Chapter - III
Selective separation of chromium(VI) from effluents using supported liquid membrane

Summary

Selective separation of chromium(VI) was carried out using supported liquid membrane (SLM) made of teflon loaded with aliquat -336 in n-dodecane. This simple, selective method is applicable for the removal of chromium from industrial effluents, synthetic wastewater and leachates from mines. The effect of feed phase, carrier concentration and stripping agent concentrations were studied and optimized. At pH 5.5, SLM transport cell would efficiently separate chromium(VI) from feed phase to stripping phase.

Part presented in 47th Annual Convention of Chemists - 2010, Raipur
INTRODUCTION

Biological toxicity of heavy elements is well known. Industries were heavy elements are used often pollute air, water and land by their discharge. One such metal, chromium is widely used in industries in the manufacture of steels, jet engines, tools, paints, photography, electric cells, rubber goods and matches. The salts of chromium are widely used in metal pickling and plating operations, in the anodizing of aluminum, in leather tanning and in several other industries. Tri-valent chromium salts such as sodium chromate or potassium chromate are generally used in ceramic and glass industries. Since chromium compounds are corrosion inhibitors, they are used to treat cooling tower water. Chromic acid in very dilute quantities are used to protect metals from corrosion [1-6].

Soil and plants contain very little chromium. Sea water and earth crust contain about 1-2.5 ppb and 200 ppm of chromium. Human body contains about 6 mg of chromium. Chromium bound to beta globulins is distributed in heart, brain, liver and spleen [7-8].

Although both trivalent and hexavalent chromium are reported to be toxic in nature, the latter one is reported to be relatively more hazardous to human being [8-9]. Since most of the industrial effluents have to pass through sewage treatment plants, bacteria in such plants are ruined by trace amounts of chromium, thereby rendering the process of water treatment useless. The U.S. Environmental Protection Agency (EPA) regulates the total chromium in drinking water and has set a maximum contamination level (MCL) of 100 µg mL⁻¹. The threshold limit value for chromium(VI) is 0.5 mg m⁻³ as proposed by the American conference of the governmental industrial hygienists. Considering its toxic effect and widespread availability it is desirable to determine micro levels of chromium in environmental matrices [9-12].

Chromium containing effluents are normally treated to convert chromium (VI) to chromium (III) by reduction using SO₂, NaHSO₃ or sodium meta bisulphate, which is then precipitated as hydroxide using NaOH. The precipitate is allowed to settle and the clear liquid is disposed off [13].

The tolerance limit of chromium (VI) in land and potable water is 0.1 ppm and 0.05 ppm (EPA, 1990). Hence, the removal of chromium (VI) from industrial effluents is important. Diphenylcarbazide is the traditional reagent used for the separation of chromium (VI) and is
determined by spectrophotometric method [14]. The sensitivity of the method is not high enough (mg/L) and the complex formed is also unstable. Azo compounds, derivatives of triphenylmethane are sensitive reagents reported for the spectrophotometric determination of hexavalent chromium. However, their specificity is not very good and it is necessary to separate the diverse ions before its determination [15-24].

Liquid membranes are widely adopted in the field of separation of toxic metals. The membrane acts as a very specific filter for suspended solids and other substances. Liquid membranes are generally used for transporting components at high rates across it through carrier molecule. Carriers alter the guest permeability and facilitate selective diffusion across the membrane. Various types of liquid membranes are reported [25-32] i.e., bulk (BLMs), emulsion (ELMs) and supported (SLMs), as well as hollow fibre contained liquid membranes (HFCLMs). SLM contains an organic solution as a carrier, which is immobilized on a porous material such as polymers. Cation transport takes place in such a way that it involves the complexation at the feed phase of the membrane and release at the receiving phase. The driving force is a proton concentration difference between the two aqueous phases (Figure 1).

The carrier-rich liquid leaving the extractor is referred to as the raffinate phase and the solvent-rich liquid leaving the extractor is the extractant phase. The technology using immobilized liquid membrane for treating industrial effluents is more economical and energy efficient. Effluents discharged from industries and leachates from mines can be directly passed through such membranes. Fractional applications of such membrane have been envisaged for the recovery of metals from lean solutions generated in hydrometallurgical operations [33-40].

Membrane separation methods of chromium reported are for removal of chromium from aqueous waste solution using liquid emulsion membrane, membrane-based hybrid processes for the removal of hexavalent chromium, removal of chromium from aqueous solution using cellulose acetate and sulfonated poly (ether, ether ketone) blend ultra filtration membranes, chromium (VI) from aqueous solutions by polymer inclusion membranes. Pilot scale membrane separation of electroplating waste water by reverse osmosis has been reported. Removal of chromium from aqueous solutions by treatment with carbon aero gel electrodes using response surface methodology, removal of chromium (VI) by solvent impregnated resins, removal of trivalent chromium contaminant from aqueous media using FAU-type zeolite membranes have also been reported [41-46].
In the present study, the separation of chromium ions is carried out using a supported liquid membrane (SLM). Which is a thin film that selectively permits the passage of a specific constituent from a mixture. Unlike solid membranes, the liquid membranes separate by its chemical property rather than size. Thus in many ways liquid membrane technology is similar to solvent extraction.

The SLM process is one of the best methods of treating waste water containing toxic metals such as chromium (VI). Selective separation and concentration of the solute of interest from dilute solution can be achieved using SLM, where a porous polymeric membrane support, impregnated with a solvent, is used as a carrier to separate metal ions. Aliquat-336 has been shown to be an effective extractant for the separation of chromium (VI) [51].

Soil samples collected from various mining sites of Chhattisgarh region of India were found to contain chromium (VI) in the range of 75 to 330 ppm. This soil when leached with aqua regia almost completely releases chromium (VI). Water leachates around the mines also show chromium (VI) in the range of 0.04-0.05 µg/mL.

**EXPERIMENTAL**

**Apparatus**

Absorbance studies were performed in Varian Cary 50 Bio UV-Visible spectrophotometer and Jobin Yvon-Ultrate-238, ICP-AES. pH measurements were made with Systronics pH meter, model 331. Stirring was done using magnetic stirrer.

**SLM support cell**

The membrane is a porous polymer membrane whose pores are filled with the organic liquid and carrier, set in between the source phase and the receiving phase, which are gently stirred [Figure 2 (a) and 2 (b)].

**Reagents**

All the chemicals used were of analytical reagent grade or the highest purity available. Double distilled water was used throughout the experiment for preparation and dilution of reagents as well as samples. Aliquat-336, n-decanol, Xylene and Kerosene were from Merck, Mumbai, India. Potassium permanganate from Loba chemie, Mumbai. Acids: H$_2$SO$_4$, HCl, HNO$_3$ and NaOH were obtained from Hi Media Laboratories Pvt. Ltd, Mumbai.
**Procedure**

**Preparation of standard solution of chromium (VI)**

Stock solution (1000 µg mL⁻¹) was prepared by dissolving 0.2829 g of K₂Cr₂O₇ in double distilled water and volume made up to 100 mL. Working standards were prepared daily by its dilution with double distilled water.

**Choice of diluents for membrane solvent**

Kerosene and xylene were found to be good diluents for the extractant, aliquat-336, but better results were obtained by n-dodecane, it was selected for dilution of the carrier liquid.

**Preparation of membrane support**

Supported liquid membrane is generally prepared by absorbing a solvent on a hydrophobic micro porous polymeric membrane using appropriate diluent. The diluent is generally immiscible with the solutions on the two sides of membrane and should have low dielectric constant. A flat sheet poly tetra fluoro ethylene (PTFE) membrane was used as the polymeric support. The commercial Teflon membrane (PTFE) membrane of 0.45 micrometer diameter, 160 micrometer pore size and 84% porosity was used. Before impregnation, the membrane support was pre saturated with water for more than two days, dried with bloating paper. Circular pieces of this PTFE membrane were soaked in the carrier solution, aliquat 336 (in nitrate medium) of different concentrations for 12Hrs before use to have uniform adsorption of carrier solution. The membrane was then removed from the organic solution, rinsed with water, wiped with filter paper to ensure the removal of excess carrier.

**Supported liquid membrane transport mechanism**

The membrane was fitted in the middle of a glass apparatus which makes the apparatus into two compartments. The feed solutions used were of various concentrations of K₂Cr₂O₇ and the strip solution was NaOH of different concentrations. These feeds and strips were separated by the membrane. Constant stirring of both the compartments were done with magnetic stirrers. Samples were taken at periodic intervals.

Schematic diagram of the SLM cell is shown in figure 3. The hydrophobic SLM whose pores are filled with the organic phase is fitted between feed phase and stripping phase. The
extraction of chromium (VI) as the chromate ion from the aqueous feed with aliquat-336 (a long chain quaternary amine) is described by the chemical equation.

\[
2R_3NCH_3NO_3 + CrO_4^{2-} = (R_3CH_3N)_2CrO_4 + 2NO_3^{-}
\]

**Procedure of supported liquid membrane (SLM) experiment**

About 30 mL 2.5x10^{-3} mol L^{-1} of chromium (VI) in nitric acid was taken in the feed compartment. The impregnated SLM - PTFE was kept at the middle of the port and in the receiving compartment, 1M NaOH solution was taken. Both feed solution and strippant solutions were stirred with a magnetic stirrer at room temperature constantly. The initial pH of the solution was maintained at 5.5. The colour reduction in the feed solution and increase in colour intensity of the strippant was visually noticeable. Samples were drawn at intervals of one hr from both compartments. The concentration of chromium (VI) was ascertained using ICP-AES. The absorption intensity of yellow color was measured at 445 nm.

**Enrichment factor**

Enrichment factor is one of the most common criteria used to evaluate a particular SLM system. The application of SLM is often aimed at the enrichment of a solute as opposed to selective separation. In the liquid membrane system the feed phase is usually composed of a more concentrated solution than the stripping phase. The enrichment factor (E), is defined as the ratio of the concentration of the species in the stripping solution \(S_s\) to the initial concentration in the feed solution \(S_f\) [29]

\[
E = \frac{(S_s)}{(S_f)}
\]

In supported-liquid membrane extractions, high enrichment factors are a result of high solubility of the analytes into the membrane and trapping metals in the acceptor phase. In this, the trapping in the acceptor phase allows additional enrichment. As described by a simple theory, infinitely large enrichment factors can be obtained with SLM extraction as the concentration of uncharged analyte in the acceptor is kept at zero. In reality, the high enrichment factors are limited by the processing time and the available sample volume.
RESULTS AND DISCUSSION

Effect of pH

pH of the system is an important factor in the selective separation and distribution of metal ion species in aqueous phase and it acts as the main variable in the extraction of Chromium (VI). The effect of feed phase on the transport of Chromium (VI) was examined from pH 2 to 8, maintaining the feed phase Cr (VI) at fixed concentration (2.5 x 10^{-3} mol L^{-1}). It is found that there was no transport of Chromium (VI) below pH 4.5 (Figure-3). Since the carrier aliquat 336 forms complex with Chromium (VI) only at pH > 4.5, chromium could not be extracted at lower pH due to lack of complex formation. From figure 3, it is clear that optimum condition for the separation of Cr (VI) is at pH 5.5 beyond which a dip in extraction is noticeable which may be due to the formation of neutral complexes.

Optimization of the SLM enrichment procedure

The carrier concentration in the SLM system is one of the important factors for selective transport of metal ions. In the case of chromium separation, aliquat-336 was found to be a suitable carrier due to higher ionization nature of aliquat-336 at 5.5 pH. Hexavalent chromium, may exist in the aqueous phase in different forms; the total amount of chromium and the pH are the main variables of the chromium species in an aqueous phase. If there is no other chemical species in the aqueous solution, the Cr (V1) equilibrium reactions are:

\[\begin{align*}
\text{H}_2\text{CrO}_4 & \rightarrow \text{H}^+ + \text{HCrO}_4^- \quad (\log K = -0.8) \\
\text{H}_2\text{CrO}_4 & \rightarrow \text{H}^+ + \text{CrO}_4^{2-} \quad (\log K = -6.5) \\
2\text{H}_2\text{CrO}_4 & \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_3\text{O} \quad (\log K = 1.52) \\
\text{HCr}_2\text{O}_7 & \rightarrow \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \quad (\log K = 0.07)
\end{align*}\]

Under the present experimental conditions, hydrogen ion present in the carrier was exchanged for metal ion complexation. Transport of chromium(VI) from the mixture of metal ions for varying concentrations of carrier (aliquat-336) were studied. The absorbance increases with an increase in the concentration of NaOH, chromium (VI) and aliquat-336 (Table-1). However high concentration of aliquat-336 is not required for the impregnation of the membrane hence for further experiments only 10\% was utilized. The strippant NaOH was also not required.
in high concentration. There is always a possibility of osmotic transfer in both compartments. Dilute solutions are better for experiments. Hence 1M NaOH was used as strippant.

**Effect of conc. of strippant solution on the transport of chromium (VI)**

Since the SLM technique involves simultaneous extraction and stripping process for the continuous transport of metal ions, it is necessary to find the effect of stripping agent in the receiving phase. The effect of stripping agent concentration on the chromium (VI) transport was investigated using various concentration of NaOH solution. The concentration of alkali varied from 1M to 4M and the result obtained are shown in table-2. The stripping efficiency is maximum at 3.35M. However, at higher concentration the excess ions tend to form an ionic atmosphere thereby causing reduction in stripping efficiency (Figure-4).

It can be seen from table-3 that though 50% transport is possible within 3 hrs, reversal takes place thereafter which may be due to the concentration barriers and osmotic pressures. As 1M NaOH also does equally good in stripping chromium, it is preferable to use 1M NaOH. In order to overcome the reverse transport, the chromium (VI) concentration in the feed compartment was reduced to 2.5x10^{-4} mol L^{-1} and 1M NaOH was used as strippent.

**Separation of chromium (VI) from effluent water**

The details of application of SLM in separating Cr (VI) from effluent samples collected from separating mixture is given in Table 3. It was seen that quantitative separation of Cr (VI) is possible with the current SLM technique.

**CONCLUSION**

Supported liquid membrane (SLM) technique is simple, sensitive and reproducible. No stringent conditions required for the separation of metal ions from aqueous solution. It requires the use of very little solvent. Thus it makes economical to use even costly solvents. In SLM technology energy requirement is minimum, loading and stripping takes place continuously. It can be successfully applied for the trace analysis of chromium (VI) content in ore leachates, steel samples, industrial effluents. Aliquat-336 is a quaternary amine and is biodegradable. Hence it posses no environmental problems. pH level suits the water resources.
Figure 1. Schematic diagram of the coupled transport mechanism for metal ion transport through a liquid membrane ($M^+$ is the metal ion, $HC$ is the ion exchange reagent, and $H^+$ is the hydrogen ion.)
Figure 2. (a) Configuration of SLM transport system
Figure 2. (b) Supported liquid membrane apparatus

Figure 3. Effect of pH in separation technique

Figure 4. Effect of concentration of strippant solution on the transport of chromium (VI)
Table 1. Transport of chromium (VI) ions across the liquid membrane

chromium (VI) concentration - $2.5 \times 10^{-3}$ mol L$^{-1}$, aliquat 336
conc. - 1%-20 %, NaOH concentration - 0.01- 4 mol L$^{-1}$

<table>
<thead>
<tr>
<th>NaOH Concentration M/L</th>
<th>Max. Absorbance value</th>
<th>Aliquat 336 Conc.%</th>
<th>Max. Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.018</td>
<td>1</td>
<td>0.101</td>
</tr>
<tr>
<td>0.05</td>
<td>0.063</td>
<td>3</td>
<td>0.297</td>
</tr>
<tr>
<td>.1</td>
<td>0.078</td>
<td>5</td>
<td>0.359</td>
</tr>
<tr>
<td>.5</td>
<td>0.122</td>
<td>10</td>
<td>0.361</td>
</tr>
<tr>
<td>1</td>
<td>0.439</td>
<td>15</td>
<td>0.362</td>
</tr>
<tr>
<td>2</td>
<td>0.445</td>
<td>20</td>
<td>0.367</td>
</tr>
<tr>
<td>3</td>
<td>0.502</td>
<td>25</td>
<td>0.368</td>
</tr>
<tr>
<td>4</td>
<td>0.468</td>
<td>30</td>
<td>0.369</td>
</tr>
</tbody>
</table>

Table 2. Chromium(VI) concentration - $2.5 \times 10^{-3}$ mol L$^{-1}$ at pH 5.42
(reagent) NaOH concentration - 1 mol L$^{-1}$ (strippent), Volume
of each compartment - 3.5 mL, Chromium taken in reagent
compartment - 449.537 µg mL$^{-1}$, Acid medium used - HNO$_3$

<table>
<thead>
<tr>
<th>Time Hrs</th>
<th>Vol. after Sampling (ml)</th>
<th>Chromium in strip µg mL$^{-1}$</th>
<th>% of Cr transport</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.5</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>1</td>
<td>3.5</td>
<td>199.794</td>
<td>44.44</td>
</tr>
<tr>
<td>2</td>
<td>3.45</td>
<td>216.356</td>
<td>48.83</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>164.70</td>
<td>37.72</td>
</tr>
<tr>
<td>4</td>
<td>3.35</td>
<td>189.21</td>
<td>43.97</td>
</tr>
<tr>
<td>5</td>
<td>3.3</td>
<td>174.45</td>
<td>41.15</td>
</tr>
</tbody>
</table>
### Table 3. Determination of chromium in leachates from open cast iron ore mines. Volume of leachate sample used (4 ml)

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Present method (µg)</th>
<th>Reported method (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.401</td>
<td>0.360</td>
</tr>
<tr>
<td>2</td>
<td>0.160</td>
<td>0.120</td>
</tr>
<tr>
<td>3</td>
<td>0.472</td>
<td>0.456</td>
</tr>
</tbody>
</table>

### Table 4. Determination of chromium in steel sample No. BS - 94614

<table>
<thead>
<tr>
<th>Steel sample</th>
<th>Certified value</th>
<th>Chromium found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Present method</td>
</tr>
<tr>
<td></td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>No. BS 94614 (0.1 g)</td>
<td>0.06</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.058</td>
</tr>
</tbody>
</table>
References

12. Reports of Committee on Water Quality Criteria, FWPCA, U.S. Dept. of Interior, **1968**.
22. EQA, *Environmental Quality Act and Regulations*.Malaysia, **2010**.