Application of Emulsion Liquid Membrane Technique for MB R 12 Red Reactive Dye-Containing Simulated Wastewater Treatment

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Abstract. The results obtained by the application of emulsion liquid membrane technique on simulated wastewater, which contained MB R 12 red reactive dye are presented. Regarding the receiving aqueous phase two type of emulsion liquid membranes were tested, and the better results were obtained for the use of HCl solution as receiving phase of the emulsion membrane versus the use of NaOH solution as receiving phase. The transport of dye from feed aqueous phase into the receiving aqueous phase occurred only in the presence of TOA as carrier agent.The optimum working conditions for removal of reactive red dye from simulated wastewaters were the following: the contact time of 300 seconds, 0.5 M HCl solution as receiving phase and the slow stirring intensity of 200 rot/min.

Keywords: wastewaters, MB R 12 red reactive dye, liquid-liquid extraction, ELM technique

1. Introduction

Dye wastewaters discharged from textile and dyestuff industries have to be treated due to their impact on water bodies, and growing public concern over their toxicity and carcinogenicity, particular. Dyes usually have synthetic origins and complex aromatic molecular structures. According to their dissociation in an aqueous solution, dyes can be classified as follows: anionic- acid, direct and reactive dyes; cationic-basic dyes; non-ionic-disperse dyes.

Dyes such as acid, basic and direct are all water-soluble but disperse dyes have low solubilities and colloidal dispersion properties. Many different and complicated molecular structures of dyes make dye wastewaters difficult to be treated by conventional biological and physico-chemical processes. Therefore, treatment technologies need to be investigated. In order to achieve the desired degree of treatment, it is necessary to integrate biological, chemical and physical processes [1]. These processes include the membrane filtration, coagulation/ flocculation, adsorption, ion exchange, advanced oxidation (chlorination, ozonation), flotation, chemical reduction, electrochemical and biological treatment. The technical and economic feasibility of each technique is determined by several factors (dye type, wastewater composition, operation costs and generated waste products). Also, the use of one individual technique is not sufficient to achieve complete decolorization, therefore dye removal strategies consists of a combination of different techniques [2].

Emulsion liquid membrane (ELM) technique is an accessible and easy way for the removal of chemicals (pollutants) from wastewaters and the transport them into desired phases, where the pollutants can be concentrated by 10-100 times. Liquid membrane permeation is an improved solvent extraction, since extraction and stripping steps are performed simultaneously. Several studies have considered removal and recovery of metals [3-11] and organic compounds [12-23]. The decisive role for application of ELM technique is the establishment of dye transport within three phases: external feed aqueous phase that contain pollutant (WIII); organic phase as permselective barrier (OII); internal receiving and concentration aqueous phase (WI). Therefore, the pollutant transport is influenced by the interfaces between the two immiscible phases (WIII/OII and OII/WI).

The objective of this work was to determine and compare the efficiency of removal of dye colour from simulated wastewaters that contain MB R 12 reactive red dye using ELM technique.

The experimental studies are carried out involving process parameters such as the initial dye concentration, carrier agent concentration, ratio of feed phase/emulsion and contact time. The study was led to understanding ELM process and optimisation of various parameters for dye removal from aqueous solution.

2. Experimental

The chemicals used for obtaining primary emulsion by type of WI/OII were the following:

- internal, receiving phase consisted of HCl or NaOH solutions with various concentrations
- organic phase was kerosene by Petrom Romanian type
- tensioactive agent, Span 80 (0.3 % ,wt versus organic phase), used for emulsion stability
- carrier agent, trioctylamine (TOA) with different concentrations
- 25 % HCl for pH adjusting

The chemicals used for obtaining emulsion by type of WIII/OII/WI were the following:

- feed aqueous phase, WIII, which contains various concentrations of MB R 12 reactive red dye, as simulated dye-containing wastewater

- primary emulsion by type of WI/OII were prepared from equal volumes of organic and receiving phases. The mixture was stirred at 1200 rpm using Sartorius stirrer RW47 type, helicoidally shape to form an emulsion.

The hydrodynamic conditions for generating the primary emulsion WI/OII were as follows: stirring intensity: 1200 rotations/minutes (fast stirring); duration: 15 minutes; the working volumes (ml) of phases OII/WI = 20/20 . To generate multiple emulsion the ratio between WIII aqueous phase and primary emulsion (WIII: primary emulsion) was ranged from 3:1 to 5:1; slow stirring intensity: 100-200 rotations/min; duration: 1-5 minutes.

After slow stirring, the next operation is settling. In this operation, the primary emulsion was separated from the treated simulated wastewater (feed aqueous phase), and dye content was analysed.

The quantitative determination of reactive red dye was made by using a Jasco V530 spectrophotometer, PC controlled, at wavelength λ=534 nm. Under these conditions, calibration plots was determined, with equation: Abs = 0.0289 conc + 0.0248 and correlation coefficient of $R^2 = 0.9989$.

To determine dye mass balance for all phases, after separation of aqueous phase, breaking of emulsion occurred, and receiving aqueous phase was analyzed. The removal efficiency was calculated based on the formula:

$$\text{Removal efficiency} = \frac{[dye]_{initial} - [dye]_{final}}{[dye]_{initial}} \cdot 100 \ (\%)$$

Symbols:

ELM – emulsion liquid membrane
ELM 1- receiving phase is HCl solution
ELM 2- receiving phase is NaOH solution
WIII- feed aqueous phase
OII- oil phase
WI- receiving aqueous phase
WI/OII-primary emulsion
WIII/OII/WI- multiple (double) emulsion
TOA – trioctylamine, as carrier agent
$[dye]_{initial}$ – initial concentration of dye in feed aqueous phase before ELM application
$[dye]_{final}$ – final concentration of dye in feed aqueous phase after ELM application

$$R = \frac{[dye]_{initial}}{[TOA]}$$

$$R' = \frac{[dye]_{initial-final}}{[TOA]}$$

3. Results and discussion

Table 1. The extraction efficiency of MB R 12 red reactive dye for various concentrations of TOA

Dye quant. in WIII (mMol)	R (Mol/Mol)	Extr. effic. (%)	Dye quant. in OII (mMol)	Dye quant., as gel aspect (mMol)	Dye quant., as gel aspect (%,vol)	R' (Mol/Mol)
0.007	0.07:1	8.6	0.0006	0.006	30	0.006:1
0.07	1.4:1	95	0.062	0.006	9.5	1.3:1
0.07	0.6:1	99	0.068	0.003	4.5	0.6:1
0.07	0.14:1	96	0.065	0.004	5.2	0.13:1

For low dye quantities in the feed aqueous phase the simple extraction efficiency was low (8.6 %) and an explanation could be low concentration gradient. It can be noticed that for higher dye quantities good values of the simple extraction efficiency was reached (99 %) (Table 1).

For all situations, during simple extraction process another phase by gel type was formed. The gel quantity (as volume) and consistence depended on initial quantities of dye and carrier agent. Higher TOA quantity, lower gel quantity and higher consistence.

Due to it was necessary to add into organic phase the carrier agent for dye transport from simulated wastewater, it can be proposed a carrier-facilitated transport occurred.

Applying suitable aqueous phase for re-extraction process, as HCl aqueous solution lead to the re-extraction efficiencies of 100 %.

Further experiments were carried out to apply ELM on dye separation using TOA as carrier agent. Two types of ELM related to the receiving aqueous phase content was applied. ELM 1 type consisted of HCl solution as the receiving aqueous phase while NaOH solution was used as receiving aqueous phase for ELM 2 type.

3.1. Application of ELM 1 for the treatment of dye-containing simulated wastewater

The further experiments were carried out using HCl with various concentrations as internal receiving aqueous phase. This receiving phase allowed high treatment efficiencies (99 %). In order to establish the working optimum conditions, different concentrations of HCl as receiving phase and emulsion stirring intensity were used. In addition, to elucidate the mechanism of carrier-facilitated transport, the influence of the different molar ratio between dye and carrier agent (R) on the treatment efficiency and R' was pursued.

Figure 1 shows the results obtained as treatment efficiency for applying ELM1 with R<1 (different values). Under these conditions, the fast and best treatment efficiency was obtained for the lowest value of R. Good results are obtained for all R, for smaller quantities of TOA a longer contact time was claimed. In figure 2 R' evolution is shown. After short contact time the experimental molar

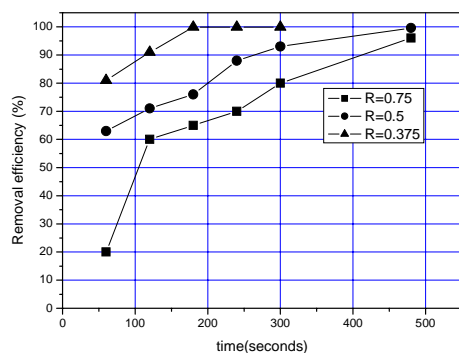ratios of dye transported by TOA were reached the proposed ones (R).

Figure 1. Removal efficiency of reactive red dye versus contact time for different subunitary molar ratios between dye and TOA (R); slow stirring intensity was 150 rpm
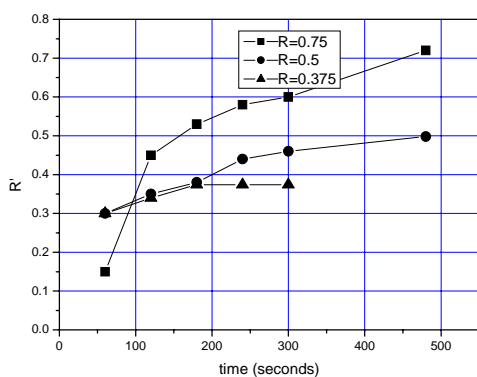

Figure 2. Evolution of experimental molar ratio between reactive red dye and TOA (R') versus time, for different molar ratios (subunitary and superunitary) between dye and TOA (R); slow stirring intensity was 150 rpm

Based on these results, the transport mechanism of the coupled transport mediated by the carrier could be supposed. In this case, carrier reacts with dye at the membrane interface and after transport through the membrane the reversible reaction takes place, and the protonated form of TOA is backed to the feed aqueous phase. Those two fluxes are stoichiometrically coupled and this is called counter current transport [6].

Results obtained for slow stirring intensity of 200 rpm for different values of R (supraunitary and subunitary) are presented in figures 3 and 4. The best results were obtained for subunitary molar ratio but the treatment of simulated dye-containing wastewater for supraunitary ratio occurred with lower treatment efficiency. Due to the transport of reactive red dye mediated by low quantity of TOA (R=10) and existing another phase into the membrane, as gel form (table 3) another type of transport mechanism could be supposed, micellar transport mechanism [7]. The definition of micelle is an aggregated

structure formed by the interaction of several surfactant molecules. More specifically, a reversed micelle is usually envisaged as a nanometer-scale droplet of an aqueous solution stabilized in a nonpolar environment by the presence of surfactant molecules at polar/nonpolar interface. An explanation for this type of transport mechanism of reactive red dye mediated by TOA could be the surfactant character of both TOA and reactive red dye. The obtaining gel was favoured by the receiving phase as HCl solution compared with NaOH solution.

The quantitative analysis of dye in every phase of the emulsion was made after the emulsion breaking by centrifugation at 10,000 rot/minutes.
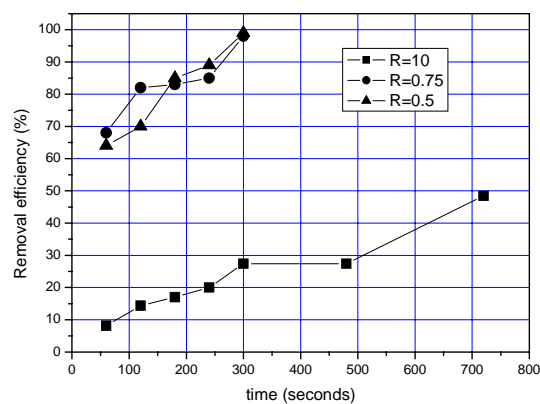

Figure 3. Removal efficiency of reactive red dye versus contact time for different molar ratios (subunitary and superunitary) between dye and TOA (R); slow stirring intensity was 200 rpm
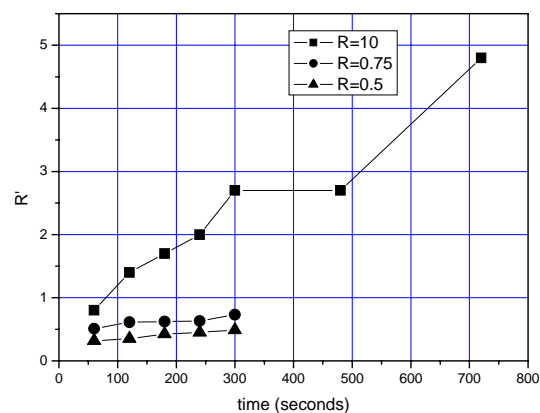

Figure 4. Evolution of experimental molar ratio between reactive red dye and TOA (R') versus time, for different subunitary molar ratios between dye and TOA (R); slow stirring intensity was 200 rpm

Table 2. The distribution of MB R 12 red reactive dye in each ELM phase; Initial quantity of dye was 0.05 mmol; WIII/WI volume ratio was 5/1; R=0.5

Removal efficiency (%)	Receiving phase	Dye transported into receiving phase (mMol)	Dye as gel form		Concen-tration factor
			mM	%, vol.	
44	0.5N NaOH	0.02	0.002	4	2.2
100	0.5N HCl	0.036	0.014	28	3.6

To determine optimum working conditions the following parameters were varied: the influence of slow stirring intensity, the influence of HCl concentration in the receiving phase and the influence of the contact time.

The better results for removal efficiency were obtained for slow stirring intensity of 200 rot/min (Figure 5). Under these conditions, no emulsion breaking or swelling occurred, this slow stirring intensity value being suitable for removal of simulated dye-containing wastewater.

The influence of the concentration of HCl as receiving phase is shown in figure 6. For the contact time shorter than 300 seconds, the better results of removal efficiencies were obtained for more concentrated HCl solution (1 M). For the contact time of 300 seconds, for both situations the removal efficiency was very good (99%). Thus, the optimum working conditions for removal of reactive red dye from simulated wastewaters were the following: the contact time of 300 seconds, 0.5 M HCl solution as receiving phase and the slow stirring intensity of 200 rot/min.
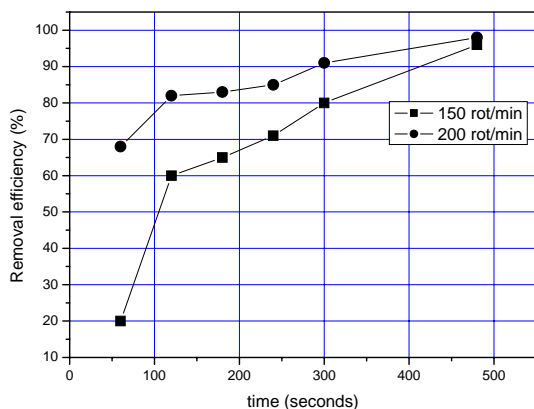

Figure 5. Removal efficiency of red reactive dye versus time for two slow stirring intensities (150 and 200 rot/min); R= 0.75; HCl 0.5 M as receiving phase
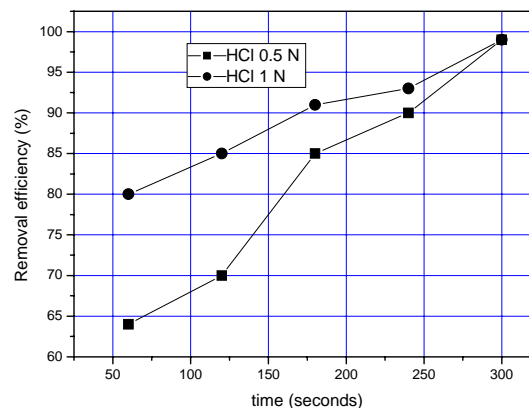

Figure 6. Removal efficiency of red reactive dye versus time for two concentrations of HCl as receiving phase (0.5 and 1 M); R= 0.5; slow stirring intensity of 200 rot/min

3.2. Application of ELM 2 for the treatment of dye-containing simulated wastewater

The composition of the receiving aqueous phase should be properly chosen in relation to the pollutant that should be removed. Thus, the receiving phase can lead to "stocking" of dye or further transformation. In addition, it has to take into account the influence of the receiving aqueous phase on the multiple emulsion stability; this involves a receiving phase that favours the emulsion stability. In order to reach the driving force of the process as proton concentration gradient, NaOH solution with various concentrations was tested as receiving phase. The results are presented in table 2.

Table 2. Removal efficiency function of R values. Initial quantity of MB R 12 red reactive dye = 0.05 mM. The slow stirring intensity of emulsion was 150 rot/min.

R<1	Internal receiving phase NaOH (mol/L)	Removal efficiency (%)
0.5	0.1	14.4
0.4	0.1	32
0.3	0.1	34
0.12	0.1	66
0.5	0.25	26
0.4	0.25	45
0.16	0.25	44
0.8	0.5	44.8
0.4	0.5	44.5
0.16	0.5	45.4

It can be noticed that the treatment efficiencies were low. At low contact time, the efficiency was higher as receiving concentration was higher. Both the contact time and the concentration of receiving phase were limited by the emulsion stability.

4. Conclusions

The separation of MB R 12 reactive red dye from simulated wastewaters can occurred by application of ELM technique.

The transport mechanism of dye could be coupled transport mediated by carrier (stoichiometrically coupled) or micelle transport (due to gel form appearance).

The best results were obtained by ELM 1 application, containing various concentration of HCl solution as receiving phase.

The optimum working conditions for removal of reactive red dye from simulated wastewaters were the following: the contact time of 300 seconds, 0.5 M HCl solution as receiving phase and the slow stirring intensity of 200 rot/min.

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