CHAPTER 2

MATERIALS AND METHODS

2.1 MATERIALS

2.1.1 Polymeric membrane support

Commercial porous flat sheet hydrophobic polytetrafluoroethylene (PTFE) membranes (47mm diameter, porosity 45%) was procured from Sartorius, India.

2.1.2 Metal salts

Metal salts K₂Cr₂O₇, CuSO₄·5H₂O, ZnSO₄·7H₂O and NiSO₄ (AR grade) obtained from Merck (I) Ltd., were used as received for the preparation of feed phase solutions. KOH, Na₂CO₃, NaOH, H₂SO₄ (AR grade) procured from Merck (I) Ltd., were used as received for preparation of the stripping phase. Deionized water was used throughout the investigation.

2.1.3 Carriers

Carriers are often the extractants employed in the conventional solvent extraction process. Carriers play a key role in making an extraction process efficient. Commercial acidic carriers di(2-ethylhexyl)phosphoric acid
(DEHPA) and phosphonic acid (2-ethylhexyl)-mono(2-ethylhexyl)ester (IONQUEST801-IQT801) were received from Albright Wilson, USA (Albright and Wilson Americas, 1995a,b). Their important physical and chemical properties obtained from manufacturer are mentioned in Table 2.1. Solvating extractants tributylphosphate (TBP), tricotylphosphine oxide (TOPO) and isobutylmethylketone (IBMK) were purchased from Merck (I) Ltd. Commercial basic carrier tricaprylmethylammonium chloride (Aliquat336) procured from CDH Chemicals Ltd., India. The appropriate concentrations of the carriers were utilized for impregnation on a polytetrafluoroethylene (PTFE) membrane.

2.1.4 Diluents

The diluents considered for metal and inorganic processing are usually hydrocarbons selected on the basis of a flash point above 60°C to minimize evaporation loss and the risk of fire and with a specific gravity of about 0.8 to aid phase separation. Commercial organic solvents n-hexane and butanol obtained from Merck India Ltd. Kerosene collected at 170-220°C (aliphatic in nature) fraction was used for separation studies.

2.2 EXPERIMENTAL DESIGN

Experimental design of supported liquid membrane (SLM) usually consists of a cell with two compartments. Cells composed of three compartments where two supports of equal (Wodzki and Sionkowski, 1995) or different nature separate the organic and aqueous phases are also in use. Kislik and Eyal (1996a,b) suggest several economical and operational advantages such as the carrier loss, durability and stability of membrane,
<table>
<thead>
<tr>
<th>Physical properties of Commercial Carriers</th>
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</thead>
<tbody>
<tr>
<td><strong>Molecular weight g/mol</strong></td>
</tr>
<tr>
<td>DEHPA (di(2-ethylhexyl)phosphoric acid)</td>
</tr>
<tr>
<td>TOPO (trioctylphosphine oxide)</td>
</tr>
<tr>
<td>IQ7801 (phosphonic acid (2-ethylhexyl)-mono (2-ethylhexyl)ester)</td>
</tr>
<tr>
<td>ALQUAT 336 (tricapryl methylammonium chloride)</td>
</tr>
<tr>
<td>TBP (C_{2}H_{7}O_{3}P) (tributylphosphate)</td>
</tr>
</tbody>
</table>

**Table 2.1 Physical properties of Commercial Carriers**
i) System-I Cr(VI), Ni(II) and Zn(II)

ii) System-II Cr(VI), Ni(II) and Cu(II)

S Ph1-Stripping phase 1: System-I Selective for Cr(VI)

System-II Selective for Cr(VI)

S-Ph2-Stripping phase 2: System-I Selective for Zn(II)

System-II Selective for Cu(II)

M1-Membrane phase 1: System-I PTFE impregnated with TBP carrier

selective for Cr(VI)

System-II PTFE impregnated with TOPO carrier

selective for Cr(VI)

M2-Membrane phase 2: System-I PTFE impregnated with IQT801 carrier

selective for Zn(II)

System-II PTFE impregnated with DEHPA carrier

selective for Cu(II)

Fig. 2.1. Flatsheet supported liquid membrane cell (FSSLM)
different driving forces and compact equipment for their three compartment cell identified as hybrid liquid membrane (HLM). A three compartment cell which contains two membrane support was used in the present study and the schematic description is illustrated in Figure 2.1.

2.3 PREPARATION OF AQUEOUS PHASES

2.3.1 Feed phase

Stock solutions were prepared by weighing appropriate quantity (100ppm) of metal salts ($K_2Cr_2O_7$, $CuSO_4$, $ZnSO_4$ and $NiSO_4$) in deionized water.

2.3.2 Strip phase

Stripping is a physical unit operation in which dissolved molecules are transferred from feed phase to strip phase. The removal of extracted metal from the loaded solvent. The driving force for mass transfer is provided by the concentration gradient between the aqueous phases. Various concentrations of $NaOH$, $Na_2CO_3$, $KOH$ and $H_2SO_4$ were prepared with deionized water.

2.4 SOLVENT EXTRACTION–PRELIMINARY INVESTIGATION

The physical-chemical process of transferring the solute between the bulk of the two immiscible phases is called solvent extraction. Conventional solvent extraction technique was used to select suitable carrier, diluent, stripping agent and effective pH for metal ion separation.
2.5 PREPARATION OF SUPPORTED LIQUID MEMBRANE (SLM)

Membrane support in general is made by adsorbing a solution of a specific carrier in a diluent medium in a microporous polymeric membrane (hydrophobic). The diluent is required to be immiscible with the solutions on the two sides of the membrane and should have low dielectric constant. A microporous PTFE (Polytetrafluoroethylene) membrane was used as a support to hold the various carriers. Before impregnation, the membrane support was presaturated with water for more than two days (Shukla et al, 1996a).

Circular pieces of these dry PTFE membranes were soaked in the carrier solution of different concentrations for 6 hr before use to have uniform adsorption of carrier solution. The membrane was then removed from the organic solution, wiped using filter paper and rinsed with water to ensure the removal of excess carrier by which the impregnated polymeric membrane support was made suitable for separation process.

2.6 SUPPORTED LIQUID MEMBRANE(SLM) - EXPERIMENTS

In the beginning of each run, the membrane impregnated with carrier was first clamped and the apparatus was assembled. Feed solution pH was adjusted to the desired value by dilute sulphuric acid (0.1N). Feed phase containing metal ions and strip phase in aqueous medium were then introduced into the feed and strip chambers respectively. The aqueous solutions were presaturated with the diluent (kerosene) solution of carrier in advance, to prevent the migration of the liquid in membrane to aqueous phase. The mixing
was done to avoid concentration polarization between membrane interfaces and bulk of solution (Anilkumar et al, 1992). When the steady state (about 30min) was reached, a sample was taken from the feed and strip phases at regular time intervals. Further, more original strip solution was added immediately to the strip phase to maintain a constant volume. A digital pH meter with glass and calomel electrodes was used to measure the pH of feed phase.

2.7 CONTROL EXPERIMENTS

Control experiments were carried out with no carrier in the membrane solvent (diluent) proved that there was no permeation of metal ions across the membrane by the membrane solvent itself.

2.8 ENRICHMENT FACTOR

The application of SLM is often aimed at the enrichment of a solute as opposed to selective separation. The flux through the SLM and the attainable enrichment are closely related. Enrichment factor is one of the most common criteria used to evaluate a particular SLM system. In the liquid membrane system the feed phase is usually composed of a more concentrated solution than the stripping phase (Kazushige Nishizawa et al, 1998). The "enrichment factor" (Y), which is defined as the ratio of the concentration of the species in the stripping solution \([S_s]\) to its initial concentration in the feed solution\([S_f]\) (Daoud et al, 1998)

\[
Y = \frac{[S_s]}{[S_f]}
\]
2.9 DETERMINATION OF METAL ION CONCENTRATION

A Varian SpectrAA-200 model atomic absorption spectroscopy (AAS) was used to measure metal ion concentration in feed and strip phases and corrections due to volume replacement were made. Metal ion concentrations were measured in AAS at appropriate wavelengths: chromium 357.9nm, copper 324.7nm, nickel 232.0nm and zinc 213.9nm.

2.10 EXPERIMENTAL DESIGN ANALYSIS AND RESPONSE SURFACE MODELLING

2.10.1 Experimental design – Statistical approach

The classical method of studying one variable at a time while holding all others constant is extremely insufficient in many cases (Stowe and Mayer 1966). Statistically designed experiments are effective because they supply the needed information about the shape of the response surface. They are also efficient because they expend minimum resources. Response surface methodology (RSM) experiments attempt to identify the output or response of a system as a function of the explanatory variables. It is a very powerful statistical tool to design experiments for optimization (Box and Wilson, 1951). It consists of a group of techniques, which are used to study the relationships between one or more measured responses and a number of input (independent) variables (Box et al 1978). The response can be thought of as a surface over the explanatory variables “experimental space”. The results of response surface experiments are used to identify a mathematical statistical relationship between explanatory variable levels and the response and to optimize the system response. The interactions among variables are taken into consideration and the block effects are nullified with RSM experimental design. Factorial design is
employed to show that the design and statistical analysis of experiments allow us to obtain a simple but efficient model for industrial control and to reduce the number and cost of experiments (Garcia et al 1993). Mathematical models have been widely used to help explain and predict the biochemical reactions. Henika (1984) developed and used response surface techniques for many industrial applications.

2.10.2 Experimental design

In order to assess the effects of separation efficiency of heavy metal ions using flat sheet supported liquid membrane (FSSLM), the response surface methodology was adopted (Khuri and Cornell, 1987).

2.10.3 Response surface methodology

Response surface methodology (RSM) was used for designing the various experiments during optimization. RSM is a set of technique that encompasses

♦ Designing a set of experiments (or setting up a series of experiments) that will yield adequate and reliable measurements of the response of interest

♦ Determining a mathematical model that best fits the data collected from the design chosen above, by conducting appropriate test of hypothesis concerning the model parameters.

♦ Determining the optimal settings of the experimental factors that produce the maximum or minimum value of the response
If obtaining the best value of the response is beyond the available resource level of the experiment, then response surface methods are aimed at obtaining at least a better understanding of the overall system. When the behaviour of the measured response of interest is governed by certain laws which lead to a deterministic relationship between the response and the set of experimental factors chosen, it should then be possible to determine the best values of the factors to optimize a desired output. However, quite often an empirical approach is necessary because the relationship is either too complex or unknown.

2.10.4 SIMILARITY BETWEEN REGRESSION ANALYSIS AND RESPONSE SURFACE METHODOLOGY (RSM)

In any system in which variable quantities change the interest might be in accessing the effects of the factors on the behaviour of some measurable quantity. Such an assessment is possible by regression analysis. Using data collected from a set of experimental trials, regression help to establish empirically, by fitting a numerical model relating the type of relationship that is present between the response variable and is denoted as response of the system. The levels of the influencing factors are called explanatory, regressor or input variables. Regression cause and effect relationships having applications in the physical biological and social sciences as well as in biotechnology. Response surface methods are additional techniques employed before doing and after a regression analysis is performed on the data. Preceding the regression analysis the experiment must be designed that is the input variables must be selected and their values during the actual experimentation designated. After the regression analysis is performed certain numerical model testing procedures and optimization techniques are applied.
Thus, the subject of RSM includes the application of regression as well as other techniques in an attempt to gain a better understanding of the characteristics of the response system under study.

2.10.5 Factors

Factors are processing conditions or input variables whose values or settings can be controlled by the experimenter.

2.10.6 Response

The response variable is the measured quantity whose value is considered to be affected by changing the levels of the factors.

2.10.7 Contour representation of a response surface

This is a technique used to help visualize the shape of a three dimensional response surface to plot the contours of the response surface. In a contour plot, lines or curves of constant response values are drawn on a graph or plane whose coordinate axis represent the levels, $X_1, X_2$ and $X_3$ of the factors. The lines (or curves) are known as contours of the surface. Each contour represents a specific value for the height of the surface (i.e. a specific value of $Y$) above the plane defined for combinations of the factors. Geometrically, each contour is a projection onto the $X_1, X_2$ plane of a cross section of the response surface made by a plane parallel to the $X_1, X_2$ plane, cutting through the surface. The plotting of different surface height values enables one to focus attention on the levels of the factors at which the changes occur in the surface shape.
The analysis of variance table

Following the program of experimentation, the data are analyzed and the results of the analysis are displayed in the table form. The table is called an ANOVA table. The entries in the table represent measures of information concerning the separate sources of variation in the data. The total variation in a set of data is called the total sum of squares (SST). The quantity SST is computed by summing the squares of the deviations of the observed Y_n's about their average value, \( Y = (Y_1 + Y_2 + \ldots + Y_n)/N \) and \( Y_n \) = observed response for \( n^{th} \) axial.

\[
SST = \sum_{U=1}^{N} (Y_n - Y)^2 \quad (2.1)
\]

The quantity SST has associated with it \( N - 1 \) degrees of freedom since the sum of the deviations, \( Y_n - Y \), is equal to zero. The total sum of squares can be partitioned into two parts; the sum of squares due to regression (or sum of squares explained by the fitted model) and the sum of squares unaccounted by the fitted model. The formula for calculating the sum of squares due to regression (SSR) is

\[
SSR = \sum_{n=1}^{N} (\hat{Y}(X_n) - Y)^2 \quad (2.2)
\]

The deviation \( \hat{Y}(X_n) - Y \) is the difference between the value predicted by the fitted model for the \( n^{th} \) observation and the overall average of the \( Y_n \)'s. If the fitted model contains \( p \) parameters, then the number of degrees of freedom associated with SSR is \( p - 1 \). The sum of squares unaccounted for the fitted model (SSE) is
The quantity $SSE$ was called the sum of squares of the residuals. The number of degrees of freedom for $SSE$ was defined previously as $N - p$ which is the difference $(N - 1) - (p - 1) = N - p$.

The usual test of the significance of the fitted regression equation is a test of the null hypothesis $H_0$: all values of $\beta_i$ (excluding $\beta_0$) are zero. The alternative hypothesis is $H_a$: at least one value of $\beta_i$ (excluding $\beta_0$) is not zero. Assuming normality of errors, the test of $H_0$ involves first calculating the value of the $F$-test

$$F = \frac{\text{Mean Square Regression}}{\text{Mean Square Residual}} = \frac{SSR/(p - 1)}{SSE/(N - p)}$$

If the null hypothesis is true, the $F$-test in the above equation follows an $F$ distribution with $p - 1$ and $N - p$ degrees of freedom in the numerator and in the denominator, respectively.

### Table 2.2 Analysis of Variance (sample table)

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Degrees of freedom(DF)</th>
<th>Sum of squares (SS)</th>
<th>Mean square(MS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Due to regression (Fitted Model)</td>
<td>$p - 1$</td>
<td>$SSR$</td>
<td>$SSR/(p - 1)$</td>
</tr>
<tr>
<td>Residual (Error)</td>
<td>$N - p$</td>
<td>$SSE$</td>
<td>$MSE = SSE/(N - p)$</td>
</tr>
<tr>
<td>Total</td>
<td>$N - 1$</td>
<td>$SST$</td>
<td></td>
</tr>
</tbody>
</table>
If the value of $F$ in above equation exceeds $F_{\alpha, p, N - p}$, then the null hypothesis is rejected at the $\alpha$ level of significance and we infer that the variation accounted for by the model (through the values of $b_{h,i} \neq 0$) is significantly greater than the unexplained variation.

An accompanying statistic to the $F$-test of the above equation is the coefficient of determination:

$$r^2 = \frac{SSR}{SST}$$

(2.5)

The value of $r^2$ is a measure of the proportion of total variation of the values of $Y_u$ about the mean $Y$ explained by the fitted model. It is often expressed as a percent by multiplying the ratio SSR/SST.

2.10.9 Predicted response surface

The response surface is the one that relates the response with the variable considered in the study. If $X_1, X_2, \ldots, X_k$ are the variables considered then the response predicted is given as

$$\hat{y} = \delta (X_1, X_2, \ldots, X_k)$$

(2.6)

The function $\delta$ is called the true response surface and is assumed to be a continuous function of $X_i$. The structural form of $\delta$ is usually unknown and therefore, an approximate form is sought using a polynomial or some other type of empirical equation. Observations are made with different combinations of the variables $(X_1, X_2, \ldots, X_k)$ and the parameters of the model is estimated.
Tests are then performed on the magnitudes of the coefficient estimates as well as on the model from itself and if the fitted model is considered to be satisfactory, it can be used as a prediction equation. The response may be a simple linear equation or may be a polynomial equation of higher order. However, the number of observations made should be always greater than the number of parameters to be estimated.

The relationship $\hat{y} = \hat{\beta}_0 + \hat{\beta}_1 x_1 + \hat{\beta}_2 x_2 + \cdots + \hat{\beta}_k x_k$ between $Y$ and the levels of $k$ factors may be represented by a "hypersurface". With $k$ factors, the response surface is a subset of a $(k+1)$-dimensional euclidean space that can be represented in a two dimensional space, whereas the solid surface is visualized in a 3D space, the third dimension representing the height of the surface above the 2D plane. In a 2D response surface, the lines indicate the locus of points that gives a particular response. The location of the point of maximum response is called the "point of maximum response" and may be obtained by measuring the response function.