

# Emulsion Liquid Membranes to Remove Volatile Organic Compounds from Surface and Underground Waters

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*To recover benzene, toluene and xylene from wastewater a separation method using emulsion liquid membranes (ELM) is studied. The membrane phase consists of octanol as diluent and lecithin as surfactant. Internal phase was Tween 60 in water, in order to enhance the aqueous solubility, especially, for xylene. Factors affecting the extraction yields were studied and the optimum conditions for extraction were determined.*

*Keywords: volatile organic compounds, emulsion liquid membranes, water purification*

Volatile organic compounds are among the most commonly found contaminants in groundwater. The main sources of waters contaminated with VOCs are industrial wastewater and groundwater, resulting from improper disposal of organic solvents, leaking storage tanks, and landfill leachates [1]. Even at low concentration, many of these substances are toxic or carcinogenic and represent a real health risks for human beings [2]. Their volatility is the reason why they can be found in surface waters only in very low concentrations. In groundwaters their concentration can be substantially higher. For this reason the cleanup of contaminated waters is necessary, but it is often difficult and expensive. The treatment methods for removing VOCs include air stripping, high temperatures incineration, photocatalytic and catalytic oxidation, adsorption and absorption, distillation, anaerobic/aerobic biological treatment, pervaporation and supported liquid membrane [1-9]. But, no single method can be used in all cases; most of the methods are specific in nature and, lately, combined methods are used, for example, adsorption and absorption, pervaporation and air-stripping [7, 10].

A promising alternative to conventional operations for many separations processes and in particular for wastewater treatment is provided by liquid emulsion membranes (LEM) [11-12]. Emulsion liquid membranes technology was first proposed by Li for the separation of hydrocarbons [13]. Several applications have been developed concerning the removal and recovery of several solutes from either aqueous or organic solutions, including biological and medical applications. In this technology, solutes are not only removed but also concentrated; extraction and re-extraction (stripping) are carried out in a single step. Liquid emulsion membranes are, in fact, double emulsions, water/oil/water (w/o/w) systems or oil/water/oil (o/w/o) systems. The membrane phase is the liquid phase that separates the encapsulated internal droplets in the emulsion from the external continuous phase. Typically, the encapsulated internal droplets in the emulsion have 1 to 3  $\mu\text{m}$  diameter. During the contact between wastewater and emulsion globules (permeation), solute transport occurs through the membrane and into the internal receiving phase, where it is concentrated.

Many organic pollutants with very low water solubility were removed using LEM systems, for example: n-heptane and aromatic hydrocarbons as toluene and xylene [14-18].

The aim of this paper is to propose a LEM system for VOCs removal from water. As VOCs model were selected xylene, benzene and toluene, alone or in different combinations.

## Materials and methods

### Materials

**Chemicals:** The oil used in this work is paraffin oil (from Merck Co.). The surfactants used were: Span 80 and Tween 60 (from Sigma-Aldrich Co.) and lecithin (from Sigma-Aldrich). HTABr (hexadecyl trimethyl ammonium bromide) was obtained from Fluka. The model VOCs: xylene, benzene and toluene were supplied from Sigma-Aldrich Co.

### Analysis of VOC's in water

The content of organic compounds was determined by GC/MS analysis with FOCUS GC DSQII system, from THERMO ELECTRON CORPORATION.

### Emulsion preparation

The LM (liquid membrane) emulsion used in this study consists of the membrane (oil) phase, SPAN 80 or lecithin as emulsifier, and an internal phase which consists of Tween 60 and distilled water. The membrane phase and the internal aqueous phase were mixed at a stirring speed of 1000 rpm for 10 min. The stability of the emulsion was verified at microscope using an Olympus microscope BX 52. For the extraction experiment a volume of prepared emulsion was dispersed in a determined volume of aqueous phase with organic pollutants (VOCs) giving different phase volume ratios. Samples of the external phase were analyzed at different time intervals.

## Results and discussions

The first experiments were done using o-xylene as test solute from VOCs. The experimental conditions for o-xylene removal from water are presented in table 1. Extraction yield was calculated as follows:

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$$\eta = \left( 1 - \frac{C_e V_{ef}}{C_{e0} V_{e0}} \right) \cdot 100 \quad (1)$$

*o*-Xylene removal was studied using an emulsion liquid membrane with the following composition: octanol as membrane phase, SPAN 80 or lecithin as emulsifier and an aqueous solution of Tween 60 or HTABr as internal aqueous phase. Because *o*-xylene has a very low solubility in water the use of an emulsifier can enhance its solubility [19].

The emulsion stability was verified using an optical microscope. The image of a fresh emulsion before contacting the aqueous phase containing *o*-xylene is presented in figure 1.



Fig. 1. Image of emulsion 1 containing octanol as membrane phase, 2.5% lecithin and an aqueous solution of Tween 60 as internal phase (x20)

The removal efficiency of *o*-xylene extraction was investigated in different conditions. The type and surfactant concentration are of critical importance to any ELM systems. In this study two emulsifiers were tested: SPAN 80 and lecithin. The first is often used to obtain emulsion systems of w/o/w type. The second is a food emulsifier and is considerably costly. Figure 2 shows the effect of these surfactants at different concentration on the concentration profile in external phase containing *o*-xylene. Lecithin is a better surfactant compared to with SPAN 80. For a surfactant, the choice of concentration must provide less membrane swelling and good membrane stability. As seen from figure 2, at low lecithin concentration the emulsion stability is poor. When lecithin concentration exceeds 3%, the removal efficiency decreases, because the surfactant can create a mass transfer barrier for solute transport. For these considerations a 2.5% concentration of lecithin was used in the following experiments.

The removal efficiency of any solute depends also on the treating ratio  $V_{em}/V_{ex}$ . For *o*-xylene removal the experimental results obtained when this parameter is varying between 1/8 and 1/5 is presented in figure 3. As seen from figure 3, *o*-xylene extraction increases with the increasing ratio  $V_s/V_e$ . The extraction degree is increasing from 79 % for  $V_s/V_e=1/8$  to 99 % for  $V_s/V_e=1/4$ .

To improve the solubility of *o*-xylene in water Tween 60 was replaced by HTABr but without success. The extraction yield decreased and emulsion swelling was observed during experiments. The best emulsion was considered to correspond to the conditions of Run 5 from table 1. This emulsion was tested for binary and multiple mixtures of VOC's and the only modification was to increase agitation speed during emulsion formation in order to improve its

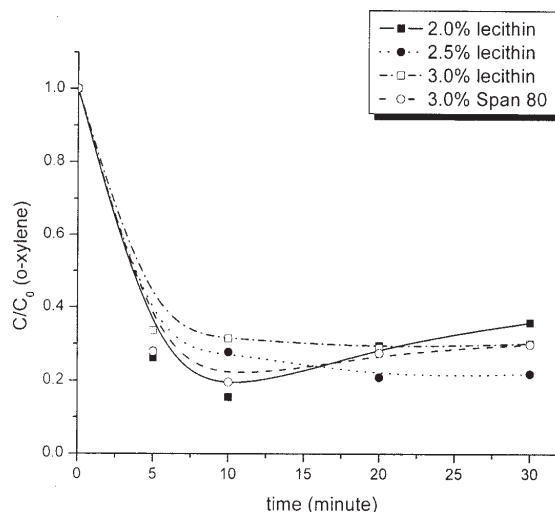


Fig. 2. Dimensionless concentration of *o*-xylene in external phase versus time for different surfactants concentration

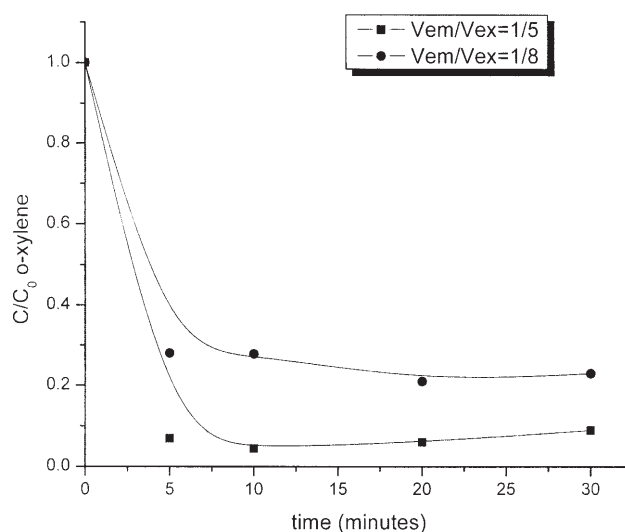


Fig. 3. Dimensionless concentration of *o*-xylene in external phase versus time for different treating ratio  $V_{em}/V_{ex}$

stability (from 1000 rpm to 2000 rpm). The results obtained, expressed as extraction yield, are presented in table 2.

As seen from table 2, for *o*-xylene the removal yield is very good, but for benzene toluene the extraction is not as good as for *o*-xylene. This is not an unexpected result for two reasons: first, benzene solubility in water is greater in comparison with *o*-xylene (1749 ppm compared to 172 ppm). The same aspect is valuable also for toluene-*o*-xylene couple (473 ppm in comparison with 172 ppm). The second reason is that the emulsion used was tested only for *o*-xylene and was improved to increase *o*-xylene removal. If a total removal is wished for benzene-toluene couple, is almost sure that another emulsion must be tested. The last experiment was done for all xylene isomers and, also, for all five components, using the same emulsion. The results obtained are presented in table 3.

For all three isomers of xylene the extraction yield is very good (>99%) and, in consequence, the emulsion tested can be used for treating wastewater. For all the components (xylene, benzene and toluene) the result is good, but unsatisfying for complete water purification. For this reason, another emulsion must be tested for benzene and toluene removal at a greater extraction yield. Another possibility, which was already investigated by the same work team [20], was to use biological systems for VOC's

**Table 1**  
EXPERIMENTAL CONDITIONS FOR o-XYLENE EXTRACTION USING ELM

	Run 1	Run 2	Run 3
Type of separation	batch	batch	batch
Agitation speed, rpm	150	150	150
External o-xylene conc., ppm	150	150	150
Membrane phase	Octanol	Octanol	Octanol
Surfactant	Lecithin	Lecithin	Lecithin
Concentration wt. %	2	2.5	3.0
Internal phase	Tween 60	Tween 60	Tween 60
Aqueous solution with emulsifier, %	1.6	1.6	1.6
$V_e/V_w$	1/8	1/8	1/8
Extraction yield (%)	64	79	70
	Run 4	Run 5	Run 6
Type of separation	batch	batch	batch
Agitation speed, rpm	150	150	150
External o-xylene conc., ppm	150	150	150
Membrane phase	Octanol	Octanol	Octanol
Surfactant	SPAN 80	Lecithin	Lecithin
Concentration wt. %	3.0	2.5	2.5
Internal phase	Tween 60	Tween 60	HTABr
Aqueous solution with emulsifier, %	1.6	1.6	1.6
$V_e/V_w$	1/8	1/5	1/5
Extraction yield	70%	99%	70%

**Table 2**

EXTRACTION YIELDS OBTAINED FOR BINARY VOC'S MIXTURES REMOVAL USING ELM SYSTEMS

No.	Components	Initial concentration (ppm)	Extraction Yields %
1	toluene	261	85.00
	o-xylene	170	94.70
2	benzene	264	77.20
	toluene	261	86.63
3	benzene	264	71.25
	o-xylene	170	99.70

removal. Three different cultures (*Candida membranes*, *Pseudomonas putida* and *Penicillium* sp) were tested for benzene toluene and xylene removal. Best results were obtained with *Candida membranes*. The cultures relieved that benzene is more resistant to microbial degradation, while xylene and toluene presents differences, with preference to o-xylene. These results may be a start point to develop a new method for VOC's removal by combining a LEM system with biological one.

## Conclusions

The present research presents experimental data obtained using emulsion liquids membranes for o-xylene removal from water. For the optimum work conditions the extraction yield achieved was 99%. The best emulsion composition was: octanol as membrane phase, lecithin as emulsifier and a solution of Tween 60 in water as internal aqueous phase. The same emulsion was tested for all xylene isomers removal (ortho, meta and para) and the results are also very good (extraction yield > 99%). When

**Table 3**

EXTRACTION YIELDS OBTAINED FOR VOC'S MIXTURES REMOVAL USING ELM SYSTEMS

No.	Components	Initial concentration (ppm)	Extraction Yields %
1	o-xylene	50	99.8
	m-xylene	50	99.4
	p-xylene	50	99.0
2	o-xylene	50	99.5
	m-xylene	50	98.0
	p-xylene	50	99.8
	benzene	261	70.8
	toluene	261	84.4

the same emulsion was tested for benzene and toluene removal in the presence of xylene isomers, the results are not as good as for xylene removal. One explanation is the relatively high solubility in water of benzene and toluene in comparison with xylene. For complete removal of benzene and toluene two solutions are proposed. The first is to try another ELM systems tailored for the two pollutants and the second, which was already tested, is to use biological systems for VOC's removal.

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## Notations

$C_{e0}$  - initial concentration of solute in aqueous external phase (g/L)  
 $C_e$  - final solute concentration in aqueous external phase (g/L)  
 $V_{e0}$  - initial volume of aqueous external phase (L)  
 $V_{ef}$  - initial volume of aqueous external phase (L)  
 $\eta$  - extraction yield % (equation 1)

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