# Chapter 10
Emulsion Liquid Membrane

Abstract Emulsion liquid membranes are widely used for recovery of metal ions and organics due to the fast extraction and are a single-stage operation of stripping-extraction. Essentially emulsion liquid membranes are double emulsions which are made stable with surfactants. Separation of dyes using such an emulsion technique is quite novel and new, being researched only for the last one or two decades. The chapter introduces the details of the technique and the efficacy of the method in removing dye-contaminated wastewater.

Keywords Liquid emulsion • Surfactant • Dye • Droplet • Alkali

Emulsion liquid membranes are demonstrated to have significant potential for treatment of various industrial wastes since their invention (Li 1968, 1971). Many studies have been carried out using emulsion liquid membrane (ELM) for recovery of metal ions (Uddin and Kathiresan 2000; Kargari et al. 2006), phenol (Ng et al. 2010), organic acids (Itoh et al. 1990; Hone and Yang 1994), cephalexin from dilute solution (Sahoo and Dutta 1998), bioactive materials (Thien and Hatton 1988), and aniline (Datta et al. 2003). A schematic showing a typical liquid emulsion membrane droplet is shown in Fig. 10.1. Recovery of textile dye from an aqueous solution has been studied by supported liquid membrane using vegetable oil as liquid membrane (Muthuraman and Palanivelu 2006). Liquid emulsion membranes are essentially double emulsion, i.e., water/oil/water (w/o/w) system or oil/water/oil (o/w/o) system. The main advantages of liquid surfactant membranes are (1) fast extraction rates due to availability of high specific surface area, (2) extraction and stripping in one stage only so that the product can be separated and concentrated simultaneously, and (3) 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 (Hou and Papadopoulos 1996). The breakdown of w/o/w-type dispersions is described through several possible mechanisms (Florence and Whitehill 1981) that include (1) coalescence of the internal aqueous droplets into larger internal droplets, (2) coalescence of the oil droplets suspended in the aqueous phase, (3) the expulsion of the internal droplets following rupture of the thin oil films during the interaction of the internal and external aqueous phases (Li et al. 1988; Sanyal et al. 1998), and (4) swelling or contraction due to water permeation through the oil membrane by diffusion (Xuan-cai and Fu-quan 1991;

Fig. 10.1 Liquid emulsion
membrane droplet

Continuous phase
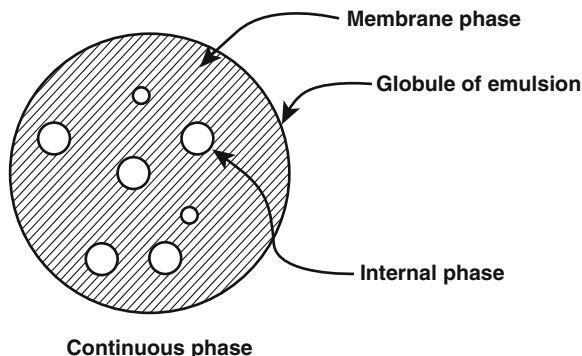
Zihao et al. 1996; Wan and Zhang 2002). In emulsion-type liquid membrane process, surfactant plays a very important role. It influences the emulsion stability and the transport rate of the solute. With the increase of surfactant concentration, emulsion stability improves; however, the extraction rate decreases due to presence of more surfactant molecules at the reaction site, aqueous-organic interface. This problem may be resolved by use of a new type of surfactant, known as bifunctional surfactant, which acts as an emulsifier and an extractant as well (Jee et al. 1985; Wodzki et al. 1990; Uddin and Kathiresan 2000).

Methylene blue (MB) and crystal violet (CV) are removed from aqueous solution using ELM technique. Removal of both single component and their binary mixture is investigated. The effects of concentration of surfactant span 80, NaOH, stirring speed, and feed dye concentration are presented herewith.

10.1   Emulsion Preparation

20 ml n-heptane was added to span 80 (concentration varying from 1 to 8 (wt/wt) %) in a beaker. NaOH concentration was varied from 0.01(M) to 0.5 (M) and added drop by drop, while the system was stirred at 2500 rpm. The final volume was 80 ml. The system was stirred for about 20 min resulting in stable emulsion. 200 ml feed containing dye was taken in a beaker, and the solution was stirred using a magnetic stirrer in the range of 300–600 rpm. 40 ml (1/5th of feed) of stable liquid emulsion was added to the feed. The emulsion slowly gets dispersed. Samples were drawn at regular intervals up to 60 min and were collected in clean and dry test tubes. Each sample was subjected to gravity settling for 25 min. The emulsion being lighter was collected at the top, and clear solution was present at the bottom in each test tube.

10.2 Effect of Surfactant Concentration

Surfactant concentration is an important factor as it directly affects the stability, swelling, and breakup of ELM. Figure 10.1 presents the variation of percentage extraction of CV for various span 80 concentrations. It is observed from this figure that the percentage extraction of CV increases up to 5% of span 80 concentration and decreases thereafter. At lower surfactant concentration (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 reducing dye extraction. It is observed from Fig. 10.2 that dye extraction is maximum (~95%) at span 80 concentration of 5%. It may be observed that the dye extraction is slightly reduced after 35 min of separation. This may be due to diffusion of sodium salt of CV from internal phase. However, this effect is marginal.

Effect of surfactant concentration on the extraction of MB is presented in Fig. 10.3. 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 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. 10.2, two trends are apparent. First, extraction profile of CV is faster than MB. Second, unlike CV, MB extraction does not fall below the maximum level at any of the surfactant concentration. It is observed that, in MB, the reacting chloride ion is surrounded by three benzene rings providing steric hindrance, and the huge electron cloud associated with these rings makes the reaction difficult. 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 of CV. Thus, the extraction

Fig. 10.2 Variation of extraction of CV with time for different span 80 concentrations (Reproduced from Das et al. (2008). With permission from Elsevier)
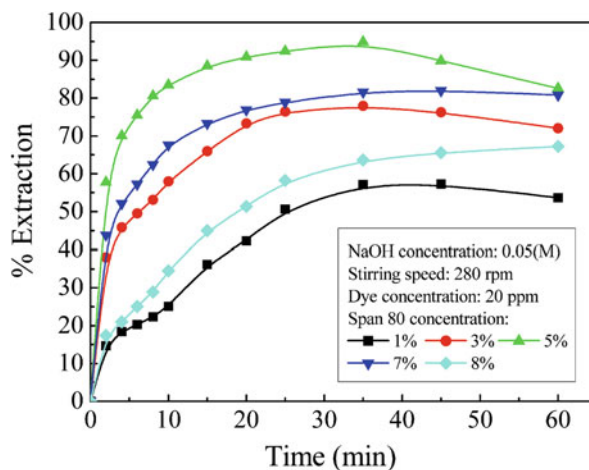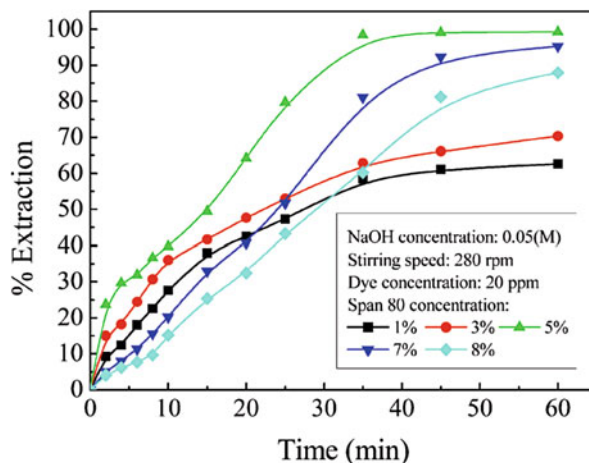
Fig. 10.3 Variation of %
extraction of MB with time
for different span
80 concentrations
(Reproduced from Das et al.
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profile of CV stabilizes at an earlier time of operation. The amount of NaOH used is
approximately equal to that required according to the stoichiometric 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 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 ELM system to
the external phase by two mechanisms: diffusive transport and breakage (Ho and Li
1984). But, solute can transfer from the external phase to the internal phase only by
diffusive transport. Our experiments indicate that for CV, the breakage and subse-
quent 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. 10.4 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, percentage extraction of CV and MB in mixture is 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 min 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. As discussed previously, the reaction
of CV is preferred over MB due to absence of pi clouds, leading to development of
extraction profiles faster in CV compared to MB. In the mixture, unlike CV, MB
extraction does not fall below the maximum level for reasons already discussed.

Fig. 10.4 Effect of span 80 concentration in binary mixture (Reproduced from Das et al. (2008). With permission from Elsevier)
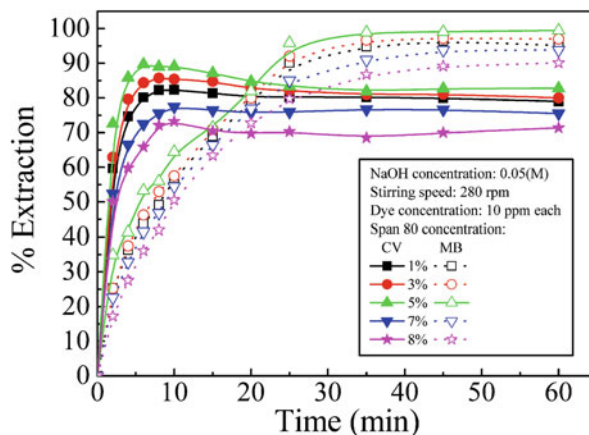
10.3 Effect of NaOH Concentration

Effect of NaOH concentration in the internal phase on the extraction of CV is shown in Fig. 10.5. 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. 10.6. The observations are similar to those in case of CV (Fig. 10.5). 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. 10.7. The optimum NaOH concentration is found to be 0.05 M in this case as well. Compared with one component system (refer to Figs. 10.5 and 10.6), 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 min 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. 10.5 Variation of
extraction of CV with time
for different NaOH
concentrations (Reproduced
from Das et al. (2008). With
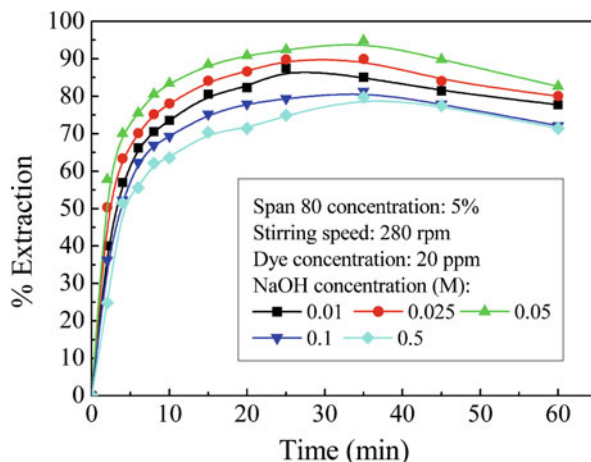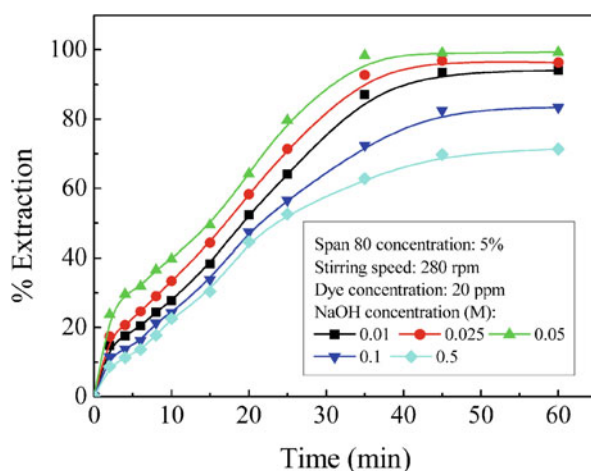permission from Elsevier)

Fig. 10.6 Variation of %
extraction of MB with time
for different NaOH
concentrations (Reproduced
from Das et al. (2008). With
permission from Elsevier)

10.4   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. 10.8. 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. 10.8 that maximum extraction (95%) occurs 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. 10.9. In this case,

Fig. 10.7 Effect of NaOH concentration in binary mixture (Reproduced from Das et al. (2008). With permission from Elsevier)
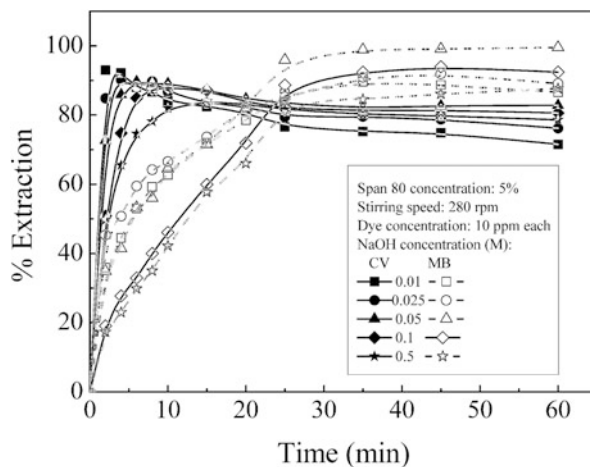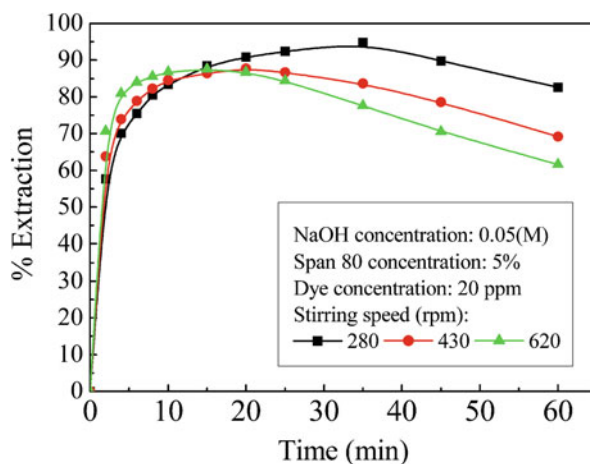

Fig. 10.8 Variation of extraction of CV with time for different stirring speeds (Reproduced from Das et al. (2008). With permission from Elsevier)

percentage extraction increases with rpm up to 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. 10.10. The trends are qualitatively similar to the single component system (Fig. 10.8 and 10.9). In the case of mixture, the maximum extraction decreases compared to single component system due to competitive transport of dyes. Maximum extraction for CV is found to be 90% and that for MB is about 97%.

Fig. 10.9 Variation of
extraction of MB with time
for different stirring speeds
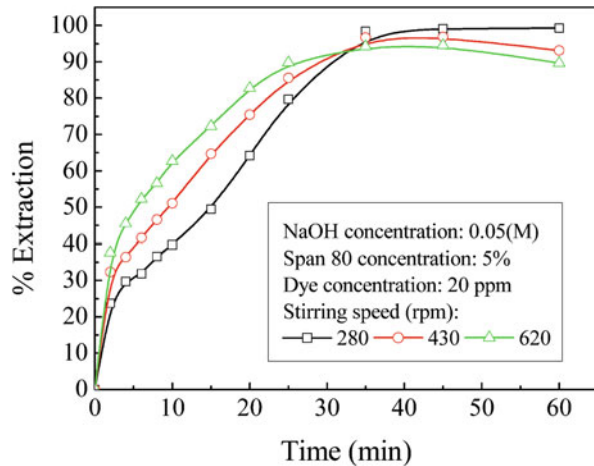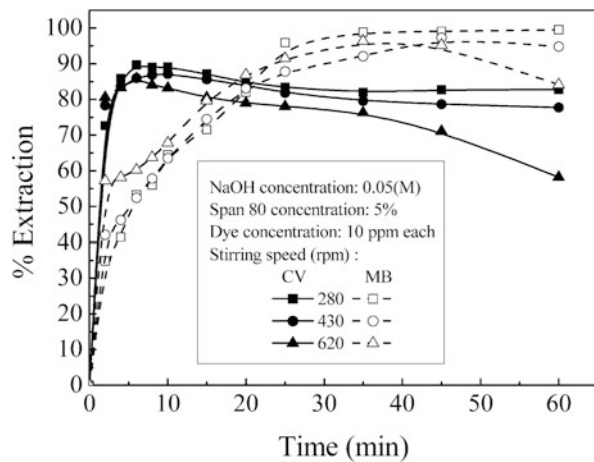(Reproduced from Das et al.
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Fig. 10.10 Effect of
stirring speed volume in
binary mixture (Reproduced
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10.5   Effect of Feed Concentration

Effects of feed concentrations of dye on the liquid membrane system are shown in
Fig. 10.11, in case of CV. It is observed from this figure that dye concentration in
the external phase decreases sharply up to 15 min and then remains almost constant
up to 35 min and increases slightly thereafter. This effect is prominent at higher dye
concentration. As dye concentration in external phase increases, more dye is
extracted in the internal phase due to enhanced driving force and after 35 min
leakage of dye to external phase occurs due to breakage of internal phase. Effects of
feed concentration on ELM system in case of MB are shown in Fig. 10.12. In case
of MB, external phase dye concentration decreases up to 40 min and remains almost
constant thereafter. As discussed earlier, there is no leakage of MB, and hence, dye

Fig. 10.11 Variation of CV concentration with time for different feed CV concentrations (Reproduced from Das et al. (2008). With permission from Elsevier)
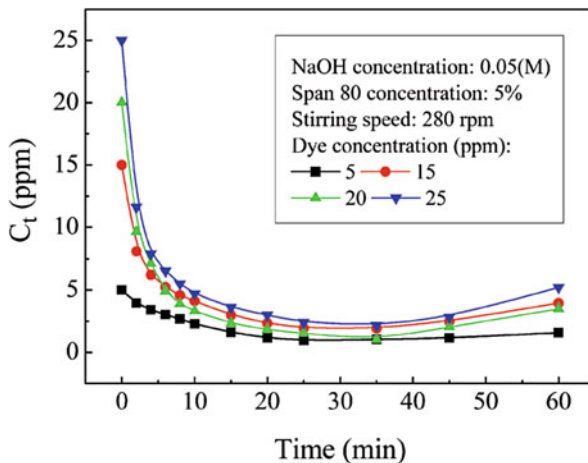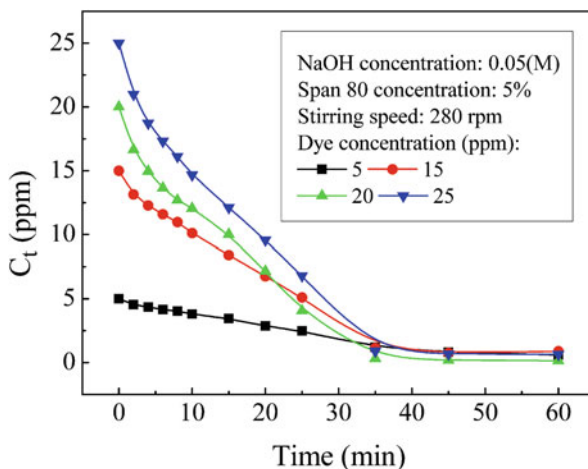

Fig. 10.12 Variation of MB concentration with time for different feed MB concentrations (Reproduced from Das et al. (2008). With permission from Elsevier)

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. 10.13. 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.

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, and composition of feed solution 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

Fig. 10.13 Effect of dye concentration in binary mixture (Reproduced from Das et al. (2008). With permission from Elsevier)
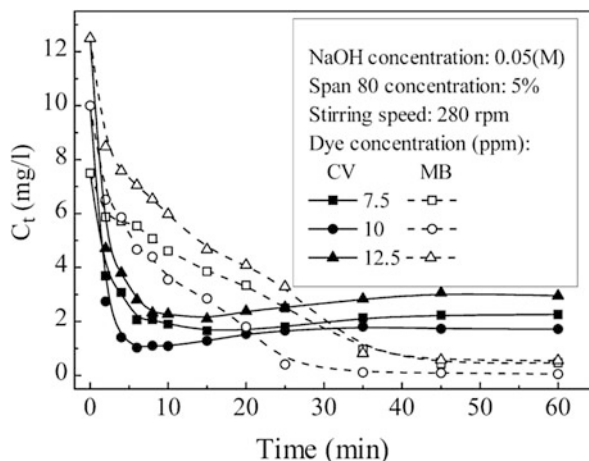
extraction of MB is found to be 99%, and that for CV is about 95% in single component system. In binary mixture, these values are 97% and 90%, respectively. Maximum extraction of CV and MB takes place at 35 min and 45 min, respectively, for single dye system, whereas maximum extraction of these dyes takes place at 5 and 35 min, respectively, in the mixture. Unlike CV, MB extraction does not fall below the maximum level for any of the parameters at its optimum conditions. This technology seems to have a promising future in the treatment of aqueous effluents containing dyes in moderate concentrations, allowing their recovery and reuse.

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