

A Review on Emulsion liquid Membranes on heavy metal separation

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Abstract: Membranes are classified into polymer, ceramic and liquid membranes. Liquid membranes are our concern and they are further classified into emulsion and immobilized(supported) membranes. Preparation method, characteristics, advantages and disadvantages of emulsion liquid membranes are being discussed. Separation of different components using emulsion liquid membrane, the surfactants used, percentage extracted, diluents, carriers and other important parameters that distinguish various methods with respect to the membrane efficiency are briefed out. Separation of Anionic dye (Congo red), Crystal violet and methylene blue dye, Silver are being considered and are discussed below.

Keywords: Cadmium, Chromium(6), aniline, emulsion, anionic dye (Congo red).

Introduction

Membrane is a selective barrier that allows the passage of certain constituents and retains other constituents found in the liquid. The most common driving force used in membrane process are pressure and concentration gradients. The two types of membranes are biological and synthetic membranes. The synthetic membranes are further classified into liquid, polymeric and ceramic membranes. The synthetic membrane are used in reverse osmosis, gas permeation, filtration etc. Liquid membrane is literally a membrane usually made of liquid. It consists of liquid phase existing either in supported or unsupported form that serves as a membrane barrier between two phases of aqueous solution or gas mixtures. There are two types of liquid membrane

- Emulsion liquid membrane (ELM).
- Immobilised(supported) liquid membrane (ILM).

Emulsion Liquid Membrane

It can be visualised consisting of “bubbles within a bubble”. The inner most bubble is the receiving phase and outer bubble is the separation “skin” containing the carriers. Anything outside the bubble is the source phase. Formation of emulsion is a disadvantage with respect to separation towards the end.

Types of emulsions

- Oil in water (o/w) – In this oil is the dispersed phase and water is the dispersion medium.
- Water in oil (w/o) – In this water is the dispersed phase and oil is the dispersion medium.
- Multiple emulsions are also available for example water-oil-water, oil-water-oil.

Materials

Emulsifiers

An emulsifier(also known as emulgent) is a substance or a material that stabilises the emulsion by increasing its kinetic stability, one type of emulsifier used is “surfactant”

Carriers

Carrier protein facilitate the movement of substances by facilitated movement or active transport. It involves in movement of molecules,ions,macromolecules etc.

Diluents

A diluent(also called fillers or thinners) is a substance added to decrease the viscosity that helps in reducing the pumping and transportation cost.Aliphatic diluents are generally used for membrane preparation because of its low solubility in water. Thinners are used to make the membrane more stable.

Determination and calculation

Percentage extraction = [(initial concentration in feed) – (concentration after extraction)] x 100 / initial concentration¹

Percentage swelling = [(volume of emulsion after extraction) – (volume of emulsion before extraction)] x 100 / initial volume²

Emulsion liquid membrane preparation

In this membrane, the organic phase is created by using diluent,carrier and emulsifiers/surfactants.organic phase is mixed with aqueous solution to form a emulsion and the emulsion is agitated with the external solution(source from recovery).After the agitation, the mixture is separated using separating funnel.

Stability of emulsion liquid membrane

The stability of membrane is the major factor for determining the separation process. The stability of the emulsion is determined by the formation of monolayer by the surfactant between the oil and aqueous phases.The stability can be found by conducting the experiment with different feed concentrations. Stability can also be found with the help of breakage ratio which is defined as

Breakage Ratio = [(Concentration of Compounds in external Aqueous Phase)(Volume of the external Aqueous Phase)]/[(Conc Of Compounds In Internal Aqueous Phase)(Conc Of Internal Aqueous Phase)]³ which is shown in (Table- 1)

Table 1: Separation of different components using emulsion liquid membrane

Parameter	Separation of					
	Anionic dye (Congo red) ⁴	Crystal violet and methylene blue dye ⁵	Cadmium ⁶	Chromium (6) ¹	Aniline ⁷	Silver ^{8,9}
Surfactant	Sorbitanmonooleate(span 80)	Span 80	Polyamine type	Span 80	Span 80	Span 80
Surfactant concentration	4%	5%	4%	3%	2%	2.5%
Diluents used	Hexane,toluene, benzene	Methylene chloride.	Toluene,cyclohexane, kerosene(less efficient)	Kerosene	Kerosene	Kerosene

Acid	Hydrochloric acid,sulphuric acid,nitric acid.	Hydrochloric acid,sulphuric acid,nitric acid	Acetic acid,nitric acid, hydrochloric acid.	hydrochloric acid,0.1N sulphuric acid,0.1N nitric acid.	Hydrochloric acid(3M)	Nitric acid
Internal solution	Sodium bicarbonate (Na ₂ CO ₃)	-	-	-	Hydrogen chloride solution	Phosphoric acid
Stirring speed(rpm)	200	280	150-200	275-350	500	3000
Emulsification time(mins)	5	-	3	4	4	3
volume ratio	1/1	1	2	30/25 (phase ratio)	1/3	1/1
Extraction efficiency	-	MB-99% CV-95%	96%	93.5%	99.5%	99.24%
De emulsifier	2 methyl 2 propanol(tertiary butyl alcohol	-	-	-	2 propanal	-

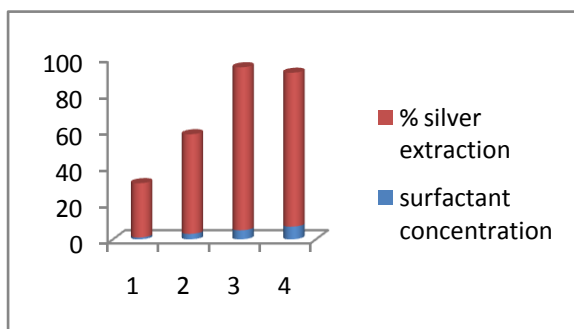
Effect of surfactant concentration

Emulsion stability increases if the surfactant concentration increases upto a certain allowable limit. In the referred paper surfactant concentration is increased from 1% to 7% ,this increases the emulsion stability and extraction which result in a decreased mass transfer. Below 1% concentration the emulsion is not stable because they break easily and the emulsion stability increases by increasing the surfactant concentration. Excess surfactant increases the resistance and viscosity of the interface as a result of that at 7% concentration extraction again decreased^{8,9} which is discussed in (Table-2 & Figure-1)

Table 2: Extraction of silver at different surfactant concentrations

Surfactant concentration	%silver extraction
1	30
3	55
5	90
7	85

Figure 1: Extraction of silver at different surfactant concentrations



Effect of emulsification time

Removal percentage increases if the emulsification time is shorter. Longer emulsification time reduces emulsion stability which results in high emulsion breakage. The extraction is increased by increasing the emulsification time from 5-20 mins. At 5 min emulsification time, the swelling is minimum. Increasing the emulsification time increases the swelling therefore emulsification time is taken as 5 mins. the time where the swelling is minimum is taken as suitable emulsification time.

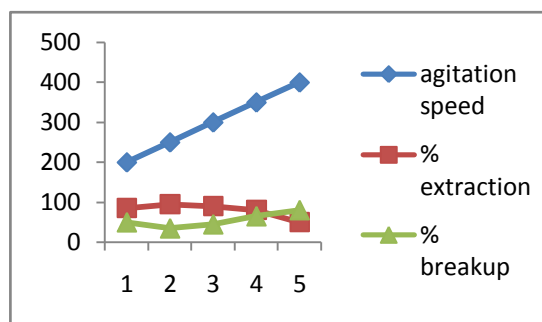
Effect of agitation speed

Extraction of compounds increases if the agitation speed increases upto a certain limit due to increase in contact area and reduction in emulsion globule size. Extraction of silver increases in the speed range between 200-250 rpm and further increase in agitation speed to 400 rpm decreases the extraction from 95-50% due to increase in the percentage breakup of emulsion. Increase of agitation speed above the critical value affects both the extraction efficiency and the emulsion stability (the emulsion becomes unstable) ^{8,9}. (Table- 3 & Figure- 2)

Table 3: Effect of agitation on extraction and emulsion breakup

Agitation speed	% extraction	% breakup
200	85	50
250	95	35
300	90	45
350	80	65
400	50	80

Figure 2: Effect of agitation on extraction and emulsion breakup



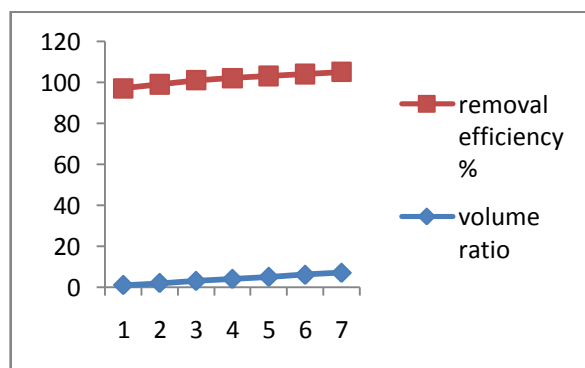
Effect of volume ratio

Increase of volume ratio of oil phase to internal phase, shifts the internal size distribution which results in increased emulsion stability for a certain range. This increased emulsion stability increases the extraction efficiency¹⁰. If the volume ratio varies from 0.3 to 1, emulsion stability increases because the rejection of internal phase is easy. Emulsion is stable for volume ratio from 1-1.5 and then decreases after 1.5 (Table- 4 & Figure- 3)

Table 4: Volume ratio on extraction efficiency

Volume ratio	Removal efficiency %
1	96
2	97
3	98
4	98
5	98
6	98
7	98

Figure 3: Volume ratio on extraction efficiency



Conclusion

Membranes currently available are vast and are used for various applications with respect to separation processes. In this review, the basic features of emulsion liquid membrane have been discussed. Factors like surfactant concentration, agitation speed, emulsification time, volume ratio which affect the percentage

extraction have been briefed with technical datas. Change in the surfactants and their concentrations along with alterations in emulsion preparation methods are the scope for new efficeient liquid membranes.

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