CHAPTER 3

REMOVAL OF TOXIC MERCURY(II) SPECIES FROM CHLOR-ALKALI INDUSTRIAL WASTES

3.1 INTRODUCTION

For many years, the chlor-alkali Industry all over the world has been a matter of concern because of the pollution due to the presence of mercury(II) in the wastage. In India, of recently, although the industries producing cast alkali have been switched over to more environmentally friendly membrane based process, still 50% of chlor-alkali industries are based on mercury cell process. Hence the contamination of mercury in brine sludge and effluents of chlor-alkali industry is more important compared to the waste from other industries such as paper and pulp, manufacture of vinyl chlorides, paints, pesticides, fungicides and cinnabar processing. Hence, the removal of mercury from these hazardous wastes assumes increasing importance.

Conventional mercury treatment technologies include precipitation [1-6], carbon adsorption [7-9], ion exchange [10-13], cementation [10-12] and roasting [13-15]. Hydrometallurgical routes [16-21] are also being considered as economic alternative for mercury(II) removal from waste streams. The above mentioned conventional mercury treatment processes are non-selective and roasting or retorting only removes mercury. However, ion exchange based methods are afford better removal of mercury. But these processes are time consuming and inherently expensive. Liquid-liquid extraction also emerged as an important technique for the removal of mercury(II) ions. Technicas Revnidas, SA, Spain [22] and Baba et al [23] have developed liquid-liquid extraction based processes for the removal of mercury(II) from waste streams of a chlor-alkali industry. But solid phase extraction now a days is emerging as a powerful
technique and in most instances replacing liquid-liquid extraction processes because of the following reasons.

(1) Absence of emulsion
(2) Minimal costs due to low consumption of reagents
(3) Higher enrichment factors
(4) Reusability of the adsorbent
(5) Safety with respect to hazardous samples, and
(6) More importantly environment friendly

Various SPE procedures described in the literature pertain to enrichment of traces of mercury(II) from dilute aqueous solutions prior to determination by suitable analytical techniques. However, none of these reports addresses to the problem of removal of mercury from chlor-alkali industrial wastes. On the other hand, activated carbon (AC) is widely used all over the world for removal of mercury(II) from chlor-alkali wastes. However, the main problem lies in the storage and disposal of mercury(II) containing activated carbon. Chelate sorbed AC is thought to be a viable alternative to address the above disposable problem as it will reduce the amount of AC required for the removal of mercury(II). The disposal process may become an alternative if it can be recycled via several adsorption-desorption processes for the removal of mercury(II).

In the present work, selective SPE procedures were developed for the removal of mercury(II) from brine sludge and cell house effluents of a chlor-alkali industry with the use of one such extractant viz, 1(2-thiazolylazo)-2-naphthol sorbed activated carbon.

3.2 PREPARATION OF 1-(2-THIAZOLYLAZO) NAPHTHOL (TAN) SORBED AC

0.20g of TAN was dissolved in minimum amount of acetone and was poured as a fine stream into 500 ml of water containing 10 g of AC with constant stirring at room temperature. The resulting slurry was stirred for 1 h and was allowed to settle for 10 min. The bulk of the supernatant aqueous solution was
decanted and then filtered through a filter paper placed in a “Buchner funnel” by suction, washed with water and dried in an oven at 80°C for several hours and then stored in dessicator.

3.3 PRELIMINARY INVESTIGATIONS

The solid phase extraction of 5 µg of mercury(II) whose pH was adjusted to 6.0±0.2 after adding 10 ml of 1.0 M of ammonium acetate onto 0.2 g of 2% TAN sorbed AC. The mercury(II) adsorbed on TAN modified AC was eluted with 2x10 ml of 1.0 M HNO₃. The mercury(II) in the eluent was determined spectrophotometrically using Iodide - Rhodamine 6G procedure [24]. These studies gave encouraging results in the removal of mercury(II) from dilute aqueous solutions and detailed optimization studies were carried out for its removal.

3.4 OPTIMIZATION OF EXPERIMENTAL VARIABLES

3.4.1 Effect of pH

The effect of pH on the removal of 5 µg of mercury(II) present in 1.0 l of solution was studied by adding 0.2 g of 2% TAN sorbed AC as SPE in the pH range 5.0-9.0. Mercury(II) preconcentrated onto TAN sorbed AC was determined spectrophotometrically via Iodide - Rhodamine 6G procedure, after eluting with 2x10 ml of 1.0 M HNO₃. The percent removal of mercury(II) onto TAN sorbed AC is constant and maximum in the pH range 5.8-6.2 (Fig.3.1). In all subsequent work, the pH was adjusted to 6.0±0.2 after the addition of 10 ml of 1.0 M of ammonium acetate buffer.

3.4.2 Effect of TAN concentration in activated carbon

The concentration of TAN in AC was varied from 0.1 to 5.0%. Mercury(II) enriched onto TAN sorbed AC was determined spectrophotometrically as described in Section 3.4.1. The results obtained are shown in Fig.3.2. The removal
of 5µg of mercury(II) present in 1.0 l of solution was quantitative when the concentration of TAN in AC was greater than 2% (Fig.3.2). Hence, 2% TAN sorbed AC was used in the subsequent studies.

Fig. 3.1 Effect of pH

Fig. 3.2 Effect of TAN concentration in AC
3.4.3 Effect of weight of chelate sorbed activated carbon

The weight of TAN sorbed AC was varied from 0.05 to 0.5 g. The removal of mercury(II) was quantitative when the amount of TAN sorbed AC was greater than 0.1 g (See Fig.3.3). Hence, 0.2 g of TAN sorbed AC was recommended for quantitative removal of mercury(II).

3.4.4 Effect of time of stirring

The time of stirring was varied from 5-60 min during the removal of 5 µg of mercury(II) present in 1.0 l of solution by using TAN sorbed AC. The results obtained are shown in Fig.3.4, from which it is clear that a minimum of 10 min of stirring was enough for the quantitative removal of mercury(II) by TAN modified AC. Ten minutes of stirring time was used in all subsequent experiments.
3.4.5 Effect of aqueous phase volume

The effect of aqueous phase volume on the removal of 5 µg of mercury(II) with TAN sorbed AC was studied in the range 25-1000 ml. The results obtained as shown in Table 3.1 indicate that quantitative removal of mercury(II) was possible even up to 1.0 l of sample solution.

<table>
<thead>
<tr>
<th>Aqueous phase volume (ml)</th>
<th>% of Hg Removal</th>
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<tbody>
<tr>
<td>25</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>50</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>100</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>250</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>500</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>1000</td>
<td>&gt; 99.5</td>
</tr>
</tbody>
</table>

3.4.6 Choice of eluting agent

The mercury(II) adsorbed on TAN sorbed AC was eluted with 1.0M of mineral acids such as hydrochloric acid, sulphuric acid and nitric acid. The results obtained are shown in Table 3.2. The quantitative removal was achieved with
sulphuric acid and nitric acid. Nitric acid eluent was used for all subsequent studies.

Table 3.2 Choice of eluent

<table>
<thead>
<tr>
<th>Eluent (1.0M) used</th>
<th>% removal of mercury(II)</th>
</tr>
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<tbody>
<tr>
<td>HCl</td>
<td>73.4</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>HNO₃</td>
<td>&gt; 99.8</td>
</tr>
</tbody>
</table>

3.4.7 Reuse studies

TAN modified AC was recycled for several times. Even after ten cycles of sorption and desorption of mercury(II) from TAN sorbed AC, the removal of mercury(II) was >99%.

3.5 EFFECT OF DIVERSE IONS

Sample solutions containing 5µg of mercury(II) and various amount of different metal ions were subjected to removal of mercury(II) by following the procedure described in section 3.4.1. No deleterious effect was observed due to 100-fold amounts of Li(I), Na(I), Ca(II), Ba(II), Sr(II), Be(II), Co(II), Pb(II), Ni(II), Al(III), La(III), Zr(IV), Th(IV), U(VI), NO₃⁻, Cl⁻, SO₄²⁻, 50 fold amounts of Cd(II), Cu(II) and Cr(III), and 10 fold amounts of Mn(II), Fe(II), and Mo(VI) in removal of mercury(II). Thus, mercury(II) can be selectively removed when present along with above metal ions through the use of TAN modified AC as SPE material.

3.6 EQUILIBRIUM LOADING OF MERCURY(II) ONTO TAN

This experiment was carried out by taking a solution containing 0.5 mg of mercury(II) and 0.2 g of TAN modified AC and 10 ml of 1.0M ammonium acetate buffer was added. The pH was adjusted to 6.0±0.2 and was diluted to 25 ml and transferred to a 60 ml separating funnel. This solution was equilibrated for 30 min and filtered through a filter paper. The amount of mercury(II) left out in the filtrate was determined by Iodide - Rhodamine 6G procedure. The equilibrium loading of TAN sorbed AC SPE material was found to be 2.24 mg/g of the
adsorbent which is much higher when compared to AC alone (~0.75 mg/g). Therefore TAN modified AC effectively removes mercury(II) approximately 3 times when compared to AC alone.

3.7 MERCURY(II) REMOVAL STUDIES

3.7.1 Aqueous solutions

Mercury(II) present at levels of 5µg in 1.0 l of aqueous solution was stirred with TAN sorbed AC. The filtrate was analysed by CVAAS. This result indicates the absence of mercury(II). This means that all the mercury(II) ions present in the aqueous solution has been removed completely. Furthermore, the amount of mercury(II) present in AC phase was also determined after the elution with HNO₃. These CVAAS studies indicate quantitative removal of mercury(II) in all tested concentration levels confirming that TAN sorbed AC can reliably be used for the removal of mercury(II).

3.7.2 Synthetic chlor-alkali effluent

Synthetic samples containing other inorganic species corresponding to composition of chlor-alkali industrial waste of M/S Travancore-Cochin Chemicals Limited, Kerala, (Table 3.3) were prepared and tested for the removal of mercury(II) by using TAN sorbed AC. The removal of mercury(II) was unaffected in presence of various extraneous ions.

Table 3.3 Typical composition of chlor-alkali industrial waste of M/s. Travancore-Cochin Chemicals Limited, Kerala

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Concentration</th>
</tr>
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<tbody>
<tr>
<td>Ca</td>
<td>38.6 mg/ml</td>
</tr>
<tr>
<td>Mg</td>
<td>5.8 mg/ml</td>
</tr>
<tr>
<td>Zn</td>
<td>21.6 µg/ml</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>6.5 µg/ml</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>2.75 µg/ml</td>
</tr>
<tr>
<td>Ba</td>
<td>45.4 µg/ml</td>
</tr>
</tbody>
</table>
3.7.3 Brine sludge

The developed solid phase extraction procedure for the extraction of mercury(II) using TAN sorbed AC was applied for the removal of mercury(II) from the brine sludge collected from M/s. Travancore-Cochin Chemicals Limited, Cochin, India. One gram of brine sludge sample was dissolved in 25 ml of 1:1 HNO$_3$ and heated until it is dissolved. The resulting solution was diluted to 100 ml with deionised water. The pH of this solution was adjusted to 6.0±0.2 and 0.2 g of 2% TAN modified AC was added. The resulting solution was stirred for 10 min and the mercury(II) adsorbed on TAN sorbed AC was eluted with 2x10 ml of 1.0M HNO$_3$. Suitable aliquots of this eluent was taken and removal of mercury(II) using TAN sorbed AC SPE was determined by Iodide - Rhodamine 6G and CVAAS procedures. The removal of mercury(II) by the developed preconcentration procedure was found to be > 99.8% (See Table 3.4) indicating the quantitative removal of mercury(II) from brine sludge sample.

### Table 3.4 Removal of mercury(II) from brine sludge and cell house effluents of chlor-alkali industry*

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Description of sample</th>
<th>Mercury(II) added</th>
<th>Mercury(II) removed**</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Present method (SPE-Spect.)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Brine sludge (µg/g)</td>
<td>60.0</td>
<td>128.0±1.0</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120.0</td>
<td>188.0±2.0</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td>2</td>
<td>Cell house effluent (µg/l)</td>
<td>0.8</td>
<td>2.42±0.02</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.60</td>
<td>3.23±0.03</td>
<td>&gt;99.8</td>
</tr>
</tbody>
</table>

*collected from M/s. Travancore-Cochin Chemicals Limited, Cochin, India

**Average of 3 determinations

3.7.4 Removal of mercury(II) from cell house effluent

Suitable aliquots of cell house effluent collected from M/s. Travancore-Cochin Chemicals Limited, Cochin, India were taken and the pH was adjusted to
6.0±0.2. The preconcentration, elution, determination by Iodide-Rhodamine 6G and CVAAS procedures were carried out as described in Section 3.7.3. The mercury left out in the aqueous phase was < 0.2%.

The mercury(II) concentration in the brine sludge cell house effluent were found to be ~125 µg/g and ~1.60 µg/l as determined by CVAAS.

3.8 EXPERIMENTAL

3.8.1 Apparatus

A Hitachi-220 double beam spectrophotometer and an ECIL make cold vapour atomic absorption spectrometer were used for the estimation of mercury(II) and LI-120 digital pH meter (ELICO, India) was used for pH measurements.

3.8.2 Reagents

Activated carbon (AC), 1-(2-thiazolyl-2-naphthol(TAN) were obtained from Aldrich Chemical Company Inc., Milwaukee, WI, USA. All other chemicals used were of analytical reagent grade.

3.8.3 Preparation of TAN sorbed activated carbon

0.2g of TAN was dissolved in minimum amount of acetone and was poured as a fine stream into 500ml of water containing 10g of AC with constant stirring at room temperature. The resulting suspension was stirred for 1 hour and was allowed to settle for 10 min. Then, bulk of the supernatant solution was decanted and filtered through a filter paper placed in a Buchner funnel by suction, washed with water and dried in an oven at 80°C for several hours and then stored in desiccator.

3.9 REMOVAL STUDIES

The SPE of mercury from the brine sludge and cell house effluent of chlor-alkali industry is comprised of the following steps:
(1) Dissolution of the brine sludge with 1:1 HNO₃.

(2) The pH of the resultant brine sludge or cell house effluent solutions were adjusted to 6.0±0.2 and extracted with 0.2 g of 2% TAN modified AC SPE material, whereupon mercury(II) was selectively removed with TAN sorbed AC.

(3) Elution of the mercury(II) bound on TAN sorbed AC SPE by using 2x10 ml of 1.0M HNO₃ to remove all the mercury(II) present in SPE.

This investigation reveals that > 99.8% mercury(II) can be decontaminated from brine sludge/cell house effluent. The flow chart for the removal of mercury(II) from brine sludge and cell house effluents of chlor-alkali industry is given in Fig. 3.5.

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**Fig 3.5 Flow chart for removal of mercury(II) from brine sludge and cell house effluents of chlor-alkali industry**
3.10 CONCLUSION

This study clearly demonstrates the use of TAN functionalized AC solid phase extractant for selective removal of mercury(II) from dilute aqueous solutions containing Mg(II), Ca(II), Ba(II) and Fe(III) ions. In addition, the results clearly demonstrated the usefulness of TAN modified AC for selective removal of mercury(II) from hazardous materials like brine sludge and cell house effluents of chlor-alkali industry. Furthermore, the higher retention/sorption capacity of TAN sorbed AC compared to AC for mercury(II) enabled the minimization of subsequent waste disposable problems. In view of the reusability over 10 cycles makes this TAN sorbed AC as an attractive material for the removal of mercury(II) from chlor-alkali industry wastes.

REFERENCES


