This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Graphical Abstract

The ‘S’ atom of thiourea functionalized polystyrene adsorbent exhibited very strong interaction with excellent separation of antimony(III and V) ions in presence of large concentration of cobalt and zirconium ions.
Experimental and DFT Studies for Selective Separation of Sb(III) and Sb(V) from Mixtures with Zr(IV)/Co(II) using Thiourea Grafted Polystyrene Adsorbent

Jyotsna S. Arora¹, Uttamkumar Joshi¹, Vilas G. Gaikar¹,*

¹Department of Chemical Engineering,
Institute of Chemical Technology,
Nathalal Parekh Marg,
Matunga, Mumbai 400019, India

and

Sk. Musharaf Ali²

²Chemical Engineering Division,
Bhabha Atomic Research Centre,
Mumbai 400 085, India

*Corresponding author: Tel.: +91-022-33612013; fax: +91-022-33611020;
e-mail ID: vg.gaikar@ictmumbai.edu.in
Abstract

A thiourea functionalized polystyrene adsorbent (TPS-DVB) is theoretically and experimentally investigated for selective sorption of antimony from acidic aqueous mixtures with CoCl$_2$ and ZrOCl$_2$. The optimal uptake of 35.6 and 24.2 mg g$^{-1}$, respectively, was obtained for antimony(III) and antimony(V), at pH 1. The isotherm data could be well explained by the Langmuir model and the adsorption kinetics was successfully fitted in the pseudo first-order kinetics. Very high separation factors of 1129 and 918 were achieved for the Sb(III)/Co(II) and Sb(V)/Co(II) mixtures, respectively. The adsorption of Sb(III) and Sb(V) ions onto the TPS-DVB adsorbent was explored using the Density Functional Theory (DFT). These theoretical studies of metal coordination with the sulfur atom in the isothiourea group of the adsorbent showed stronger interaction of Sb(III) and Sb(V) ions over Co(II) and ZrO(II) ions. The inclusion of solvation model in the theoretical calculations improved the agreement between the experimental and the calculated metal-sulphur bond distances.

Keywords: zirconium, thiourea, adsorption, DFT, separation factor
1. Introduction

The zirconium (98%)-tin (1.5%) alloy is used as a structural cladding material in nuclear plants owing to its low cross-sectional area for capture of thermal neutrons and corrosion resistance.\textsuperscript{1} Cobalt, < 20 mg.kg\textsuperscript{-1}, is present as an impurity in the zirconium-tin alloy.\textsuperscript{1} The radionuclides, \textsuperscript{58}Co and \textsuperscript{125}Sb are formed as the activation products of cobalt and tin present in the cladding material. Several efforts have been directed to separate these radionuclides when dissolved in aqueous acidic solutions.\textsuperscript{1-5} The current state-of-art separation processes are heavily dependent on inorganic adsorbents and ion exchangers.\textsuperscript{4}

The oxidation state and co-ordination structures of metal ions in aqueous solutions play important roles in the formation of metal-extractant complex, thus enabling separation.\textsuperscript{6} The aqueous acidic solutions of cladding material comprises of cobalt in +2 oxidation state, zirconium in +4 form while antimony exhibits two oxidation states (+3,+5).\textsuperscript{1,2,4,7} Kumar \textit{et al.}\textsuperscript{8} reported selective sorption of Co(II), from aqueous HCl solutions of concentrated ZrO(II) ions, using \textit{penta}-aza and \textit{hexa}-aza macrocyclic ligands, starting with the molecular design of these ligands using Density Functional Theory (DFT) calculations. Bishay\textsuperscript{3} has reported effective separation Co(II) and Sb(III) using Amberlite C-G 400 resin (separation factor, $\alpha_{\text{Sb}^{3+/\text{Co}^{2+}}} = 850$). Devi \textit{et al.}\textsuperscript{1} used Dowex 50-X8 and Dowex 1-X8 resins for adsorptive separation of radioactive \textsuperscript{60}Co and \textsuperscript{125}Sb ions. However, these ion exchange resins get loaded mainly with Zr because of their strong affinity for zirconium ions at 1-3 M acid concentrations, resulting in poor selectivity.\textsuperscript{1,8} Further, the separation of antimony and cobalt using ion chromatography poses several processing problems\textsuperscript{9,10} along with use of concentrated acid solutions (6-11 M)\textsuperscript{1,3,5} for adsorption/elution and exhibiting little selectivity simultaneously.
The properties of a solid polymer matrix can be tailored to achieve the desired selectivity for separating a metal ion from the aqueous mixtures and operational flexibility by selecting an available ligand or by designing a specific complexing molecule. The derivatization may alter the acid/base properties of the adsorbent as well as may help in the preorganisation of the ligands. Understanding the metal ion-ligand interaction becomes, therefore, necessary to design the metal selective adsorbents. Deorkar and Tavalarides have used pyrogallol-silica gel ceramics in an adsorption column to separate Sb(III) from aqueous copper and lead salt solutions with the adsorption capacity of 5.0 mg Sb(III)/g of ceramics. Saito et al. and Kawakita et al. used porous hollow-fiber membrane containing N-methylglucamine (NMG) that gave uptake of 96 mg and 130 mg of Sb(III) and Sb(V), respectively per gram of the membrane.

According to Pearson’s acid-base theory, the chemical hardness or the softness of a metal ion may decide its selectivity and coordination properties toward a donor atom. Zr(IV) in ZrO(II) ion is classified as a hard acid, while Co(II) and Sb ions (III and V) are borderline and soft acids, respectively. Hence, taking advantage of this weak acidity of antimony, sulfur in thioether and thiols as soft base, is considered as the best choice for the donor atom. The S-containing organics, mainly thiourea, have been reported for antimony complexation and also as antimony eluting agent from ion exchange columns. In addition, thiourea immobilized as thiol and isothiouronium resins have also been reported for selective removal of heavier transition metals.

The current work reports the use of thiourea based polystyrene adsorbent (TPS-DVB) for selective and optimum adsorption of antimony(III and V) ions from mixtures with cobalt and zirconium. The DFT studies were also performed for the complexation of the metal ion with the functionalized adsorbent providing structural, energetics and electronic information.
2. Materials and Methods

2.1. Materials

Chloromethylated polystyrene (CMPS) beads cross-linked with 2% divinylbenzene, was obtained from Auchtel Pvt. Ltd. (Mumbai, India) with 3.5 meq/g of chlorine content. Thiourea, K$_2$CO$_3$ and tartaric acid (all AR-grade) were obtained from s.d. Fine Chemicals, Mumbai, India. Deionized water was used to prepare the stock solutions. The Sb(V) and Sb(III) stock solutions were prepared from potassium hexahydroxoaantimonate(V) (Sigma-Aldrich, >99%) and antimony trichloride (Thomas baker, >99%), respectively, in aqueous HCl solutions. Cobalt chloride (s.d. Fine Chemicals) and zirconyl chloride (s.d. Fine Chemicals) were used for the preparation of cobalt and zirconium solutions. Standard solutions (ICP grade, 1000 mg.dm$^3$) of Co, Zr and Sb were obtained from Sigma-Aldrich.

2.2. Methods

The carbon, hydrogen, nitrogen and sulphur contents of the adsorbent, after the grafting process, were analysed using a Perkin-Elmer 240B Elemental Analyser. A Bruker-VERTEX 80V FT-IR spectrophotometer, aligned with Ultra-Scan interferometer, was used to record the spectra of TPS-DVB with KBr pellets. Inductively coupled plasma atomic emission spectroscopy (ICP–AES) (ARCOS, MS Spectro, Kleve, Germany) was used to measure the metal-ion concentrations with an instrument detection limit (IDL) of 10 ppb for all metal ions. A radiofrequency (RF) generator with 1400 W power and 27.12 MHz frequency was used along with charge-coupled device (CCD). Argon gas was used as the nebulizer gas, auxiliary gas, and also for the generation of plasma with flow rates of 0.8, 1, and 12 dm$^3$.min$^{-1}$, respectively. The samples were injected into the plasma by maintaining the pump speed of 30 rpm. Post metal adsorption, the energy-dispersive X-ray analysis (EDX) by JEOL scanning electron microscope
was used for the elemental analysis of the polymer beads after coating with platinum. The accelerating voltage was 20-30 kV and the electric current was 15 mA.

3. Experimental and Computational Section

3.1. Experimental Section

3.1.1. Synthesis of thiourea grafted poly(styrene–DVB) resin (TPS-DVB)

The synthesis (Scheme 1) and characterization of thiourea grafted on poly(styrene–DVB) copolymer (TPS–DVB) was performed according to previous reports.\textsuperscript{30,31}

\textit{Scheme 1: Synthesis of thiourea grafted adsorbent (TPS-DVB)}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{scheme1.png}};
\end{tikzpicture}
\end{center}

3.1.2. Batch Adsorption Studies

The competitive batch sorption of antimony ions (III and V) in the presence of cobalt and zirconium ions was investigated by suspending 20 mg of the adsorbent in stoppered conical flasks containing 10 cm\textsuperscript{3} of solutions after adjusting the pH of the solution to an optimum value. The pH of the solution was adjusted by using dilute aqueous solutions of HCl or NaOH, each of 0.1 M concentration. The flasks were kept on an orbital shaker with an agitation rate of 100 strokes.min\textsuperscript{-1} at an ambient temperature of 303 ± 2 K for 24 h equilibration. The residual metal-ion concentrations in the solutions were measured by ICP–AES.
The metal-ion uptake by the adsorbent was estimated from the difference in the initial and residual metal-ion concentrations \( (C_0 \text{ and } C_e, \text{ respectively}) \) in the aqueous solutions. The adsorption capacity per unit weight of adsorbent, \( Q_{av}, \) (Eqn (1)) and percentage adsorption (%R) (Eqn (2)) were calculated as

\[
Q_{av} = \frac{(C_0-C_e) \times V_s}{W_s} \tag{1}
\]

\[
%R = \left(\frac{C_0-C_e}{C_0}\right) \times 100 \tag{2}
\]

where \( W_s \) is the weight of the solid adsorbent \( (g) \) and \( V_s \) is the volume of the solution \( (dm^3) \). The distribution coefficient, \( K_d \) \((dm^3 \cdot g^{-1})\) (Eqn (3)) was calculated as

\[
K_d = \frac{(C_0-C_e) \times V_s}{W_s \times C_e} \tag{3}
\]

and separation factor \((\alpha)\) is given by Eqn (4)

\[
\alpha = \frac{K_{d,SB}}{K_{d,Co}} \tag{4}
\]

The kinetics of antimony(III) and antimony(V) adsorption was studied at 303 K and pH = 1 with 100 cm\(^3\) \((V_0)\) of 100 ppm initial antimony concentration and 200 mg of TPS-DVB. The samples \((V_t)\) were withdrawn at regular intervals and an equal amount of 0.1 M HCl was added into the bulk solution so as to maintain the volume of the solution constant during the adsorption study. The metal uptake at any time \( t_i \), \( Q_{t_i} \) \((mg \cdot g^{-1})\) is given by Eqn (5)

\[
Q_{t_i} = \frac{(C_0-C_{ti}) \times V_0 - \sum_2^{t_i-1} C_{t_i-1} t_i \times V_t}{W_s} \tag{5}
\]

where, \( C_{t_i} \) is the metal concentration at any time \( t_i \).

The desorption studies were performed by using 0.05 M tartaric acid and 0.1 M NaOH solution.\(^{10}\) The metal loaded TPS-DVB was equilibrated with the eluent for 3 h. The adsorbent was then filtered and the resulting solution was acidified with dilute HCl solution prior to ICP-
AES analysis. The adsorbent was washed thoroughly with deionized water, dried at 363 K and was used in the subsequent three-cycle of adsorption–desorption experiments.

3.2. Computational Section

DFT studies on thiourea, TPS-DVB and the metal-adsorbent complexes in the presence of chloride counter-ions were performed for understanding the atomistic interactions between antimony, cobalt and zirconyl ions with TPS-DVB. The Gaussian 09 program\textsuperscript{34} was used for investigating the structural and electronic properties. The B3LYP functional\textsuperscript{20,35-38} with LANL2DZ-ECP basis set was considered for the metal ions\textsuperscript{20,35-38}. The 6-311+G(d,p)\textsuperscript{39} basis set was considered for the rest of the atoms as it was found to successfully predict various molecular properties. The geometry optimization of all the molecules was performed without imposing any initial symmetry restriction. The cobalt(II) ion (possessing three unpaired electrons) has quartet multiplicity while in all antimony(III), antimony(V) and zirconyl(II) ions, there are no unpaired electron. Hence for the simulation studies of Co(II)-TPS-DVB (weak ligand) complexes surrounded by chloride ions, unrestricted formalism (\textit{viz.} UB3LYP) was employed. The absence of imaginary frequencies during the Hessian calculations characterized these as stationary points. For all the complexes, corrections to the interaction energy were calculated by considering the basis set superposition error (BSSE) with counterpoise correction (CPC).\textsuperscript{40}

Geometry optimization of the complexes including the solvent effects were further performed with the Integral Equation Formalism Polarized Continuum Model (IEFPCM)\textsuperscript{41} in Gaussian 09. The dielectric constant (\(\varepsilon\)) for bulk water was taken as 78.4 and Natural Bond Order (NBO) method was employed to calculate the natural population analysis.
4. Results and Discussion

The functional group loading, specific Brunauer-Emmett-Teller (BET) macropore surface area, average pore size and pore volume of TPS-DVB were measured in co-ordination with our previous reports on the similar adsorbents. 

4.1. Equilibrium metal adsorption studies on TPS-DVB

The pH of the solution significantly affects the nature of functional groups on the adsorbent surface and the speciation of metal ions. The plots of single component adsorption of Sb(III) and Sb(V) on TPS-DVB as a function of pH are shown in Fig. 1. In the pH range of 0-2, a considerable change in the $Q_{av}$ values were observed while the amount of antimony adsorbed was almost constant beyond pH = 4. The highest uptake of Sb(III) as well as that of Sb(V) occurs at pH 1 viz. 35.6 and 24.2 mg.g$^{-1}$, respectively. A similar adsorption behavior of the maximum uptake at pH 1 was reported for Sb(V) ions on pyrogallol bonded to silica gel ceramic support. However, when the pH was increased from 2 to 6, antimony adsorption decreased significantly due to the formation of hydroxide species ($\text{Sb(OH)}_3$ and $[\text{Sb(OH)}_6]$) in the solutions. Further, at pH conditions, below 1, thiourea leaches out from the polystyrene surface decreasing the adsorption capacity of TPS-DVB for Sb.

To evaluate the selectivity of TPS-DVB for Sb ions from Co/Zr mixtures, competitive sorption experiments were performed at pH = 1 since TPS-DVB exhibited the highest adsorption capacity ($Q_{av}$) of Sb ions at this pH. It was noted that zirconium had almost negligible adsorption on TPS-DVB while cobalt to some extent showed an interaction, but antimony interacted very well with TPS-DVB. The adsorption constants, $K_d$, for Sb(III) and Co(II) from their binary mixtures are 1.242 and 0.0011 dm$^3$.g$^{-1}$, respectively while for Sb(V) and Co(II) mixtures the values are 1.010 and 0.0016 dm$^3$.g$^{-1}$, respectively (Table 1). The selectivity factor
(α) for Sb(III) and Co(II) mixtures is \( \alpha_{\text{Sb(III)/Co}} \) 1129 while that of Sb(V) and Co(II) mixtures is \( \alpha_{\text{Sb(V)/Co}} \) 918. These results clearly indicate much stronger interaction of Sb(III) and Sb(V) with TPS-DVB as compared to that of cobalt and zirconium. The bonding of the metal ions with TPS-DVB was further confirmed by elemental analysis using EDX. The peaks in the EDX spectrum at 2.31 and 6.92 keV correspond to the binding energies of SKa\(^{31}\) and CoKa\(^{42}\) (Fig. 2(a)), respectively, while peak at 3.60 keV corresponds to the binding energy of SbLa\(^{43}\) (Fig. 2(b)).

Figure 1: Effect of pH on sorption of Sb(III) and Sb(V)
Figure 2: EDX spectrum of Co (a) and Sb (b) on TPS-DVB after adsorption.

Table 1

Experimental results for co-adsorption of antimony and cobalt on TPS-DVB at pH = 1

<table>
<thead>
<tr>
<th></th>
<th>Antimony</th>
<th>Cobalt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_o$; ppm</td>
<td>$C_e$; ppm</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>96.9</td>
<td>27.8</td>
</tr>
<tr>
<td>Sb(V)</td>
<td>71.6</td>
<td>23.7</td>
</tr>
</tbody>
</table>

The experimental equilibrium adsorption data for the uptake of antimony and cobalt ions were further analyzed by Langmuir adsorption model (Eqn (6)) to estimate the maximum loading capacity of TPS-DVB.

$$Q_{av} = Q_{max} \cdot \frac{K_d C_e}{1 + K_d C_e}$$ (6)
where, $Q_{max}$ is the maximum metal ion adsorption capacity per unit weight of adsorbent (mg·g$^{-1}$), $C_e$ is metal ion concentration in the aqueous phase at equilibrium in ppm. $K_L$ (dm$^3$·mg$^{-1}$) represents the Langmuir adsorption constant. The plots of $Q_{av}$ of Sb(III), Sb(V) and Co(II) vs. $C_e$ show that the $Q_{max}$ for Sb(III) and Sb(V) as 40.01 and 25.64 mg·g$^{-1}$ resin, respectively, as against 0.65 mg·g$^{-1}$ resin for Co(II) (Fig. 3). These plots exhibit a good correlation between the experimental ($Q_{exp}$) and the Langmuir model ($Q_{fit}$) confirming monolayer coverage of metal ion on TPS-DVB surface.

![Figure 3: Effect of metal concentration on the adsorption density](image)

The suitability of the adsorbent ($R_L$) for the uptake of metal ions can be determined by the Langmuir model described according to Eqn (7)\textsuperscript{30},

$$R_L = \frac{1}{1+(K_LC_0)}$$

(7)
The $R_L$ values for TPS-DVB for Co(II) and Sb (III as well as V) ions are less than one suggesting that TPS-DVB was suitable for adsorption of these metal ions. In addition, the spontaneity of the adsorption process can be elucidated from $\Delta G$ values which can be calculated according to Eqn (8)

$$\Delta G = -RT \ln K_L$$

where $R$ (J.mol$^{-1}$.K$^{-1}$) is the gas constant, $T$ (K) is the temperature, and $K_L$ (dm$^3$.mol$^{-1}$) is the Langmuir constant. Table 2 also gives the $\Delta G$ values for the adsorption of antimony and cobalt ions by TPS-DVB at 303 K, suggesting their spontaneous adsorption.

The adsorption kinetics studies were also performed for the time-dependent uptake of both Sb(III) and Sb(V) ions. Initially, the adsorption rate is high and reaches 67 and 53%, for Sb(III) and Sb(V), respectively, within 5 h (Fig. 4). However, as time progresses, adsorption becomes slower and reaches the equilibrium values of 89 and 66%, for Sb(III) and Sb(V), respectively, after 24 h. Hence the solution was equilibrated for a minimum of 24 h. The experimental data was modeled using the pseudo first-order kinetics given by Eqn (9) and the Lagergren’s plot is given in Fig. 4 (inset).

$$\log(Q_e - Q_t) = \left(-\frac{k}{2.303}\right)t + \log Q_e$$

The kinetic parameters, $Q_e$ value and the rate constant $k$ are 30.70 mg.g$^{-1}$ and 0.36 h$^{-1}$ for Sb(III) while 24.90 mg.g$^{-1}$ and 0.41 h$^{-1}$ for Sb(V) ions. The adsorption kinetics is well represented by Lagergren’s model as the calculated values are in agreement with the experimental data (Fig. 4 (inset)).

In order to show the reusability of TPS-DVB, the adsorbed metal was eluted with 0.1 M NaOH with 0.05 M tartaric acid mixture. After three consecutive cycles of adsorption-
desorption, the removal percentage was 67 and 60% for Sb(III) and Sb(V), respectively, viz. less than 12% decrease in the adsorption efficiency occurred.

Figure 4: Effect of contact time on adsorption of antimony (inset: Lagergren’s plot)

Table 2
Adsorption Constants Degree of Suitability Values and free energy change parameters for TPS-DVB

<table>
<thead>
<tr>
<th></th>
<th>$Q_{max}$; mg.g$^{-1}$</th>
<th>$K_L$; dm$^3$.mg$^{-1}$</th>
<th>$R_L$</th>
<th>$\Delta G$, kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(III)</td>
<td>40.01</td>
<td>0.39</td>
<td>0.19-0.03</td>
<td>-9.73</td>
</tr>
<tr>
<td>Sb(V)</td>
<td>25.64</td>
<td>0.18</td>
<td>0.36-0.53</td>
<td>-7.79</td>
</tr>
<tr>
<td>Co(II)</td>
<td>0.65</td>
<td>0.024</td>
<td>0.46-0.08</td>
<td>-0.86</td>
</tr>
</tbody>
</table>
4.2. Metal-adsorbent Coordination Mechanisms

The DFT calculations were performed to comprehend the fundamental atomic interactions between the functionalized adsorbent and the metal ion surrounded by counterions during the complexation studies.44-46

4.2.1. Structure and properties of thiourea and TPS-DVB

The DFT optimized structure of thiourea and its mapped electrostatic potential surface (MESP) are shown in Fig. 5(a) and 5(b), respectively. The ‘S’ in thiourea possesses two lone pairs of electrons considering its \( sp^2 \) hybridization and hence, the MESP has significant negative charge around ‘S’ atom which is capable of attracting metal ions. These calculated geometrical parameters are in close agreement with the reported experimental and computed values obtained at B3LYP/6-311++G** level (Table 3).47 The orbital analysis of thiourea exhibit that the main atomic contributions to highest occupied molecular orbital (HOMO) of thiourea (Fig. 5(c)) come from 89% “\( p \)” character of sulfur while 73% “\( p \)” character of sulfur contributes towards the next occupied orbital (HOMO-1) (Fig. 5(d)). Hence, the HOMO and HOMO-1 are mostly constituted of a lone pair \( 3p \) orbital contribution from ‘S’. The simultaneous consideration of MESP surface and the two molecular orbitals, shows the hybridized lone pairs of ‘S’ (Fig. 5(e)). The arrow along the ‘S-C’ double bond indicates the direction along which the metal ion could approach ‘S’. The complex formation with the metal ions is expected through π bonding as shown in Fig. 5(e).

For simplified molecular simulations, the thiourea grafted polystyrene resin (TPS-DVB) was represented as the isothiouronium group bonded to a benzyl group.49 The DFT optimized structure of the grafted adsorbent is shown in Fig. 5(f) along with its MESP in Fig. 5(g) where the electron rich region is towards C=N group. 2\( p \) orbitals of nitrogen are more radially
contracted and thus difficult to approach by the metal ion for bonding, while the lone pairs of ‘S’
are easily available for bonding with the metal ion. The HOMO of TPS-DVB (Fig. 5(h)) is
mostly constituted of a lone pair orbital contribution from ‘S’ while the lowest unoccupied
molecular orbital (LUMO) is localized mainly on the polystyrene backbone (Fig. 5(i)). The
calculated geometrical parameters are given in Table 3. In addition, the calculated gas phase
vibrational frequencies of TPS-DVB are in very good agreement with the experimental FTIR
values (Table 3).

The HOMO-LUMO energy difference ($E_{eg}$) was calculated by using Eqn (10)

$$E_{eg} = E_{LUMO} - E_{HOMO}$$  \hspace{1cm} (10)

The calculated values of the frontier orbital energy difference $E_{eg,PCM}$ and $E_{eg,g}$ of TPS-DVB
are 5.496 and 5.597 eV, respectively. The lower value of $E_{eg,PCM}$ than $E_{eg,g}$ is due to solvation.
The orbitals of the ligand (isothiourea supported on polystyrene backbone) being less bulky get
substantially influenced by the presence of surrounding medium (water in this case). This results
in decreased frontier ligand orbital gap $E_{eg,PCM}$ compared to the gas phase orbital gap $E_{eg,g}$.

Table 3

| Comparison of experimental values with DFT optimized bond lengths and bond angles of
| thiourea and TPS-DVB. |
|-----------------------|------------------------|
|                        |                        |
| **Isothiourea**        | **TPS-DVB**            |
|                        | **Vibrational frequency, cm$^{-1}$** |
|                        | **Cal.** | **Exp.$^{a,b}$** | **Cal.** | **Exp.** |
| $r_{C-S}$, Å           | 1.676   | 1.671           | 1.689   | 1.863   |
| $r_{C-N}$, Å           | 1.359   | 1.365           | 1.329   | 1.382   |
| $\theta_{S-C-N}$, deg  | 122.3   | 122.6           | 121.6   | 122.9   |

$E_{eg} = E_{LUMO} - E_{HOMO}$, eV
<table>
<thead>
<tr>
<th>deg</th>
<th>$\theta_{S-Ct-N}$, deg</th>
<th>$E_{eg,S}$</th>
<th>$\theta_{CT-S-Cb}$, deg</th>
<th>$E_{eg,PCM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>115.9</td>
<td>5.597</td>
<td>104.1</td>
<td>5.496</td>
</tr>
</tbody>
</table>

*a* (B3LYP/ 6-311++G**)  
*b* experimental values  
*C*$_B$ is the C atom of benzyl group  
*C*$_T$ is the C atom of thiourea moiety
Figure 5: The DFT optimized structure of thiourea (a), its mapped electrostatic potential surface (MESP) (b), the Highest occupied (c) and the next occupied molecular orbitals of thiourea (d). The visualization of atomic lone pair orbitals of the S atom and the possible direction with mode of metal ion bonding is shown (e), the optimized TPS-DVB moiety (f), mapped electrostatic potential surface of TPS-DVB (g), the highest occupied (h) and the lowest unoccupied MOs (i) of TPS-DVB. The electron density around the S atom ranges from -2.01 to 2.11e⁻³².
4.2.2. Interaction of TPS-DVB with Sb(III & V), Co(II) and Zr(IV)

The interaction between TPS-DVB and metal chlorides can be rationalized by the quantum chemical properties *viz.* electronegativity \( \chi \), hardness \( \eta \) and the electrophilicity index \( \omega \) as calculated by Eqn (13), (14) and (15), respectively. Pearson (2005)\(^{50} \) stated that for an interacting system of two species differing in its electronegativities, the electronic flow will occur from the molecule with the lower electronegativity (the organic molecule) towards that of higher value (metal species). Further, a lower value of \( \omega \) signifies a more reactive nucleophile while the converse is stated for an electrophile (high value of \( \omega \))\(^{51} \). The \( \chi \) and \( \omega \) values for all the species in the present study are listed in Table 4. These values indicate that the TPS-DVB adsorbent is nucleophilic and hence interact with the electrophilic metal chlorides.

\[
\chi = \frac{(E_{LUMO} + E_{HOMO})}{2} \tag{13}
\]

\[
\eta = E_{LUMO} - E_{HOMO} \tag{14}
\]

\[
\omega = \frac{\chi^2}{2\eta} \tag{15}
\]

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>( \chi )</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS-DVB</td>
<td>0.1375</td>
<td>0.0467</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>0.2022</td>
<td>0.0930</td>
</tr>
<tr>
<td>Sb(V)</td>
<td>0.2004</td>
<td>0.0755</td>
</tr>
<tr>
<td>Co(II)</td>
<td>0.1794</td>
<td>0.0566</td>
</tr>
<tr>
<td>ZrO(II)</td>
<td>0.1709</td>
<td>0.0451</td>
</tr>
</tbody>
</table>

The gas phase interaction energy \( \Delta E_g \) between the metal ion and TPS-DVB surrounded with counter-ions to maintain electroneutrality was calculated using Eqn (11) and are given in Table 5.\(^{52} \)
\[ \Delta E_G = E_{\text{complex}} - (E_{\text{TPS-DVB}} + E_{\text{metal-chloride}}) \]  

(11)

where, \( E \) is the total energy of the respective optimized structures. The interaction energies of all the metal complexes with TPS-DVB and counter-ions are negative showing attractive interactions. The BSSE correction was also performed using by Eqn (12) and the BSSE corrected binding energy \( \Delta E_{\text{corr}} \) and \( (M - S)_G \) bond length are given in Table 5.

\[ \Delta E_{\text{corr}} = \Delta E_{\text{gas}} + \text{BSSE} \]  

(12)

From the gas phase calculations it is seen that, the effect of BSSE as well as the comparison of \( (M - S)_G \) bond length with the experimental values, exhibit a discrepancy for antimony viz. the trend in \( \Delta E_G \) was found to be reversed when compared to the experimental selectivity of metal ion adsorption (Table 5). Since, adsorption of the metal ion occurs from aqueous acidic solutions, the metal-adsorbent interaction is largely influenced by the presence of solvent molecules. Hence, the implicit solvation model was employed for the metal-counterion-TPS-DVB complexation.

The optimized structures of the adsorbent–metal complexes from solvation studies are shown in Fig. 6. The value of \( \Delta E_{\text{PCM}} \) for Sb(III) is more negative than Sb(V) and Co(II) ions (Table 5) exhibiting an attractive interaction, while slightly positive \( \Delta E_{\text{PCM}} \) was observed for ZrO(II) ion, thus exhibiting unfavorable interaction (Table 5). This indicates that Sb(III and V) gets selectively adsorbed on TPS-DVB due to their strongest interaction with S of TPS-DVB. The trend in interaction energy Sb(III) > Sb(V) > Co(II) > ZrO(II), is now consistent with the experimental adsorption data. Similarly, Hocking et al.\textsuperscript{43} and Song et al.\textsuperscript{45} inferred that favorable coordination between the chelating adsorbents and metal
Figure 6: DFT optimized interaction of Sb$^{3+}$ (a), Sb$^{5+}$ (b), Co$^{2+}$ (c) and ZrO$^{2+}$ (d) with TPS-DVB and the counter-ions with implicit solvation model. The grey, blue, yellow, green, white, and red represents C, N, S, Cl, H, and O atoms, respectively. Sb, Co and Zr atoms are represented by purple, cyan and silver spheres, respectively.

Table 5
DFT optimized parameters for metal with TPS-DVB in gas phase as well as implicit solvation model.

<table>
<thead>
<tr>
<th>Resin+metal+ Counter-ion</th>
<th>$\Delta E_{\text{Gas}}$, kcal.mol$^{-1}$</th>
<th>BSSE, kcal.mol$^{-1}$</th>
<th>$\Delta E_{\text{corr}}$, kcal.mol$^{-1}$</th>
<th>$(M - S)_G$, Å</th>
<th>$\Delta E_{\text{PCM}}$, kcal.mol$^{-1}$</th>
<th>$(M - S)_{PCM}$, Å</th>
<th>M-S$_{exp}$, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ZrO]$^{2+}$</td>
<td>-29.99</td>
<td>2.99</td>
<td>-25.13</td>
<td>2.74</td>
<td>0.44</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>-37.60</td>
<td>3.61</td>
<td>-31.79</td>
<td>2.46</td>
<td>-8.74</td>
<td>2.83</td>
<td>$^a$2.35-2.37</td>
</tr>
<tr>
<td>Sb$^{5+}$</td>
<td>-13.05</td>
<td>3.14</td>
<td>-9.9</td>
<td>2.81</td>
<td>-12.42</td>
<td>2.76</td>
<td>$^b$2.70-2.77</td>
</tr>
<tr>
<td>Sb$^{3+}$</td>
<td>-6.22</td>
<td>1.98</td>
<td>-4.24</td>
<td>2.92</td>
<td>-16.21</td>
<td>2.67</td>
<td>$^c$2.52-2.79</td>
</tr>
</tbody>
</table>

$^a$Silvestru et al. $^{53}$, $^b$Sharutin et al. $^{54}$, $^c$Ozturk et al. $^{20}$
cations can be correctly evaluated by considering the solvation effect during DFT calculations. Further, the $M - S_{PCM}$ is the least for Sb(III) while the highest for ZrO(II). These calculated values of $(M - S)_{PCM}$ bond length are in good correlation with the reported XRD values.$^{20, 53, 54}$

The charge transfer values ($Q_T$) were calculated by summing up the NPA charges on metal chlorides in the adduct$^8$ and changes in the optimized geometrical parameters of TPS-DVB adsorbent post metal complexation are given in Table 6. For all the metal-adsorbent complexes, negative $Q_T$ signifies flow of electrons from the lone pair of ‘S’ atom to metal ion which is consistent with the Pearson’s acid-base theory.$^{14, 50}$ Maximum charge transfer occurs in Sb(III) complex, followed by Sb(V), Co(II) and least for Zr(IV). On comparing the chemical groups of all the complexes, considerable distortions of bond lengths of TPS-DVB with Sb(III) and Sb(V) were observed. However, very little changes in TPS-DVB adsorbent post Co(II) and ZrO(II) complexation occurred confirming lesser interaction and lowered stability.

Table 6

Comparison of bond lengths, bond angle computed with implicit solvation model of TPS-DVB (before and after complexation) and charge transfer from TPS-DVB to metal.

<table>
<thead>
<tr>
<th></th>
<th>$r_{CT-S}$, Å</th>
<th>$r_{CB-S}$, Å</th>
<th>$\theta$ C$_T$-S-C$_B$, deg</th>
<th>$Q_T$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS-DVB</td>
<td>1.805</td>
<td>1.862</td>
<td>105.61</td>
<td></td>
</tr>
<tr>
<td>[ZrO]$^{2+}$</td>
<td>1.831</td>
<td>1.854</td>
<td>105.68</td>
<td>-0.159</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>1.837</td>
<td>1.831</td>
<td>105.72</td>
<td>-0.218</td>
</tr>
<tr>
<td>Sb$^{5+}$</td>
<td>1.877</td>
<td>1.828</td>
<td>105.98</td>
<td>-0.515</td>
</tr>
<tr>
<td>Sb$^{3+}$</td>
<td>1.886</td>
<td>1.825</td>
<td>106.12</td>
<td>-0.608</td>
</tr>
</tbody>
</table>

$^*$C$_B$ is the C atom of benzyl group, $^{**}$C$_T$ is the C atom of thiourea moiety

Comparative study with Literature Reports
Although it is difficult to directly compare the adsorption efficiency of TPS-DVB with other adsorbents because of the different experimental conditions used, it is still apparent that the selectivity for antimony over cobalt is much higher with the current adsorbent at low acid concentrations than the reported ion exchanger adsorbents. Devi et al.\(^1\) reported \(\alpha_{\text{Sb}^{3+}/\text{Co}^{2+}} = 16\) for an anion exchanger Dowex 1-X8 with quaternary ammonium functional group in Cl\(^-\) form in 8 M HCl while the cation exchanger Dowex 50-X8 with sulfonic acid functional group, exhibited \(\alpha_{\text{Sb}^{3+}/\text{Co}^{2+}} = 50\) in the presence of 9 M HCl. However, with 0.5 M HCl, the Dowex 1-X8 and Dowex 50-X8 resins exhibited selectivity towards cobalt with \(\alpha_{\text{Sb}^{3+}/\text{Co}^{2+}} = 1.25\) and 0.06, respectively. These separation factors are at much lower level as compared to the TPS-DVB giving good separation factors which ensure very selective pick-up of antimony ions at low acid concentrations. Further, Bishay\(^3\) reported the simultaneous adsorption of cobalt and antimony(III) from 8 M HCl solutions on an anion exchange column filled with Amberlite CG-400 resin having quaternary ammonium functional groups in Cl\(^-\) form. These metal ions are selectively eluted with 3 M HCl and 0.1 M HClO\(_4\), respectively with \(\alpha_{\text{Sb}^{3+}/\text{Co}^{2+}} = 850\). Though the separation of cobalt and antimony using the ion exchange process was effective, the major disadvantages of this process are the handling of highly concentrated solutions for adsorption and the nuclear waste streams contains other metal ions which might also get adsorbed on these non-selective resins.

The TPS-DVB adsorbent can overcome the demerits of the usual ion-exchange process resulting in effective separation of antimony from Co and Zr mixture. Further, DFT results are in agreement with the experimental data, indicating that DFT is helpful to determine the complexation of metal cations with the functionalized adsorbent.

5. Conclusions
Thiourea modified polymeric adsorbent having styrene backbone was evaluated as an excellent antimony selective adsorbent in the presence of cobalt and zirconium. The maximum adsorption capacity of the adsorbent for Sb(III) and Sb(V) was 40.01 and 25.64 mg.g\(^{-1}\) with a high separation factor 1129 and 918, respectively. The results of DFT calculations on inclusion of solvation are in accordance with the experimental adsorption data. The HOMO is located on ‘S’ atom of TPS-DVB which interacts with the metal ion. The computed M-S bond distances (under solvation conditions) are in good agreement with the XRD values for similar systems.

**Acknowledgements**

We acknowledge the Department of Atomic Energy, Government of India, for the financial support and IITB SAIF, IITB Department of Earth Science, for the analytical support.
References


53.
