Investigation of Organic Matter Release in Emulsion Liquid Membrane Treatments

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Abstract

The emulsion liquid membrane (ELM) technique is a process used for separation. It uses organic diluents, extractants, and surfactants. Due to the organic nature of these constituents, an unwanted organic matter release to the external phase occurs during the separation process. The present study demonstrates this organic matter release to the external phase in the ELM process used for the removal of lead ions from industrial storage battery wastewater. Toluene, kerosene, mineral oil, and xylene, as organic diluents, sorbitan monooleate (Span 80) and polyoxyethylene (20) sorbitan trioleate (Tween 85), as surfactants, and di-2-ethylhexyl phosphoric acid (D2EHPA), as extractant, were used. In the process of lead ion removal from storage battery wastewater, while lead ion concentration decreased to < 0.4 mg/l from its initial value of 2.8 mg/l, the organic matter load (COD) of the treated wastewater increased to about 160 mg/l. Additionally, Span 80 exhibited better results than Tween 85 in terms of CODs and lead removal. Kerosene had a more stable membrane than the other organic diluents used. The optimum membrane components and their rates were 70% kerosene, 18% mineral oil, 3% Span 80, and 9% D2EHPA. When wastewater pH was adjusted to improve lead ion removal, COD of the treated wastewater increased to > 200 mg/l.

Key words: Emulsion liquid membrane, Industrial storage battery wastewater, Lead ion, Organic matter release.

Introduction

The emulsion liquid membrane (ELM) technique, invented by Li in 1968, was regarded as an emerging separation technology and was extensively examined for potential applications in such fields as hydrometallurgy, environmental engineering, biochemical engineering, pharmaceutical engineering, and food technology (Wan and Zhang, 2002; Reis and Carvalho, 2004). With this technology solutes are not only removed, but also concentrated (Kumaresan et al., 2003). Some kinds of chemicals that can be removed or recovered from industrial streams using ELMs are organic acids, phenols, cresols, and amines, as well as metallic ions such as lead, copper, cadmium, and mercury (Yan and Pal, 2001).

ELM systems are created by forming an emulsion with 2 immiscible phases (internal and membrane phases) and then dispersing this emulsion into a third phase, the continuous phase (in the present study this phase is industrial storage battery wastewater). In general, the internal and continuous phases are miscible; however, the membrane phase does not have to be miscible with the internal and continuous phases. To make a stable emulsion during the treatment process, some surfactants and stabilizing agents are added to the membrane phase containing one or more solvents. A lot of emulsion globules are

desired in the continuous phase. In this way, a large membrane surface area occurs and the mass transfer from the continuous phase to the internal phase increases in speed (Datta et al., 2003).

ELMs have some important advantages, such as ease of operation, low power consumption, and a modular design (Kumaresan et al., 2003). Nevertheless, as with any technique, ELMs exhibit some drawbacks, such as membrane rupture, swelling, and stability (Dzygiel and Wieczorek, 2000). Furthermore, because of the contact between the oil phase and the wastewater (external phase) to be treated in this technology, a small amount of the oil membrane may remain in the raffinate, which is another drawback of ELM technology (Hayworth et al., 1983).

In our previous work (Gurel et al., 2005), the removal of lead ions from industrial storage battery wastewater using the ELM technique was investigated and we obtained > 98% efficiency with the treatment.

In another previous study (Turan et al., 2004) that was conducted to investigate the effect of different membrane component ratios on COD of industrial storage battery wastewater, the following membrane components gave the minimum COD to the external phase: 70% (vol.) kerosene, 18% (vol.) mineral oil, 9% (vol.) D2EHPA, and 3% (vol.) Span 80. An increase in D2EHPA and Span 80 content increased COD of the wastewater. Organic matter content of the wastewater increased as the treatment process progressed. Additionally, in the removal of cyanide from synthetic water it was found that COD of synthetic water following the treatment increased according to the organics used and time (Turan et al., 2004).

To the best of our knowledge, except for our previous work, the literature does not contain any reports about organic input as it relates to removal efficiency. Therefore, the present study was conducted to demonstrate the organic input problem associated with multiple membrane components and to demonstrate the importance of optimizing this membrane technique.

In the present work, the problem of organic matter release to the external phase was solved using the same membrane parameters and wastewater as used in our previous work (Gurel et al., 2005).

Materials and Methods

Materials

The organic diluents kerosene, mineral oil, xylene, and toluene were obtained from Aldrich (Steinham, Germany), Acros (Morris Plains, NJ, USA), Atabay (Turkey), and Lab-Scan (Dublin, Ireland), respectively. The extractant di-2-ethylhexyl phosphoric acid (D2EHPA) and the surfactant sorbitan monooleate (Span 80) were obtained from Sigma (St. Louis, MO, USA). The surfactant polyoxyethylene (20) sorbitan trioleate (Tween 85) was supplied by Acros (Morris Plains, NJ, USA). The other chemicals used in the study, H_2SO_4(sulfuric acid) (95%-98%), NaOH (sodium hydroxide), ferroin indicator, and Ag_2SO_4 (silver sulfate), were supplied by Merck (Darmstadt, Germany), $Fe(NH_4)_2(SO_4)_2.6H_2O$ (ferrous ammonium sulfate hexahydrate) and $K_2Cr_2O_7$ (potassium dichromate) were obtained from Carlo Erba (Rodano, Italy), and $HgSO_4$ (mercuric sulfate) was obtained from Baker Analyzed (Phillipsburg, NJ, USA). All the chemicals used were of analytical grade. Industrial storage battery wastewater was obtained from Yiğit Battery Co., Ankara, Turkey.

Equipment

The emulsions used in all experiments were prepared using a PRO 200 homogenizer (0-30,000 rpm). The solution formed by the emulsion and external phases was stirred by a jar test apparatus (Velp Scientifica F.6/s; 0-300 rpm). The samples taken from the external phase at definite intervals were analyzed to determine lead concentration by means of flame atomic absorption spectrometry (FAAS) (Unicam-929 AA). The pH values of the samples were measured using a Sartorius PB-20 standard pH meter. The stirring speed of the homogenizer was adjusted with a digital stroboscope (Lutron DT-2249). Chemical oxygen demand (COD) tests were conducted using a Velp Scientifica Eco 6 thermoreactor. Whatman glass microfiber filters (11.0 cm GF/C) were used to separate the emulsion globules that remained in the external phase after the settling process. An Olympus microscope (Melville, NY, USA) was used for observing the state of the internal phase droplets at the beginning of the treatment. Photos were taken with a Canon Powershot S50 digital camera attached to the microscope at the same magnification for all systems.

Procedure

The emulsion phase (20 ml) was prepared by adding stripping solution (H_2SO_4 1.8 N; 9 ml) to the membrane phase solution (11 ml) that formed from the membrane components (mineral oil, kerosene, xylene, toluene, D2EHPA, Span 80, and Tween 85) at various compositions and then by stirring in the homogenizer. A pre-treatment (with a lab scale sand filter) was applied to the industrial storage battery wastewater for suspended solids removal. The 250 ml of wastewater, which was passed through the sand filter, was placed into a vessel with 4 baffles and then stirred using a propeller with 4 flat blades. Simultaneously, the emulsion was rapidly added to the external phase. The solution containing the emulsion and external phases was stirred at 300 rpm for 20 min, except during the pH adjustment study (the pH adjustment study was conducted separately for 1, 3, 4, and 5 min at 300 rpm). In the pH adjustment study, diluted sodium hydroxide was used to increase the pH from 1.65 to 4.00. In this study, 4 systems that had the same membrane components were created. After all treatment periods, 20-ml samples were taken and filtered to separate the emulsion globules from the external phase (treated industrial storage battery wastewater). COD tests were conducted with 10 ml of treated wastewater and finally the lead and pH measurements were obtained. COD and lead analyses were performed according to the Standard Methods for the Examination of Water and Wastewater (Clescerl et al., 1999). The phase ratios of the membrane and all the other parameters used in these studies were the same as the optimum values of our previous study (Gurel et al., 2005). The phase ratios of all the ELM systems are given in Table 1.

Results and Discussion

In the analysis performed for determining the contents of the industrial storage battery wastewater, which was passed through a sand filter, average lead concentration, pH value, and COD value of the wastewater were 2.8, 1.65, and 16 mg/l, respectively.

A study was conducted to investigate the effects of several membrane components, such as xylene, toluene, and Tween 85, and the effects of other components used in a previous study on COD of wastewater. There was no pH adjustment made to the wastewater and during the first minute of the treatment there was no investigation for COD in the work conducted by Turan et al. (2004). As a part of these ongoing studies, another study was performed to see the effect of pH adjustment on COD of wastewater, and to measure COD change that occurs in the first minute of treatment.

The effect of several diluents and surfactants on COD of external phase

In these experiments, membrane phases were constituted from different membrane components, but the membrane phase ratios were kept constant. The component ratios of the ELM systems and other parameters are given in Table 2. The external phase lead concentrations, pH values, and COD values that were obtained after the treatment studies are shown in Figure 1, and emulsion phase droplets of each system before treatment are shown in Figure 2. In the studies conducted to determine the internal phase droplet sizes (average) of each system before the treatment, it was found that the average droplet size of systems I, II, III, V, and VI was 6, 7, 5, < 2, and ≤ 2 μm, respectively. The droplet size of system IV was not determined because of low viscosity.

Table 1. The phase ratios of the ELM systems created in this study.

The Ratios of Membrane, Emulsion, and External Phases	
Membrane Phase/Emulsion Phase: 0.550	Internal Phase/External Phase: 0.036
Membrane Phase/External Phase: 0.044	Internal Phase/Emulsion Phase: 0.450
Emulsion Phase/External Phase: 0.080	Internal Phase/Membrane Phase: 0.818

Membrane phase (11 ml): 70% kerosene, 18% mineral oil, 3% span 80, and 9% D2EHPA.

Internal phase (9 ml): 1.8 N H_2SO_4.

Emulsion phase (20 ml): membrane phase + internal phase.

External phase (250 ml): storage battery industry wastewater.

Table 2. The component ratios of the ELM systems made with several surfactants and organic diluents, and the system parameters used in the study.

| Membrane and System Components	ELM Systems					
	Systems, Component Ratios, and Amounts					
	I	II	III	IV	V	VI
Kerosene (vol. %)	-	-	70	-	-	70
Xylene (vol. %)	-	70	-	-	70	-
Toluene (vol. %)	70	-	-	70	-	-
Mineral Oil (vol. %)	18	18	18	18	18	18
Tween 85 (vol. %)	-	-	-	3	3	3
Span 80 (vol. %)	3	3	3	-	-	-
D2EHPA (vol. %)	9	9	9	9	9	9
Internal P. (H_2SO_4) Normality (N)	1.8	1.8	1.8	1.8	1.8	1.8
External P. (ml)	250	250	250	250	250	250
Internal P. (ml)	9	9	9	9	9	9
Parameters						
Total Treatment Period (min)	20	20	20	20	20	20
Emulsification Rate (rpm)	7940	7940	7940	7940	7940	7940
Emulsification Period (min)	1	1	1	1	1	1
Reactor Stirring Rate (rpm)	300	300	300	300	300	300
Temperature of external phase (^{o}C)	15	15	15	15	15	15
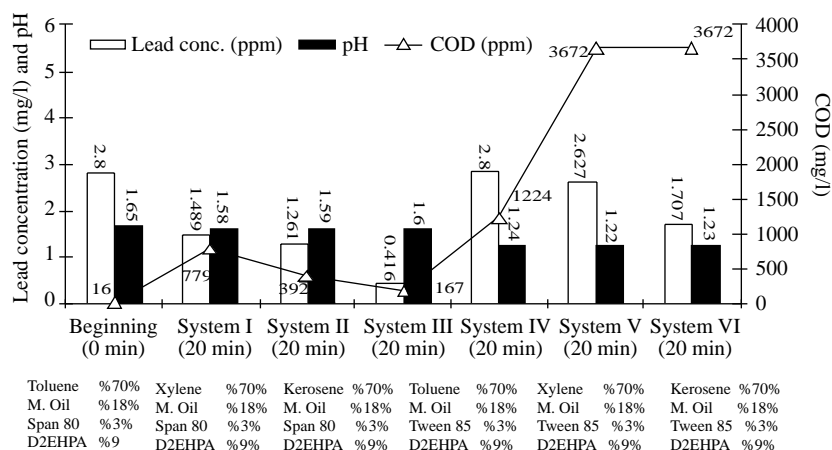
Figure 1. The external phase lead concentrations, COD, and pH values obtained after the treatment studies performed with several surfactants and organic diluents.

When lead removal efficiency was investigated after the treatment period, it was observed that the first 3 systems (I, II, and III) constituted from the surfactant Span 80 exhibited removal efficiency values of approximately 50%. The other 3 systems (IV, V, and VI) composed of Tween 85 showed much lower efficiency when compared to the other 3 systems composed of Span 80.

Although Span 80 is highly soluble in aqueous phases, it is a very good emulsifier and has low resis-

tance to mass transfer (Ho and Sirkar, 1992). Based on this information, it can be stated that Span 80 can dissolve in industrial storage battery wastewater. Additionally, if the concentration of this surfactant is not optimized, then the membrane can break down due to low stability, and Span 80 and the other ingredients in the membrane phase can permeate into the wastewater to be treated. Therefore, Span 80 has an important role in increasing COD values.
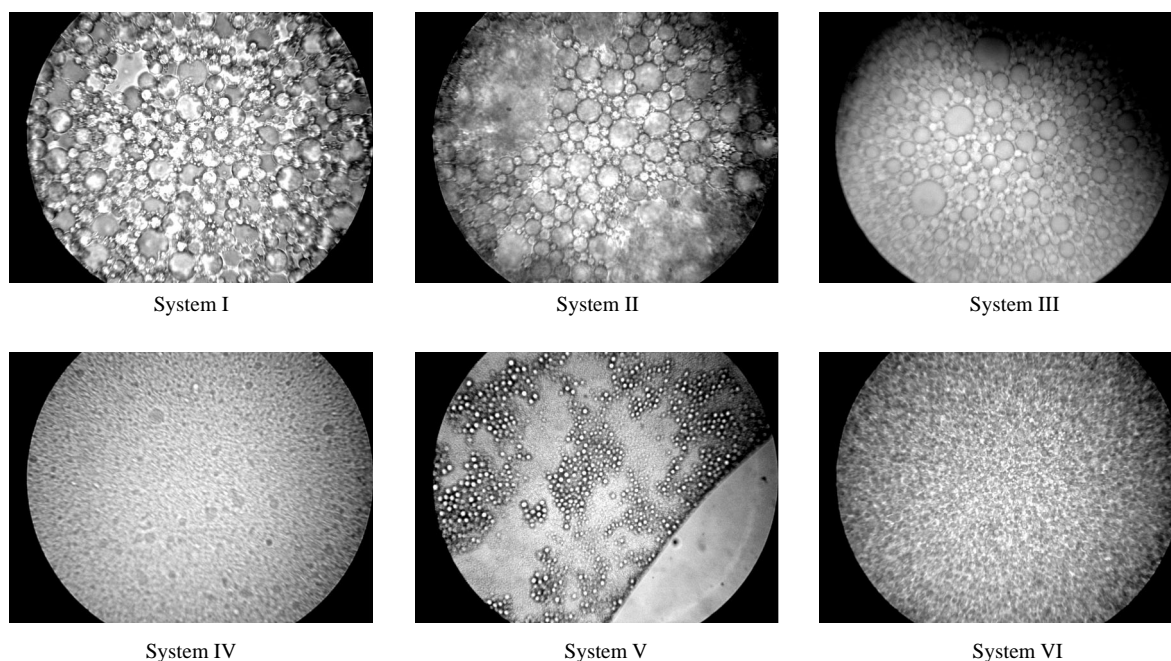
Figure 2. The emulsion phase droplets of each system before the treatment process.

After a treatment period of 20 min, COD values of the external phases were determined. When the systems composed of surfactant Span 80 were examined, it was noted that toluene caused the highest organic matter input to the treated wastewater. It was seen that the kerosene did not contribute to COD of the external phase as much as the other diluents used in these experiments. Kerosene has a higher viscosity value (2.71 $\mathrm{m^2/s}$ at 20 °C) than the diluents, toluene (0.68 $\mathrm{m^2/s}$ at 20 °C) and xylene (mixture of isomers; with a range of 0.72-0.86 $\mathrm{m^2/s}$ at 20 °C); hence, it is thought that kerosene supports membrane stability due to its high viscosity.

In the systems composed of Tween 85, COD values obtained after treatment were higher than those of the other systems constituted with Span 80. When the HLB (hydrophilic-lipophilic balance) values of these surfactants (Span 80: 4.3; Tween 85: 11.0) were taken into consideration, it was seen that Tween 85 could dissolve more easily in the wastewater than Span 80. In addition, Tween 85 has less viscosity than Span 80. Subsequent studies can be conducted to decrease COD values encountered in the present study by adjusting the membrane component ratios according to Tween 85.

In systems IV and V, emulsion globules did not form after the dispersion of the emulsion phase to the external phase, and the external phase turned a milky color. In system VI very small emulsion glob-

ules formed during the dispersion process, but the system remained stable for only 40 s of stirring. After this period, the formed emulsion globules were broken and then the external phase turned a milky color. After the treatment period, the pH values of the external phases of these 3 systems (IV, V, and VI) were very low. It can be stated that this phenomenon occurs due to the transfer of the internal phase reagent (H_2SO_4 with a normality value of 1.8) to the external phase as a result of the breakdown in membrane stability. All these findings demonstrated that the emulsion stability of systems IV, V, and VI broke down extraordinarily. As a result of the breakdown of emulsion stability, water soluble parts of the membrane components increased COD of the wastewater. System III, which had the best lead removal efficiency in our previous studies, also had the best lead removal efficiency and the lowest COD (167 mg/l) in the present study. Moreover, when the internal phase droplet form of system III was compared to the other systems, it was observed that it had the best internal phase droplet form (Figure 2).

The investigation of change in COD of the external phase adjusted to the optimum pH value

In our previous work (Gurel et al., 2005), a pH value of 4.0 and a treatment period of 5 min were the op-

timum conditions for removal of lead from industrial storage battery wastewater. To investigate COD of wastewater and the lead removal with a treatment period < 5 min, another study was conducted. The component ratios and the other parameters of ELM systems are given in Table 3. Post-treatment lead concentrations, CODs, and pH values of the systems are displayed in Figure 3.

It is known that the pH value of the external phase in ELMs affects the rate of mass transfer because of the driving force that results from the transport of H^+ ions from the internal to external phase, which is the inverse of the metal ions. When the pH value was adjusted to 4.0, the transport of lead ions from the external phase to the internal phase was facilitated, and after 5 min the lead concentration that remained in the external phase was > 0.1 mg/l.

In the first minute of the treatment it was clearly seen that COD increased tremendously. In particular, this increase occurred because of the high shearing forces that resulted from stirring during the dispersion of the emulsion phase to the external phase. The membrane components escaped to the external phase due to the emulsion drops, which initially did not completely form.

Table 3. The component ratios of the ELM systems, and the system parameters used in the study of pH adjustment.

ELM Systems				
Membrane and System Components	Systems, Component Ratios, and Amounts			
	I	II	III	IV
Kerosene (vol. %)	70	70	70	70
M. Oil (vol. %)	18	18	18	18
Span 80 (vol. %)	3	3	3	3
D2EHPA (vol. %)	9	9	9	9
Internal P. (H_2SO_4) Normality (N)	1.8	1.8	1.8	1.8
External P. (ml);	250	250	250	250
Internal P. (ml)	9	9	9	9
Parameters				
Total Treatment Period (min)	1	3	4	5
Emulsification Rate (rpm)	7940	7940	7940	7940
Emulsification Period (min)	1	1	1	1
Reactor Stirring Rate (rpm)	300	300	300	300
Temperature of external phase (°C)	17	17	17	17
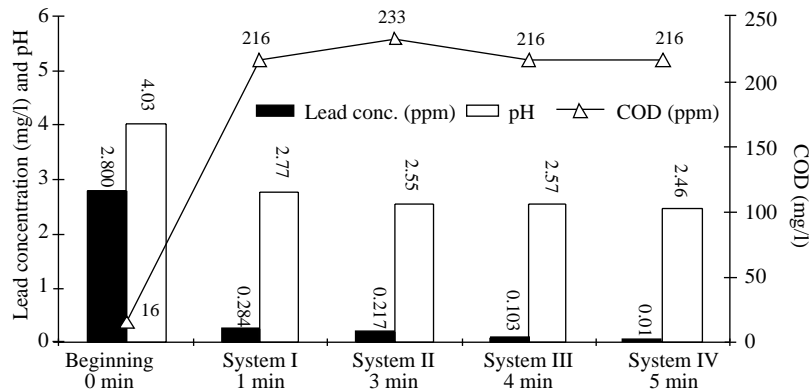
Figure 3. The pH adjusted external phase lead concentrations, COD, and pH values obtained after the treatment studies.

In the third minute of the treatment, COD was higher than after the first, fourth, and fifth minutes of treatment, with an experimental error. Between the first and fifth minutes of the treatment process, except the third minute, COD remained stable by demonstrating that the stability of the emulsion did not break down during the 5 min of treatment. At the end of 5 min, the lead concentration decreased to 0.01 mg/l with an efficiency of over 99%. COD in this experiment was higher than that of the other experiment (system III: 167 mg/l) that was conducted to determine the effect of several diluents and surfactants on COD of the external phase. This was due to extraction rates occurring more rapidly. An increase in the extraction rate decreased membrane stability; thus, COD of the wastewater increased due to the leakage of membrane material.

Conclusions

In the present study conducted for determining the effect of several organic diluents and surfactants on COD of industrial storage battery wastewater, the ELM systems released some of the organic matter to the external phase. Moreover, in studies performed with different surfactants, Tween 85 contributed to COD of the wastewater more than Span 80 did. Kerosene showed more resistance to the release of organic matter than the other organic diluents used. The optimum values of membrane components were kerosene 70% (vol.), mineral oil 18% (vol.), D2EHPA 9% (vol.), and Span 80 3% (vol.). As a result of organic matter release, COD of the wastewater increased from 16 mg/l to about 160 mg/l after treatment with ELM. Therefore, future studies of ELM systems for the removal of several contaminants and tests of new membrane components must investigate the organic matter input to the external phase. When the pH value of industrial storage battery wastewater was adjusted to 4.0, lead removal efficiency reached approximately 90%, but additionally COD of the wastewater increased to >200 mg/l in the first minute of the treatment. It can therefore be stated that the increase in COD occurs at the beginning of the treatment. In conclusion, for reducing this organic matter release at the beginning of the removal study, the reactor stirring rate can be enhanced gradually; thus the shearing forces arising from stirring can be lowered. Furthermore, the dispersion of the emulsion phase into the external phase with different dispersion techniques can be studied to see the change in organic matter release. Finally, the release of COD can be reduced by preparing much more stable membranes, but in this case the removal of lead cannot be achieved. Consequently, when these options are tested, the release of organic matter into effluent can be minimized without negatively influencing lead removal efficiency.

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