



Removal of dyes and their mixtures from aqueous solution using liquid emulsion membrane

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ABSTRACT

Extraction of dyes from aqueous solution was studied using liquid emulsion membrane. Study was carried out using two dyes, namely, crystal violet (CV) and methylene blue (MB). Extraction of single component system of each dye and their binary mixture were investigated. Liquid emulsion membrane was formed using *n*-heptane as membrane phase, sodium hydroxide solution as the internal phase and dye solution as the external phase. Surfactant span 80 was used as the emulsion stabilizer. Effects of concentration of span 80, concentration of NaOH, stirring speed, composition of feed solution and the volume ratio of the oil phase to the aqueous phase (O/A) were studied in detail both for single and binary system. Maximum extraction of MB was found to be 99% and that for CV was about 95% in single component system. In binary mixture, these values were 97% and 90%, respectively.

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1. Introduction

Disposal of large volume of wastewater containing toxic organic solutes is a common problem, of many industries. Adequate treatment is therefore required before disposal of industrial waste. Continuous research efforts are being made either to treat such effluents for facilitating easy disposal, or to recover the chemicals and recycle the process water.

Emulsion liquid membranes are demonstrated to have significant potential as an effective tool for treatment of various industrial wastes since their invention [1,2]. Many studies have been carried out using emulsion liquid membrane (ELM) for the recovery of metal ions [3,4], phenol [5], organic acids [6,7], sephalexin from dilute solution [8], aniline [9] and bioactive materials [10]. Recovery of textile dye from an aqueous solution has been studied by supported liquid membrane using vegetable oil as liquid membrane [11]. Liquid emulsion membranes are essentially double emulsion, i.e., water/oil/water (w/o/w) systems or oil/water/oil (o/w/o) systems. The main advantage of liquid surfactant membranes are: (i) fast extraction rates due to availability of high specific surface area; (ii) extraction and stripping in one stage only so that the product can be separated and concentrated simultaneously; (iii) possibility of extraction from very dilute solutions.

Stability of w/o/w emulsions is generally understood as the resistance of the individual globules against coalescence [12]. The breakdown of w/o/w type dispersions is described through several possible mechanisms (Florence and Whitehill, 1981), which include: (i) coalescence of the internal aqueous droplets into larger internal droplets; (ii) coalescence of the oil droplets suspended in the aqueous phase; (iii) the expulsion of the internal droplets following rupture of the thin oil films during the interaction of the internal and external aqueous phases [13,14]; and (iv) swelling or contraction due to water permeation through the oil membrane by diffusion [15–17]. In emulsion-type liquid membrane process, surfactant plays a very important role. It influences the emulsion stability and the transport rate of the solute. With the increase of surfactant concentration, emulsion stability improves; however, the extraction rate decreases due to the presence of more surfactant molecules at the reaction site, aqueous–organic interface. This problem may be resolved by the use of a new type of surfactant, known as bi-functional surfactant, which acts as an emulsifier and an extractant as well [3,18,19].

In the present work, experimental studies have been carried out to remove dyes, methylene blue and crystal violet, from aqueous solution using LEM technique. Removal of both single component and their binary mixture are investigated. The effects of concentration of surfactant span 80, NaOH, stirring speed, feed dye concentration and ratio of oil phase to aqueous phase (O/A) have been examined in detail. The optimum operating conditions for the

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extraction of two dyes (methylene blue and crystal violet) in single as well as in binary mixture are evaluated experimentally.

2. Experimental

2.1. Materials

Surfactant span 80 (sorbitan monooleatet), methylene blue (MB) and crystal violet (CV) were obtained from Loba Chemie, Mumbai, India and SD Fine-Chem Ltd., Mumbai, India, respectively. *n*-Heptane was procured from SRL, Mumbai, India. Sodium hydroxide (NaOH) pellets were obtained from Merck. All the chemicals were used without further treatment.

2.2. Procedure

2.2.1. Emulsion preparation

Twenty milliliters of *n*-heptane was added to accurately measured span 80 (concentration varying from 1% to 8% (w/w)) in a beaker. NaOH concentrations were varied from 0.01 to 0.5 (M) and added drop by drop while the system was being stirred at 2500 rpm. The final volume was around 80 ml. The system was stirred for about 20 min resulting in stable emulsion.

2.2.2. Extraction process

Around 200 ml dye-containing feed was taken in a beaker and the solution was stirred using a magnetic stirrer in the range of 300–600 rpm. Around 40 ml (1/5th of feed) of stable liquid emulsion was added to the feed. The emulsion slowly begun to get dispersed. Samples were drawn at regular interval upto 60 min and were collected in clean and dry test tubes. Each sample was subjected to gravity settling for around 25 min. The emulsion being lighter was collected at the top and clear solution was present at the bottom in each test tube. The clear solution was sent for analysis. The extraction of dye is evaluated as Extraction (%) = $100 \times (C_0 - C_t)/C_0$, where C_0 is the initial concentration and C_t is the concentration at time t .

2.3. Analysis

The concentration of dyes at the clear solution extracted from the feed was determined by UV spectrophotometer (make: Thermo Spectronic, USA; model: GENESYS 2). The standard method was used to calculate the concentration of dyes in their binary mixture [20].

2.4. Operating condition

The operating parameters were span 80 concentrations, NaOH concentration, feed dye concentration and stirring speed during extraction. Operating conditions for single dye system and binary mixture are shown in Tables 1 and 2, respectively.

3. Results and discussion

3.1. Effect of surfactant concentration

Surfactant concentration is an important factor as it directly affects the stability, swelling and break up of LEM. Fig. 1 represents the variation of percentage extraction of CV for various span

Table 1
Experimental scheme for single component

Span 80 (% w/w)	1, 3, 5, 7, 8
NaOH (M)	0.01, 0.03, 0.05, 0.1 and 0.5
Stirring speed (rpm)	280, 430 and 620
Feed conc. (ppm) CV/MB	5, 15, 20 and 25
Oil phase/aqueous phase (v/v)	1, 2, 4 and 10

Table 2
Experimental scheme for binary mixture

Span 80 (% w/w)	1, 3, 5, 7, 8
NaOH (M)	0.01, 0.03, 0.05, 0.1 and 0.5
Stirring speed (rpm)	280, 430 and 620
Feed conc. (ppm)	
CV	2.5, 7.5, 10 and 12.5
MB	2.5, 7.5, 10 and 12.5
Oil phase/aqueous phase (v/v)	1, 2, 4 and 10

80 concentrations. It is observed from this figure that the percentage extraction of CV increases upto 5% of span 80 concentrations and decreases thereafter. At lower surfactant concentrations (less than 5%), emulsions break easily leading to poor extraction. At higher surfactant concentration (beyond 5%), although the membrane stability increases, mass transfer resistance also increases due to presence of more surfactant at aqueous–organic phase interface, resulting in less transfer of dye molecules to internal phase. Thus the dye extraction is reduced. It is observed from Fig. 1 that dye extraction is maximum (~95%) at span 80 concentrations of 5%. It may be observed from Fig. 1 that the dye extraction is slightly reduced after about 35 min of separation. This may be due to diffusion of sodium salt of CV from internal phase. Although this effect is marginal.

Effect of surfactant concentration on the extraction of MB is presented in Fig. 2. In case of MB, almost 100% extraction is achieved at the surfactant concentration of 5%. Below 5%, the extraction is reduced as discussed earlier. It may be observed from this figure that extraction of MB reaches a constant value after about 45 min, due to reduction in driving force (i.e., the concentration gradient of MB between external and internal phase). Comparing this figure with Fig. 1, two trends are apparent. Firstly, extraction profile of CV is faster than MB. Secondly, unlike CV, MB extraction does not fall below the maximum level at any of the surfactant concentration. The structure of MB is shown in Appendix A, Fig. A1. The chloride ion in MB is surrounded by three benzene rings. These benzene rings provide steric hindrance to any molecule trying to reach the reacting chloride ion in MB. This is a plausible explanation for the reduced reaction rates in case of MB. On the other hand, although CV molecule is bigger in size, less hindered chloride ion reacts easily. Therefore, reaction of CV in internal phase favors faster transport

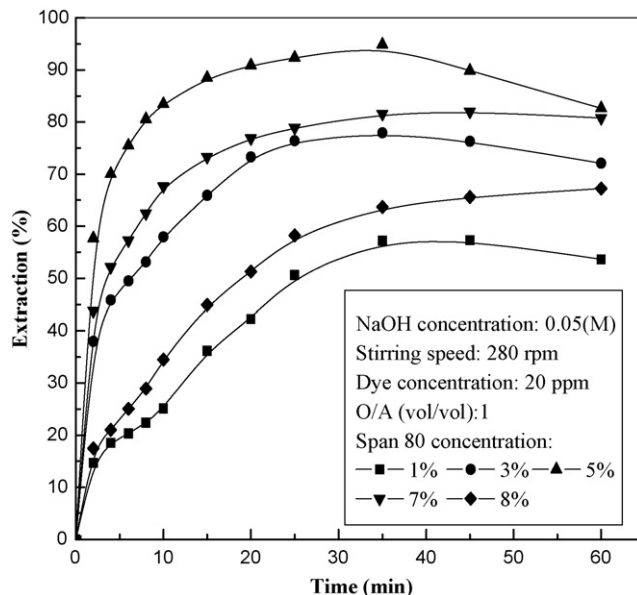


Fig. 1. Variation of % extraction of CV with time for different span 80 concentration.

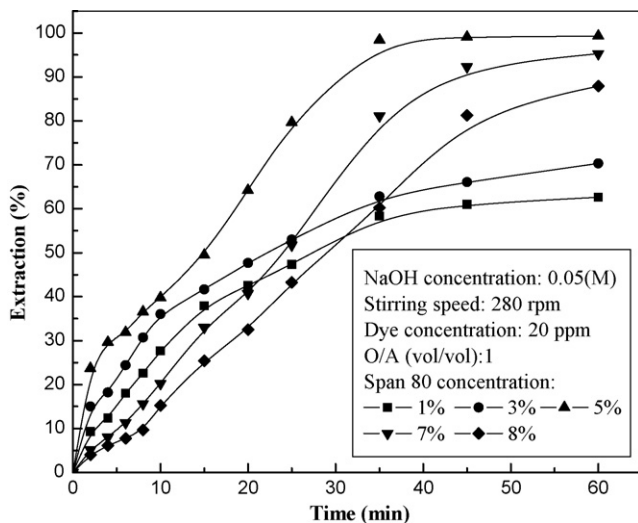


Fig. 2. Variation of % extraction of MB with time for different span 80 concentration.

of CV to the internal phase. Thus the extraction profile of CV stabilizes at an earlier time of operation. The amount of NaOH used is approximately equal to that required according to the stoichiometry of its reaction with the respective dyes. As the reaction with CV is very fast, NaOH present in the inner phase gets depleted at an earlier time as compared to the case with MB. Therefore the chance of leakage of MB into the external phase is small. Ho and Li presented a concept where the solute can transfer from the internal phase of an LEM system to the external phase by two mechanisms: diffusional transport and breakage [21]. But, solute can transfer from the external phase to the internal phase only by diffusional transport. Our experiments indicate that for CV the breakage and subsequent leakage of CV into the external phase, over time, manifests itself as a drop in percentage extraction, whereas this phenomenon is absent for experiments with MB for the time of operation used herein.

Extraction profile of the dye mixture is presented in Fig. 3 for various concentrations of surfactant. The qualitative observations are similar to those of one-component system as discussed earlier. Two distinctly new observations are evident from this figure. Firstly, the extraction values of both components are slightly less than the single component system. For example, at 5% surfactant concentration, percent extractions of CV and MB in mixture

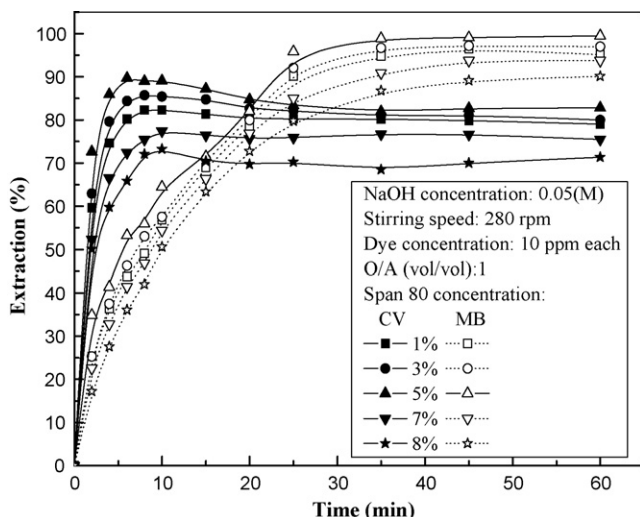


Fig. 3. Effect of span 80 concentrations in binary mixture.

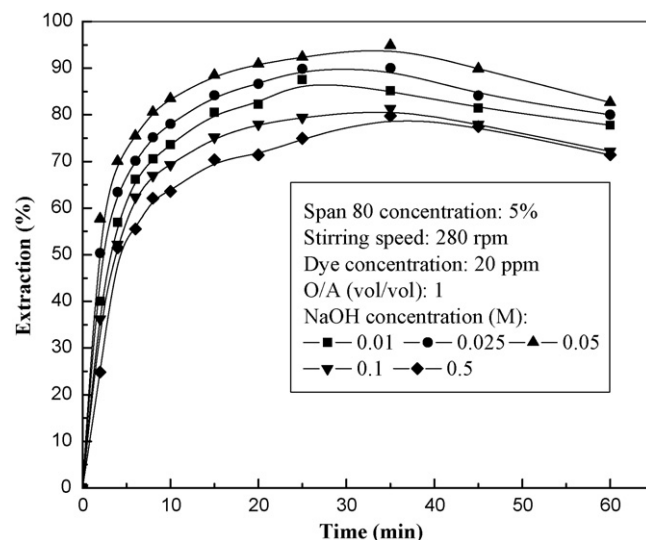


Fig. 4. Variation of % extraction of CV with time for different NaOH concentration.

are 90% and 97%, respectively, compared to 95% and 99% in their single-component system. This is due to competitive transport and reaction of two dyes. Secondly, percentage extraction of both CV and MB is quicker compared to one component system. For example, maximum extraction of CV and MB takes place at 35 and 45 min, respectively for single dye system whereas maximum extraction of these dyes takes place at 5 and 35 min, respectively in case of mixture. The presence of three benzene rings around the reactive chloride ion in MB causes steric hindrance. No such hindrance to the reaction site is present in CV and hence the extraction CV is faster as compared to MB. In the mixture, unlike CV, MB extraction does not fall below the maximum level for reasons already discussed.

3.2. Effect of NaOH concentration

Effect of NaOH concentration in the internal phase on the extraction of CV is shown in Fig. 4. It is observed that maximum extraction (95%) occurs at NaOH concentration of 0.05 (M). At higher concentration (beyond 0.05 (M)), extraction of dye decreases. At lower concentration (below 0.05 (M)) of NaOH, almost all reactant (NaOH) is consumed in the internal phase resulting in lower extraction efficiency. At concentration above 0.05 (M), excess NaOH causes swelling of emulsion leading to destabilization of liquid membrane system, causing reduction in percentage extraction.

Effect of NaOH concentration on the extraction of MB is presented in Fig. 5. The observations are similar to those in case of CV (Fig. 4). In this case also, the optimum value of NaOH concentration is found to be 0.05 (M). Effect of NaOH concentration on the extraction of CV–MB mixture is shown in Fig. 6. The optimum NaOH concentration is found to be 0.05(M) in this case as well. Compared with one component system (refer Figs. 4 and 5), it is observed that percentage extraction of each dye is slightly less than the single component system as discussed earlier. It is interesting to note that time required for stabilization of percentage extraction profile is much less in case of dye mixture compared to single component system. For example, 35 and 45 min are required for stabilization for CV and MB, respectively in single dye system whereas only 5 and 35 min are required for these dyes in their mixture. This is due to preferential reaction of CV with NaOH in the internal phase as discussed earlier.

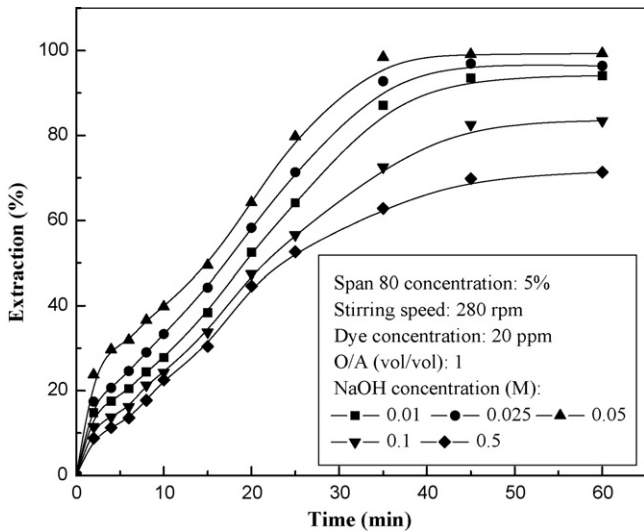


Fig. 5. Variation of % extraction of MB with time for different NaOH concentration.

3.3. Effect of stirring speed

Stirring speed during extraction is an important factor. Effects of stirring speed on the extraction of CV are shown in Fig. 7. It is observed that at earlier period of operation, extraction is more at higher stirring speed. This trend is observed during initial 15 min. At higher stirring speed, smaller sized emulsion droplets are formed leading to more surface area for mass transfer. But at the same time, higher stirring speed adversely affects the stability of emulsion globules leading to breakage. Therefore percentage extraction decreases in the long run. It is observed from Fig. 7 that maximum extraction (95%) occurred at 35 min and with a stirring speed of 280 rpm. Beyond 15 min, percentage extraction decreases with rpm. Similar observations are made in case of extraction of MB from Fig. 8. In this case, percentage extraction increases with rpm upto about 35 min. Beyond that, breakage of emulsion occurs and extraction of MB decreases with rpm. Maximum extraction observed is about 99% at 280 rpm at the end of operation. Effects of rpm on extraction of dye mixture are presented in Fig. 9. The trends are qualitatively similar to the single component system (Figs. 7 and 8). In the case of mixture, the maximum extraction decreases compared to single component system due to competitive transport of

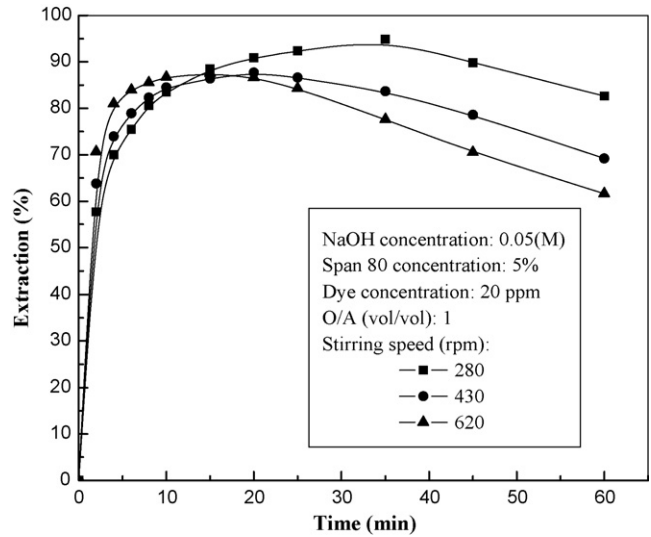


Fig. 7. Variation of % extraction of CV with time for different stirring speed.

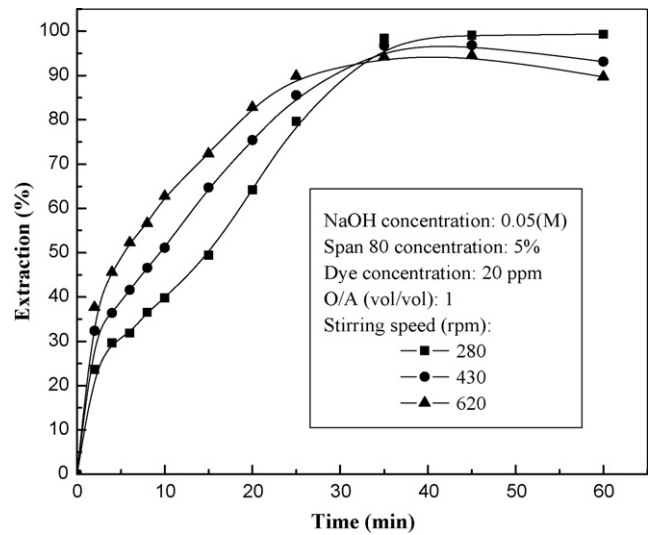


Fig. 8. Variation of % extraction of MB with time for different stirring speed.

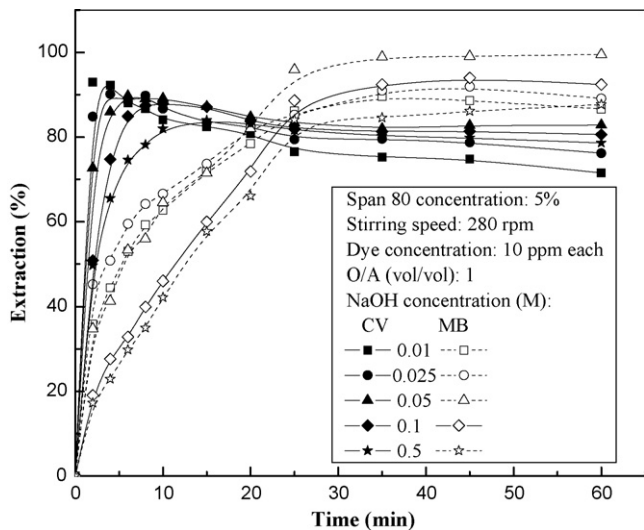


Fig. 6. Effect of NaOH concentration in binary mixture.

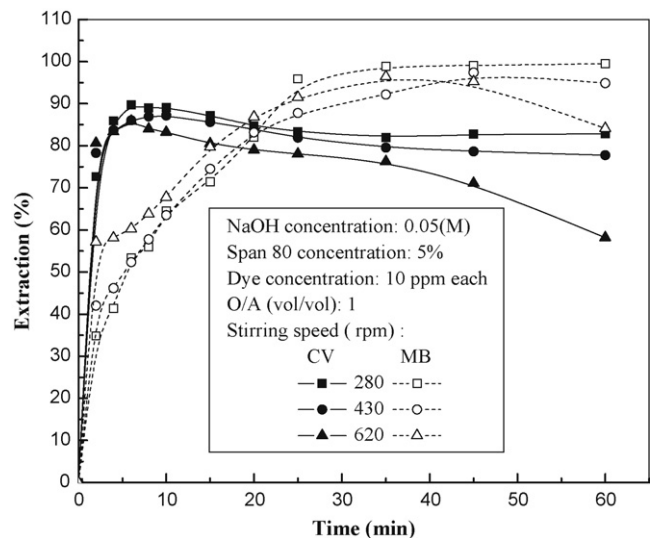


Fig. 9. Effect of stirring speed in binary mixture.

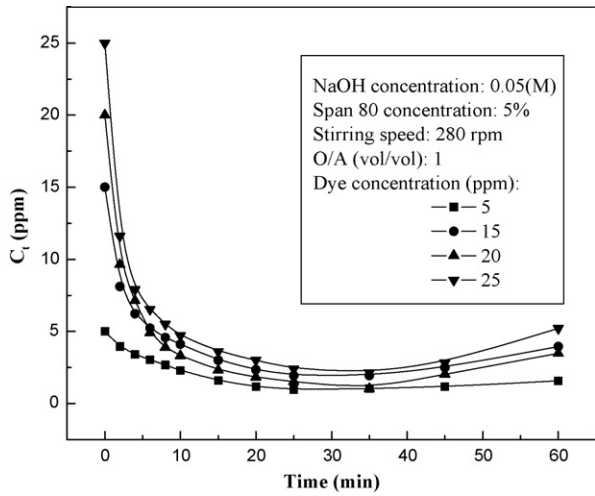


Fig. 10. Variation of CV concentration with time for different feed CV concentrations.

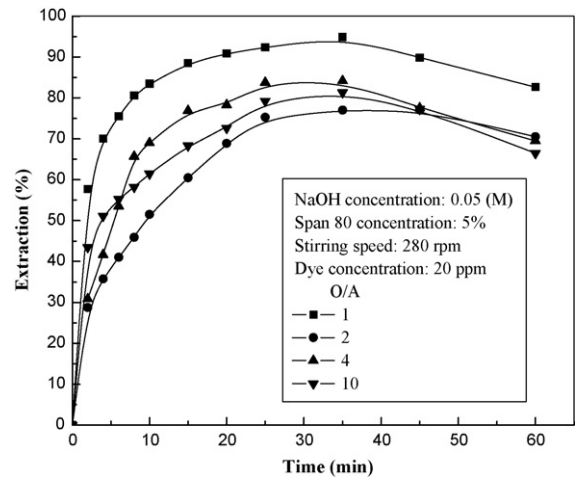


Fig. 13. Variation of % extraction of CV with time for different O/A ratio.

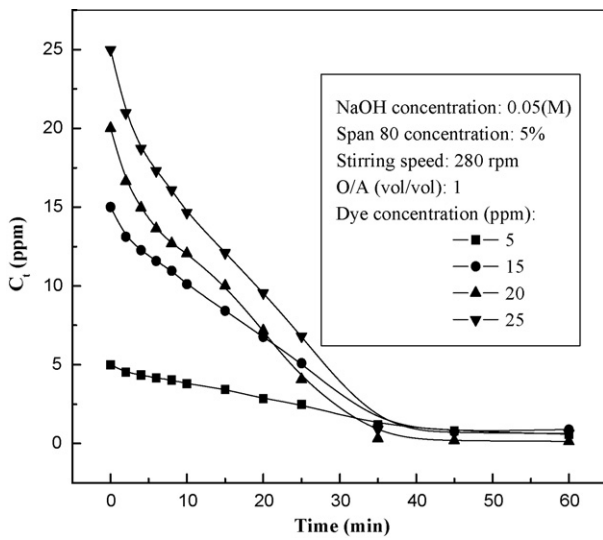


Fig. 11. Variation of MB concentration with time for different feed MB concentrations.

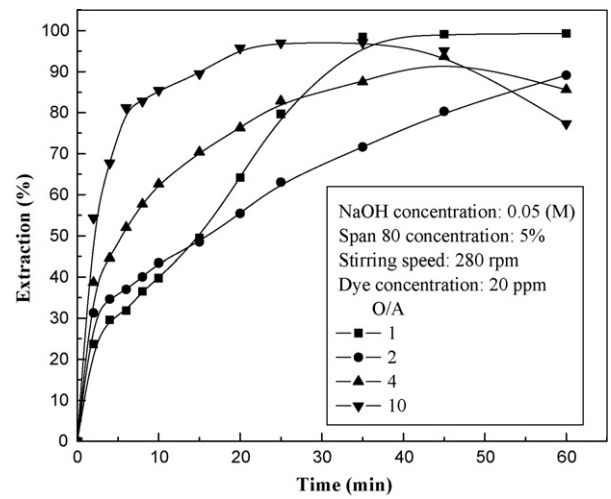


Fig. 14. Variation of % extraction of MB with time for different O/A ratio.

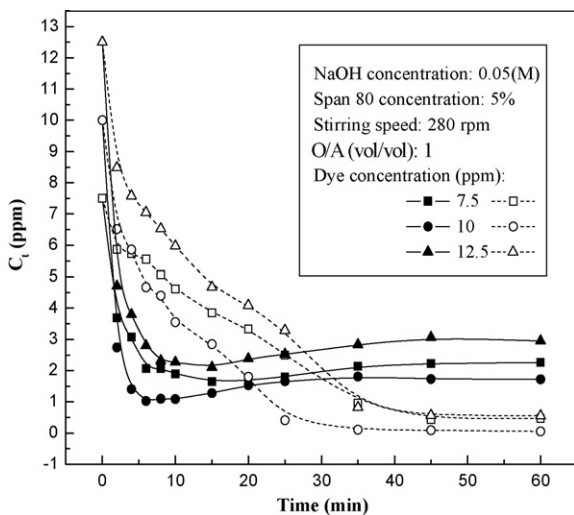


Fig. 12. Effect of dye concentration in binary mixture.

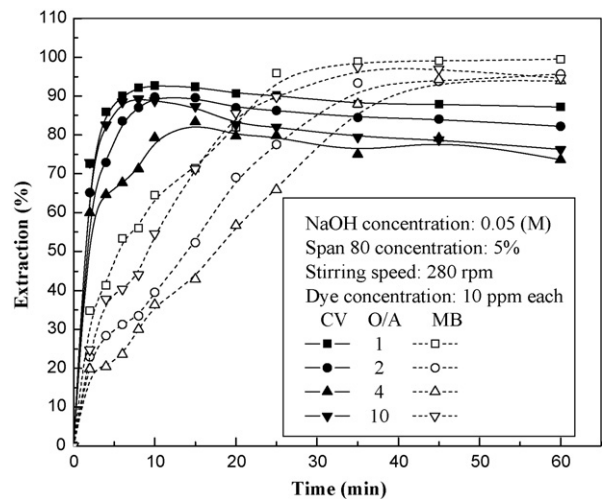


Fig. 15. Effect of volume ratio of the oil phase to the aqueous phase (O/A) in binary mixture.

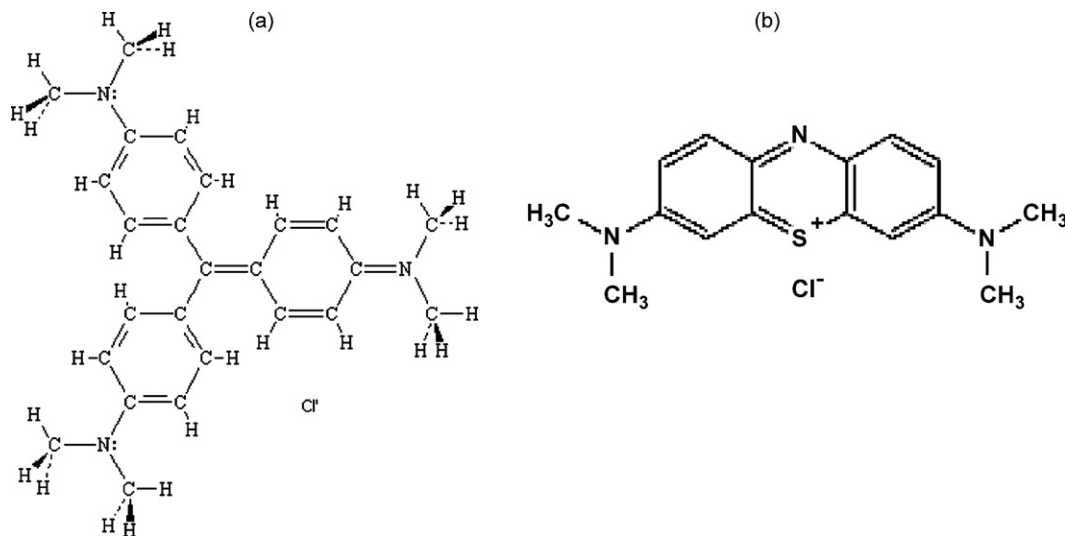


Fig. A1. Structure of: (a) crystal violet and (b) methylene blue.

dyes. Maximum extraction for CV is found to be 90% and that for MB is about 97%.

3.4. Effect of feed concentration

Effects of feed concentrations of dye on the liquid membrane system are shown in Fig. 10, in case of CV. It is observed from this figure that dye concentration in the external phase decreases sharply upto about 15 min and then remains almost constant upto about 35 min and increases slightly thereafter. This effect is prominent at higher dye concentration. With increase in dye concentration in the external phase, the driving force for dye transport to the internal phase increases. This leads to a sharp decline of dye concentration of the external phase up to about 10 min (see Fig. 10). The dye concentration in the external phase remains approximately constant after that. The slight increase in dye concentration in the external phase beyond 35 min can be explained by possible breakdown of some of the globules and/or leakage of CV through the liquid membranes back to the external phase. Effect of feed concentration on LEM system in case of MB is shown in Fig. 11. In case of MB, external phase dye concentration decreases upto about 40 min and remains almost constant thereafter. As discussed earlier, there is no leakage of MB and hence, dye concentration in external phase remains constant almost at zero level indicating almost 99% extraction. Effects of feed concentration in dye mixture are presented in Fig. 12. The trends obtained are similar to single component system. Compared to single component system, the dye concentration in the external phase at the end of operation is slightly higher (indicating lower percentage extraction) due to competitive transport of dyes as discussed earlier.

3.5. Effect of volume ratio of the oil phase to aqueous phase (O/A)

In the removal of organic and inorganic pollutants from the solutions using the liquid emulsion membrane (LEM) technology, the volume ratio of the oil phase to the aqueous phase (O/A) plays an important role. Oil phase provides more resistance to the solute transport but at the same time it offers more stability to emulsion droplets [21]. Fig. 13 shows that extraction of CV is achieved best when the volume ratio of the oil phase to aqueous phase is 1. With increase in this ratio, the extraction decreases as concentration of NaOH in the aqueous phase decreases. It is also seen from this figure that there is little emulsion breakage in most of the cases and it is most profound in case of minimum aqueous phase volume. The

effect of volume ratio of oil phase to aqueous phase for the extraction of MB is presented in Fig. 14. The extraction efficiency is also maximum for the ratio (O/A) of 1. The trend is almost similar to that of CV. Effect of volume ratio of the oil phase to the aqueous phase (O/A) in binary mixture is shown in Fig. 15. It is seen that the breakage in the emulsion takes place earlier in case of mixture. Here also best extractions of two dyes are achieved with O/A ratio of 1.

Recovery of dyes using liquid membrane system is scant in literature [11], whereas removal of metal ions and aromatic compounds is well studied [3–5,7,9]. Recovery of textile dye (astacryl golden yellow) from its synthetic solution was studied by supported liquid membrane using various vegetable oils as liquid membrane [11]. The optimum stirring speed was found to be 350 rpm. The maximum recovery of dye was in the range of 80–95%. Maximum efficiency for removal of dyes found in this work is about 96–99% for single component system and that is from 90% to 95% for binary mixture.

4. Conclusion

A study of recovery of two dyes, namely CV and MB, separately and simultaneously by emulsion liquid membrane is undertaken. The effects of concentration of span 80, concentration of NaOH, stirring speed, composition of feed solution and the volume ratio of the oil phase to the aqueous phase are studied both for single and binary system. The optimum span 80 and NaOH concentrations are found to be 5% and 0.05 (M), respectively for a feed concentration of 20 ppm. The optimum stirring speed for extraction is 280 rpm. Maximum extraction of MB is found to be 99% and that for CV is about 95% in single component system. In binary mixture, these values are 97% and 90%, respectively. The maximum extractions of both the dyes are achieved with the volume ratio of the oil phase to the aqueous phase (O/A) of 1. Maximum extraction of CV and MB takes place at 35 and 45 min, respectively for single dye system whereas maximum extraction of these dyes takes place at 5 and 35 min, respectively. Unlike CV, MB extraction does not fall below the maximum level for any of the parameters at its optimum condition. This technology seems to have a promising future in the treatment of aqueous effluents containing dyes in moderate concentrations, allowing their recovery and reuse.

Appendix A

Fig. A1

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