Investigation of the oxalic acid extraction with different extractant in the emulsion type liquid membrane

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ABSTRACT

Emulsion liquid membranes have been studied for since the last thirty years. It is one of the most advantageous techniques of separation at the present. Biosynthetic products separation (antibiotics, amino acids, and carboxylic acids), metals recovery from hydrometallurgical and nuclear industry wastes is important applications. In the present work, oxalic acid was extracted and concentrated from aqueous solutions. The emulsion liquid membrane system was used. This system consists of a diluent (Escaid 100, Toluene and Kerosene) a surfactant (Span 80) and an extractant (Alamine 300, Amberlite LA-2, TOPO, TBP) and Na\textsubscript{2}CO\textsubscript{3} were used as a stripping solution. In order to find an optimal operating condition, we investigated the effects of various experimental variables, such as type of diluent and extractant, mixing speed of feed solution, extractant concentration, feed solution pH, stripping solution concentration, surfactant concentration. It was optimized by Artificial Neural Networks (ANN).

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1. INTRODUCTION

Organic acids, widely used in the food, pharmaceutical and chemical industries, are important chemicals. Oxalic acid and oxalates are useful as reducing agents for photography, bleaching, and rust removal. They are widely used as a purifying agent in pharmaceutical industry, precipitating agent in rare-earth metal processing, bleaching agent in textile and wood industry, rust-remover for metal treatment, grinding agent, waste water treatment. Fermentation technology for the production of organic acids in particular has been known for more than a century and acids have been produced in aqueous solutions. They have severe inhibiting effects on the rate of conversion and thus several separation methods, such as liquid extraction, chromatographic methods, evaporation, ultrafiltration, reverse osmosis, dialysis, crystallization, precipitation and drying, have been practised to remove acids from reactants in Kahya (2001) and Hauer (1994). These steps increase the production costs. So the conventional route of organic acid production is uneconomical.

The classical process to recover a carboxylic acid from a wide variety of dilute aqueous effluents including wastewaters is based on precipitation of the calcium salt upon addition of calcium hydroxide to the acid aqueous solution. After a complete filtration, the treatment of the solid phase with sulphuric acid leads to preferential precipitation of calcium sulphate. The free organic acid in the resulting aqueous filtrate is first purified by ion exchange resins and then evaporated to give crystals of the acid. In a few cases, since the yield of final crystallization was relatively low, a solvent extraction technique can be considered as an attractive alternative to recover the valuable organic acid in Malmary (1997). Reactive liquid-liquid extraction of organic
acids by a suitable extractant has been found to be a promising alternative to the conventional processes in Wennersten (1983), Kertes (1986), Poposka (1998), Uslu (2009). Tertiary and quaternary amines such as Alamine 336 and Aliquate 336 form ion pairs with the undissociated carboxylic acids, which result in higher extraction efficiencies. With a phosphorus-bonded oxygen donor extractant such as tributyl phosphate, the extraction process results from the solvating character of the phosphoryl group, which acts as a strong Lewis base. The specific behaviour of phosphorus extractants in the process of acid extraction has been investigated in previous works in Shevchenko (1963), Shah (1981). Oxalic acid was extracted by various extractant in Kirsch (1996), Qin (2001), Lebedev (2008), Bames (1999), Qui (2010). Various solvents have been used for extraction of carboxylic acids. The use of liquid membranes offers an alternative method to solvent extraction process for selective separation and concentration of various solutes from aqueous dilute solutions. Solute transport across a liquid membrane is a combination of extraction and stripping in a single stage unit operation process. This process provides maximum yield of the extracted solute with minimum inventory and power consumption. Recently, Manzak (2004, 2010, 2011) have studied the extraction of some carboxylic acids with trioctyl amine (TOA), trioctyl methyl ammonium chloride (Aliquate 336) and Alamine 336 as extractants in emulsion liquid membranes.

2. EXPERIMENTAL

2.1. Reagents

The emulsion liquid membrane consists of a surfactant, an extractant, and a diluent. The non-ionic surfactant is Span 80, which is also called sorbitan monooleate. The
carrier Alamine 300 was obtained from Cognis Corp. A carrier is a secondary amine. Also, Amberlite LA-2 is a mixed N-lauryltrialkyl-methyl amine. A commercial kerosene, (TUPRAS Oil Company, Turkey), Toluene, Escaid 100 (from ExxonMobil) were used as diluents. Amberlite LA-2, TOPO (Tri-\textit{n-}octylphosphine oxide), TBP (tributyl phosphate), Na$_2$CO$_3$ were purchased from Merck.

2.2. Membrane preparation

The liquid membranes consisted of a carrier, a surfactant and a diluent. This mixture is emulsified at mixing speed of 2000 rpm by speed mixer. The stripping solution (50 mL Na$_2$CO$_3$) was added drop wise to the membrane solution. The solution is stirred continuously for 30 min to obtain a stable ELM. The liquid membrane was added to a feed solution in 600 mL beaker. A variable speed mixer stirred the two-phase system. Diluent type, mixing speed, carrier concentration, pH, the stripping solutions and surfactant concentration were varied to observe their effect on the extraction of oxalic acid.

2.3. Analysis of carboxylic acid

All experiments were performed at room temperature. All aqueous solutions were prepared using deionized water. The concentrations of oxalic acid in the feed from the batch ELM experiments were analyzed using an HPLC apparatus equipped with a 4.6 mmx250 mm Hypersil C18 ODS column and detected with UV detector (Shimadzu SPD-M20A) at 210 nm.

3. RESULTS AND DISCUSSION

3.1. Effect of the extractant type
The efficiency of tertiary amines in recovery of various organic acids has since been proposed and proved in many works in Yabannavar (1987), Thakur (2008). Amberlite LA-2 (seconder amine), Alamine 300 (tertiary amine), TOPO and TBP were used as an extractant. Amberlite LA-2 provided a better performance compared to the other extractant, as shown in Figure 1.

Fig. 1 The effect of extractant type on the extraction of oxalic acid [Diluent: Escaid 100, (90%, w/w), surfactant: Span 80 (5%, w/w), extractant: Amberlite LA-2, Alamine 300, TOPO, TBP (5%, w/w), feed phase concentration: (1.52, w/v), feed mixing speed: 300 rpm, stripping phase: 50 mL (5%, w/v) Na$_2$CO$_3$, treatment ratio (V$_F$/V$_E$): 5/2, phase ratio (V$_S$/V$_M$): 1/1, feed mixing speed: 300 rpm, emulsion mixing speed: 2000 rpm].
Fig. 2 The effect of extractant type on the extraction of oxalic acid [Diluent: Kerosen (90%, w/w), surfactant: Span 80 (5%, w/w), extractant: Amberlite LA-2, Alamine 300, TOPO, TBP (5%, w/w), feed phase concentration: (1.52, w/v), feed mixing speed: 300 rpm, stripping phase: 50 mL (5%, w/v) Na$_2$CO$_3$, treatment ratio ($V_F/V_E$): 5/2, phase ratio ($V_S/V_M$): 1/1, feed mixing speed: 300 rpm, emulsion mixing speed: 2000 rpm].

3.2. Effect of diluent

Different organic diluents produce changes in emulsion stability, percentage of extraction, enrichment factor and swelling in Kulkarni (2000). Kerosene, Toluene, Escaid 100 were used as diluents. Escaid 100 is the commercial product of ExxonMobil.
and aliphatic kerosene, which is a complex mixture. Escaid 100 provided a better performance compared to the other diluents (Fig. 1, Fig. 2 and Fig. 3). The amines can be dissolved in various solvents such as aliphatic, aromatics, C4 or higher alcohols, and combinations of these. Usually different diluents were used to modify the physical properties of the extractants (viscosity, density, and surface tension). Diluents help in reducing the viscosity of the amines and thus increasing the diffusion rate of the complex. The role of diluent is not only to improve the physical properties of the extraction system, but it also removes the interaction product. The organic diluent with lower viscosity does not seem to have a better extraction rate. It is shown in toluene (Fig. 3). The properties of the diluents are given in Table 1.

Table 1: Some properties of diluents

<table>
<thead>
<tr>
<th>Diluent type</th>
<th>Dielectric constant</th>
<th>Viscosity (mPa s)</th>
<th>Density (kg/m³)</th>
<th>Aromatics (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.24</td>
<td>0.59</td>
<td>860</td>
<td>100</td>
</tr>
<tr>
<td>Kerosene</td>
<td>2.2</td>
<td>1.6</td>
<td>830</td>
<td>15</td>
</tr>
<tr>
<td>Escaid 100</td>
<td>—</td>
<td>1.6</td>
<td>815</td>
<td>24</td>
</tr>
</tbody>
</table>

3.3. Effect of mixing speed of feed solution

Effects of mixing speed on the extraction of oxalic acid are shown in Fig. 4. It was observed that for an increase in mixing speed from 300 to 500 rpm, the extraction rate of oxalic acid was increased, when the mixing speed increases, the size of emulsion globules dispersed in the external phase decreases, and thus leading to a higher surface area for mass transfer in Kulkarni (2000), Lee (2010). Unlimited increase in the rate of stirring speed can cause unwanted situation. Emulsion may be broken. As a result, the most appropriate mixing speed was 500 rpm.
Fig. 4 The effect of mixing speed of feed solution [Diluent: Escaid 100 (90%, w/w), surfactant: Span 80 (5% w/w), extractant: Amberlite LA-2 (5%, w/w), feed phase concentration: (1.52, w/v), stripping phase: 50 mL (5%, w/v) Na$_2$CO$_3$, treatment ratio ($V_F/V_E$): 5/2, phase ratio ($V_S/V_M$): 1/1, emulsion mixing speed: 2000 rpm]

3.4. Effect of extractant concentration

Extractant plays a significant role in ELM process. The effect of Amberlite LA-2 concentration on the extraction of oxalic acid was studied from 5 to 7 wt%. It was shown in Fig. 5. Considering of data, it is seen that an increase in concentration from 5 to 7% leads to an increase in the extraction rate. The enhanced stability of the emulsions containing higher concentration of carrier could be attributed to their higher viscosities.
3.5. Effect of feed solution pH

The pH value of aqueous feed solution affects the ionisation of carboxylic acids. The pH of the feed phase varied from 1.8 to 3, as shown in Fig. 6. The extraction of oxalic acid decreases with increasing pH. As the pH increases, the resulting decrease in the external phase hydrogen ion concentration decreases the extent to which the amine can couple with the oxalic acid, and thus the rate of extraction decreases.
Fig. 6 The effect of feed phase pH on the extraction of oxalic acid [Diluent: Escaid 100 (90%, w/w), surfactant: Span 80 (5%, w/w), extractant: Amberlite LA-2 (5%, w/w), feed phase concentration: (1.52, w/v), stripping phase: 50 mL (5%, w/v) Na₂CO₃, treatment ratio (V_F/V_E): 5/2, phase ratio (V_S/V_M): 1/1, feed mixing speed: 300 rpm, emulsion mixing speed: 2000 rpm]

3.6. Effect of stripping solution concentration

The selection of suitable stripping solution is considered to be one of the main factors to occur for an effective ELM. A driving force for extraction of oxalic acid in the ELM system can be prepared from a pH difference between the feed and the stripping phases. The transport of organic acids necessarily requires a simultaneous back-extraction or stripping step at the opposite side of the membrane. In the stripping process, the extractant is regenerated and the organic acid is stripped. Na₂CO₃ was used as the stripping solution. The effect of Na₂CO₃ concentration in the stripping solution was investigated and the results are shown in Fig. 7. The extraction increases with the increase in sodium carbonate concentration. The stripping concentration of 5% (w/v) was accepted as the most stable concentration.
Fig. 7 The effect of stripping phase concentration on the extraction of oxalic acid
[Diluent: Escaid 100 (90%, w/w), surfactant: Span 80 (5% w/w), extractant: Amberlite LA-2 (5%, w/w), feed phase concentration: (1.52, w/v), feed mixing speed: 300 rpm, stripping phase: 50 mL (5%, w/v) Na₂CO₃, treatment ratio (V_F/V_E): 5/2, phase ratio (V_S/V_M): 1/1, feed mixing speed: 300 rpm, emulsion mixing speed: 2000 rpm]

3.7. Effect of surfactant concentration

The selection of suitable surfactant is important factor for solute extraction. Increasing of surfactant concentration enhanced the stability of emulsion liquid membrane. The membrane breakage ratio usually led to diminish with the increase in surfactant concentration. Too little surfactant renders the membrane weak. The experiments were performed with the surfactant concentration ranging 5% to 9% and the results are shown in Fig. 8. Excess surfactant leads to lower extraction due to make the higher interfacial resistance. It was observed that a concentration of 7 wt.% was accepted as the best surfactant concentration for oxalic acid.
Fig. 8 The effect of surfactant concentration on the extraction of oxalic acid [Diluent: Escaid 100 (90, 88, 86%, w/w), surfactant: Span 80 (5, 7, 9% w/w), extractant: Amberlite LA-2 (5%, w/w), feed phase concentration: (1.52, w/v), feed mixing speed: 300 rpm, stripping phase: 50 mL (5%, w/v) Na$_2$CO$_3$, treatment ratio (V$_F$/V$_E$): 5/2, phase ratio (V$_S$/V$_M$): 1/1, emulsion mixing speed: 2000 rpm]

3.8. Extraction mechanism

Amberlite LA-2 is a high molecular weight, oil soluble secondary amine that can be reaction with acids to form the corresponding amine salts. It ensures the removal of acids from aqueous solutions. Furthermore, the anions which are associated with the amine salt in the organic phase are free to enter into an exchange reaction with other anions in an aqueous solution to form a new, oil-soluble but water-insoluble amine salt. The steps of the proposed transport mechanism are as follows:

In the extraction step, the Amberlite LA-2 reacts with the oxalic acid and forms an acid-amine salt at the interface between the feed and membrane phases in Eq.1

\[
R_2 NH_{(org)} + H_2C_2O_4_{(aq)} \leftrightarrow (R_2 NH_2^+)_2 C_2 O_4^{2-}_{(org)} \]

(1)

Transport of the amine salt followed by stripping at the interface between the membrane and internal phase, after the amine salt had diffused across the membrane, the complex reacts with the stripping solution (Na$_2$CO$_3$) at the membrane-stripping phase interface, as indicated in Eq.2.

\[
(R_2 NH_2^+)_2 C_2 O_4^{2-}_{(org)} + Na_2CO_3_{(aq)} \rightarrow (R_2 NH_2^+)_2 CO_3^- + Na_2C_2 O_4_{(aq)} \]

(2)
Transport of amine carbonate with CO$_2$ disengagement and seconder amine regeneration at the interface between the membrane and external phases in Eq.3

\[(R_2 NH_3^+)_2 CO_3^{2-} \rightarrow 2R_2 NH_{(org)} + CO_2 + H_2O\]  

3.9. ANN model

The standard network that is used for function fittings is a two-layer feedforward network, with a sigmoid transfer function in the hidden layer and a linear transfer function in the output layer. The number of hidden layers was set to 20 and output layer was 1. The training continued until the validation error failed to decrease for 7 iterations.

Figure 9 shows regression plots. They display the network outputs with respect to targets for training, validation and test sets. All the data sets fall along the perfect line that shows the network outputs are almost equal to the targets. For our case fit is reasonably good for all data sets, with R values close to 1 in each case.

![Regression plots](image-url)
Figure 10 shows the error bars for training, validation and testing. The blue bars represent training data, the green bars represent validation data, and the red bars represent testing data. This histogram clearly indicates the outliers in the experimental data. Most of the data fall in a very small area that shows very small error values.

![Error Histogram with 20 Bins](image)

**Fig. 10** The error bars for training, validation and testing

The model predicts efficiency of extraction with average error <1%. The performance of the ANN models were assessed through mean square error (RMSE), mean absolute error (MAE), and correlation coefficient (R). The modeling results indicated that there was an excellent agreement between the experimental data and predicted values (Fig.11).

![Comparison of measured and predicted results for train and test sets](image)

**Fig.11** The comparision of measured and predicted results for train and test sets (a,b)
4. CONCLUSION

An emulsion liquid membrane process using Amberlite LA-2, Alamine 300, TOPO, TBP as a carrier to extract the oxalic acid from aqueous solutions was conducted. The influence of such parameters as extractant type, diluent type, mixing speed, extractant concentration, feed solution pH, stripping concentration, surfactant concentration were examined and the optimum conditions were experimentally determined. Among the diluents of toluene, kerosene and Escaid 100, the diluent Escaid 100 showed better performance than the others, that is, the extraction efficiency of more than 90% could be achieved within about 20 min. It appears that the organic diluents with lower viscosity do not seem to have a better extraction rate. In this study, the best extractant was found as Amberlite LA-2 for oxalic acid extraction. The extraction rate is sensitive to the feed pH. The extraction rate and ultimate yield of oxalic acid increase with decreasing pH. The modeling results indicated that there was an excellent agreement between the experimental data and predicted values.

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