Separation of aniline from aqueous solutions using emulsion liquid membranes

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Abstract

An emulsion liquid membrane process is developed to separate aniline from dilute aqueous solution. Aniline (amino-benzene) is a carcinogenic chemical common in industry and industrial wastewater. Due to aniline's high boiling point (183°C) and low concentration in wastewater, more traditional methods of separation such as distillation are very energy intensive. This emulsion process is offered as a low energy alternative. All separations occur in a Rushton stirred tank. The membrane phase consists of kerosene and the surfactant sorbitan monooleate (span 80). Hydrogen chloride solution is the internal phase. This study also examines the effects of HCl concentration, aniline concentration, and the amount of emulsion on separation. Up to 99.5% of the aniline is removed from solutions containing 5000 ppm in as little as 4 min depending on process conditions. Leakage is minimal and swelling is only about 3% after 5 min of processing. Approximately 98% of the membrane phase (both kerosene and span 80) is successfully recovered and recycled by using heat and/or adding 2-propanol for demulsification. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aniline is an aromatic amine $(C_6H_5NH_2)$ used as an intermediate in the manufacture of many dyes, pesticides, pharmaceuticals, and feedstock chemicals used to make rubber. In the United States, 62 facilities have reported the use or manufacture of aniline. It is a hazardous substance that readily dissolves in water up to 3.5%. Thus,

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aniline solubility in water not only increases its risk of possible pollution in wastewater but also in drinking water sources in case of a chemical spill. During the period 1981–1983, the National Institute for Occupational Safety and Health (NIOSH) estimated that over 35,000 workers were potentially exposed to aniline [1].

Aniline has produced tumors in animals and has been known to increase the risk of bladder cancer in humans. OSHA regulates the permissible exposure limit for aniline at 2 ppm on an 8-h time weighted average (TWA) for skin absorption. In addition, the American Conference of Governmental Industrial Hygienists has put a threshold limit value (TLV) for aniline at 2 ppm on the 8-h TWA with a skin notation. The aquatic toxicity rating, TLm96, for aniline is 10 ppm, which is the concentration that will kill 50% of the exposed organisms within 96 h [2].

The objective of this project is to develop an emulsion liquid membrane process to separate aniline from wastewater. Due to aniline's high boiling point (183°C), and generally low concentration (usually about 1% or less) in wastewater, distillation columns and other heat intensive separations require a large amount of energy to vaporize the low boiling material. The extraction scheme developed here is offered as a low-energy alternative.

Li [3] introduced emulsion liquid membrane (ELM) processes for the separation of hydrocarbons in 1971. Such processes consist of three phases: an external phase, a membrane phase and an internal phase. The external phase contains the solute (here a pollutant) to be extracted. The membrane phase physically separates the external and internal phases and contains a surfactant to maintain emulsion stability. In the internal phase or the receiving phase, the solute gets converted into a species that cannot diffuse back to the external phase. The solute diffuses from the external phase to the membrane phase, permeates through the membrane phase and reaches the internal phase where it is converted into another substance by reaction. The mass transfer depends on the concentration difference (driving force) of the solute between the external phase and the internal phase. The solute concentration in the internal phase is always zero in ELM systems, thus maximizing the concentration driving force. The solute removal rate also depends on the distance it must diffuse. A high concentration of emulsion droplets decreases the distance a solute molecule must travel, therefore increasing the rate of removal.

Two phenomena that are important in the study of ELM separation processes are leakage and swelling. Leakage of internal phase material is usually associated with a rupture of the membrane phase. Whenever the membrane phase is subjected to high shear, the emulsion globule may rupture and some of the internal phase leaks through the membrane phase to the external phase. This leak not only contaminates the external phase but also affects the separation process by reducing the driving force available. Swelling is the movement of external phase material through the membrane phase into the emulsion globule.

Li used liquid membranes to separate mixtures of hydrocarbons. He studied the effect of surfactant concentration on membrane selectivity and the effect of surfactant structure on permeation rate for heptane/toluene and heptane/hexadecane mixtures.

Shah and Owens [4] used liquid membranes for the separation of benzene and hexane. They investigated the effect of composition of feed, contact time with solvent,

and ratio of solvent volume to volume of hydrocarbon feed. Their results suggested that this technique might be more effective than distillation for a benzene/hexane system.

Phenol has been removed from wastewater using sodium hydroxide as the receiving phase [5,6]. The effects of NaOH concentration, phenol concentration, and the amount of emulsion on the separation factor have been established. Acetic acid has also been extracted from aqueous solution using NaOH as the receiving phase [6,7].

Borwanker et al. [8] studied the effect of internal phase leakage on separation and its deleterious effects on performance. High shear (due to high impeller stirring speed) and lengthy separation times are responsible for most leakage. Baird et al. [9] studied the removal of aromatic amines by injecting a concentrated solution of amine after an emulsion was introduced in the mixing tank. They also investigated the importance of reaction reversibility on the separation. Goswami et al. [10] studied ELM hydrocarbon separation processes under unsteady state conditions for continuous and batch devices. They presented analytical solutions for unsteady state diffusion equations. However, modeling has thus far had little influence on ELM system design. ELM processes are always developed experimentally as in this study.

Liquid membranes have often been employed to recover heavy metals from water systems. See, for example, Salazar et al. [11] on the recovery of chromium, or Larson and Wiencek [12] on the recovery of mercury. There are also some applications of ELM systems where the reaction in the internal phase creates a usable product. Wang and Jones [13] produced silicon dioxide spheres with diameters of about one micrometer using a sodium silicate internal phase reacting with sulfuric acid introduced into the external phase.

A schematic of an emulsion liquid membrane globule suspended in the external phase using the materials of this study is shown in Fig. 1. The emulsion is made by dispersing the internal phase in the membrane phase in a stirred tank in the presence of a surfactant. Shear introduced by the stirrer breaks the internal phase substance into spherical droplets. Surfactants help to keep the emulsion stable by preventing the droplets from coalescing. Small-sized droplets have a larger surface area per unit volume allowing excellent mass transfer. Typically, the size distribution of the dispersed internal phase droplets is about 1 to 100 μm. This emulsion is then mixed with the external phase in another stirred tank. Membrane phase globules with a size range of 0.1–2 mm are formed. This process results in an internal mass transfer area in the order of 10^6 m^2/m^3 [14] and an external mass transfer area of about 3000 m^2/m^3 [15]. After the separation process is completed, the agitator is stopped, and the mixture separates into two phases due to buoyancy. The treated external phase separates to the bottom, and the spent emulsion collects at the top. The top phase is then decanted and further processed to recover the membrane phase, and the reaction products of the internal phase. The recovered membrane phase (both kerosene and surfactants) can then be recycled.

The intent of the work is to develop a process for removal of aniline from wastewater using an ELM system. This study examines the effects of the amount of emulsion, aniline concentration, acid fraction in the emulsion and acid concentration on the removal of low concentrations of aniline in water solution. It is found that a system using kerosene as the membrane phase, and hydrochloric acid as the internal phase, and span 80 as a stabilizer gives excellent separation in a short time. The influence of
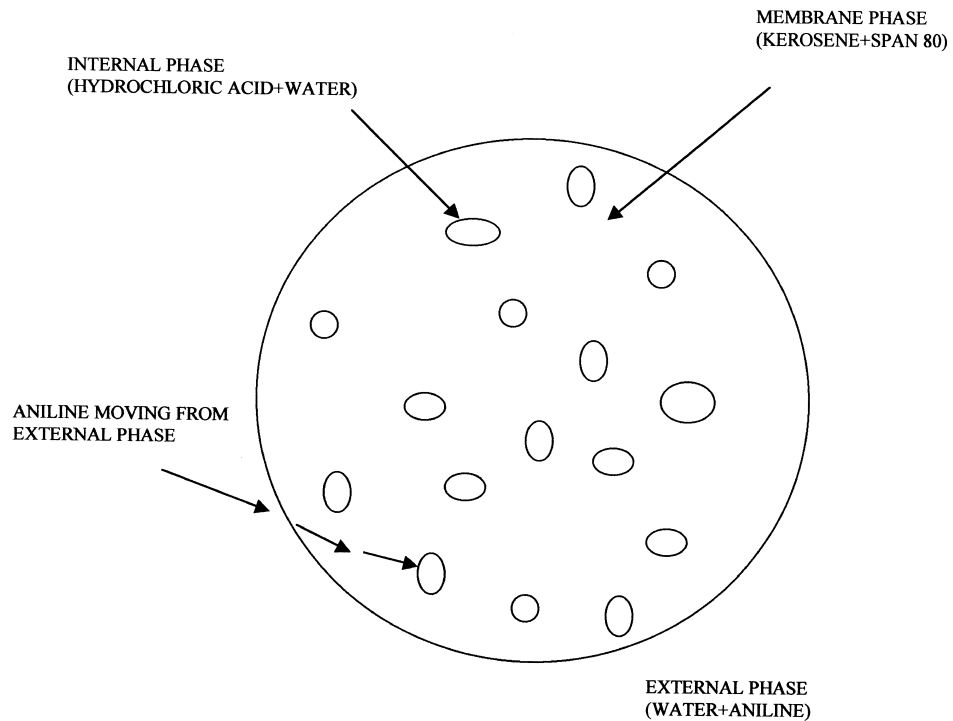
Fig. 1. An emulsion globule suspended in the external phase. The chemical contaminant (aniline) transports from the external phase (water) through the membrane phase (kerosene) to the internal phase (hydrochloric acid solution).

swelling and leakage is investigated as well. Demulsification is achieved by adding 2-propanol and by the application of heat.

2. Experimental

2.1. Equipment and materials

   The experimental set-up consists of two identical baffled tanks: one for emulsion preparation and the other for the separation process. The dimensions of a tank are shown in Fig. 2. The tanks are made of Plexiglas tubing and have an inner diameter of 15.4 cm and a height of 30 cm. They have four baffles, 90° apart, that extend one-tenth (1.54 cm) of the way into the tank. For all experiments, the liquid level is equal to the tank depth. This makes the liquid volume approximately 2.835 l. The agitating equipment is an electrically driven, variable speed motor with a 0–1750 rpm range supplied by Aldrich. This motor is connected to a shaft with a three-bladed marine propeller 5 cm in diameter. The propeller is located mid-way between the bottom of the tank and the liquid level. The stirring speed was measured by a model TAC-10 optical tachometer supplied by SPM Instrument. Aniline, hydrochloric acid, and span 80 (sorbitan monooleate), were of ACS grade and supplied by Sigma. Spectrum Chemical supplied kerosene.
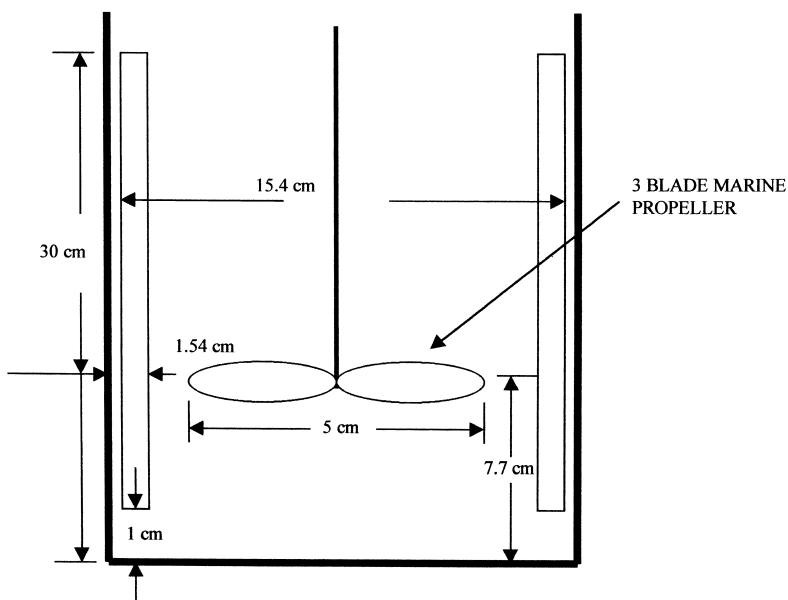

Fig. 2. Dimensions of the preparation and processing tanks.

2.2. Procedure

The membrane phase is prepared by pouring kerosene into the emulsion preparation tank, and bringing the stirring speed to 500 rpm. Then span 80 (2% of kerosene by volume) is added. After 5 min of mixing, the speed is slowly increased to 1600 rpm and held there for another 5 min. Hydrochloric acid is then introduced into the tank and mixed for 15 min at 1600 rpm. This results in an emulsion of hydrochloric acid particles in kerosene that has roughly a 1 to 20 μm drop size distribution of as measured by a microscope.

Aniline wastewater is prepared by dissolving aniline in distilled water in a mixing tank at 800 rpm for 10 min. The stirring speed setting is then decreased to 200 rpm and emulsion is added. All separation experiments were conducted at 200 rpm since preliminary experiments showed significant leakage above this stirring speed. Separation duration times were fixed at 1, 2, 4, 8, and 15 min. Final aniline concentrations were determined by averaging several titrations. Analysis showed the error (standard deviation) in measuring aniline by volumetric titration to be ±22 ppm. All separation experiments were begun at room temperature of about 22°C. A slight temperature rise of 2°C to 3°C occurred in each experiment due to heat of reaction and the addition of mechanical energy (stirring) to the system.
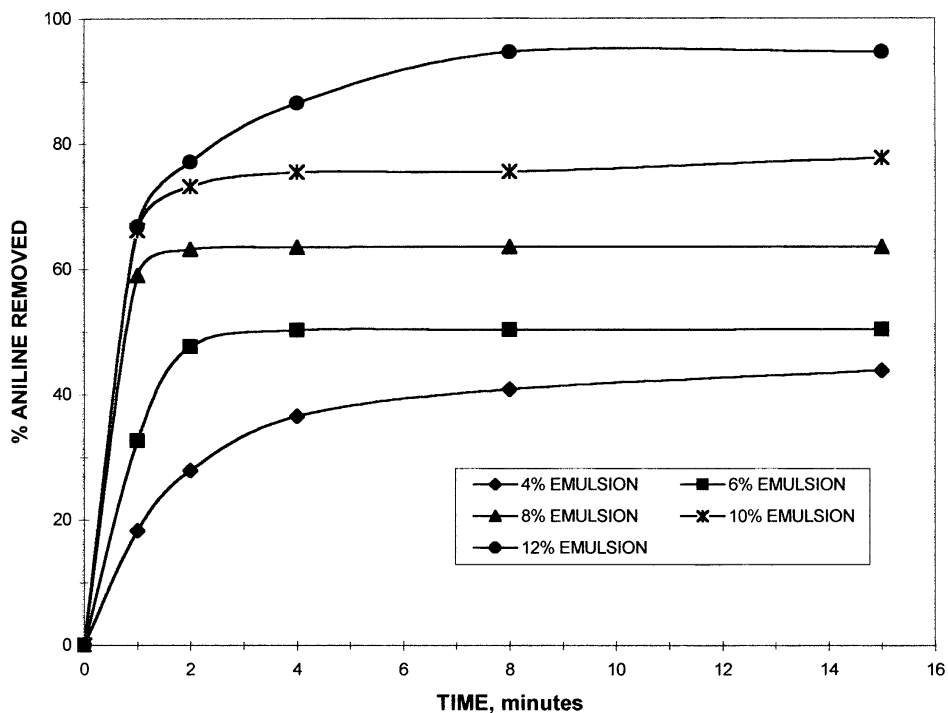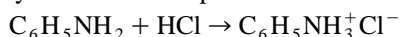

Fig. 3. The effect of emulsion fraction on aniline removal. External phase = 0.5% aniline in water; acid (3.0 M) fraction in emulsion = 0.25.

At the conclusion of each experiment, the addition of heat and/or an additive (2-propanol) were used for demulsification. The membrane phase (both kerosene and stabilizer) was then recovered and recycled.

3. Results and discussion

3.1. Process development

In order to establish the ELM process, variations in concentration of aniline in aqueous solution, emulsion quantity, and acid fraction in emulsion were observed over (separation) time. The range for amount of emulsion was chosen to be 4% to 20%. At values greater than 20%, it was found that the separation of spent emulsion from treated water was difficult due to the formation of a gelatinous white mass. For all separation experiments in this study, kerosene was the membrane phase, hydrochloric acid was the internal phase, and span 80 was used to stabilize the emulsion. The reaction of aniline with hydrochloric acid proceeds to an aniline salt in the internal phase as [16]:

$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+Cl^-$$

Surfactant fraction in emulsion was fixed at 2% of membrane phase by volume and the stirring speed was 200 rpm.
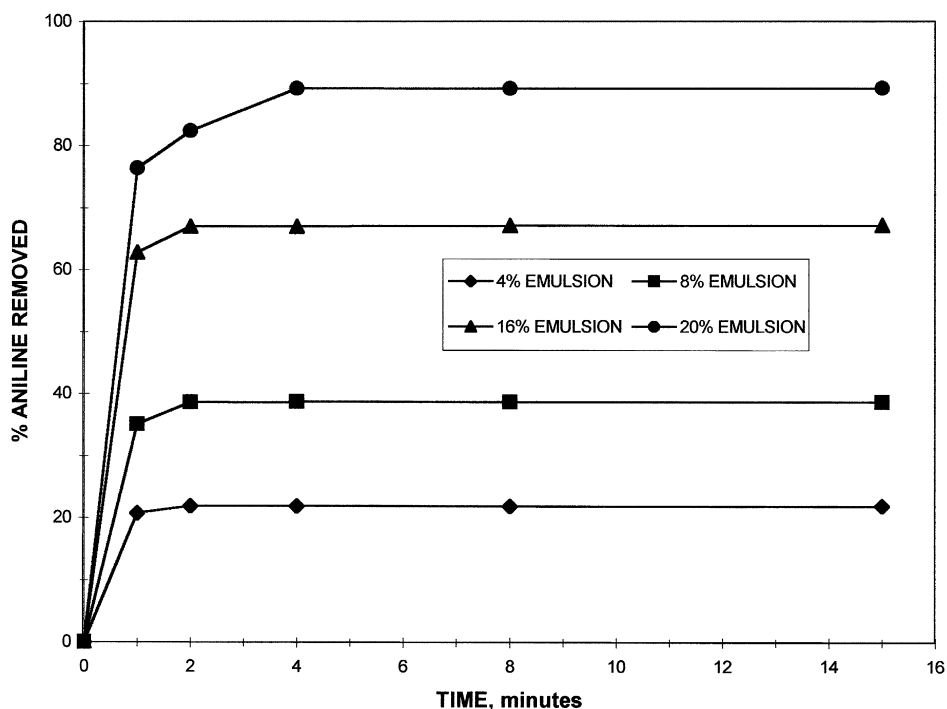

Fig. 4. The effect of emulsion fraction on aniline removal. External phase = 1% aniline in water; acid (3.0 M) fraction in emulsion = 0.25.

As a first step, the effect of processing time on aniline removal was studied using 4% emulsion, a 0.25 (25% of emulsion by volume) acid fraction, and 3.0 M acid, for a 0.5% (5,000 ppm) aniline solution. As shown in Fig. 3, 20% of the aniline is removed in the first minute and almost 40% is removed in 4 min. As emulsion fraction was increased, separation increases. For 12% emulsion, 70% of the aniline is removed in the first minute and 94.7% is removed in 8 min. The increase in initial removal rates and total removal with emulsion fraction is due to the nearer proximity of emulsion droplets, a greater total transfer area, and a greater acid amount (capacity). To approximate inter-droplet distance, assume a cubic array of emulsion droplets with diameters of 1 mm. The inter-droplet distance is then $(4/3\pi a^3/\phi)^{1/3} - 2a$, where a is the droplet radius and ϕ is the emulsion volume fraction. For a 4% emulsion fraction ($\phi = 0.04$), the inter-droplet distance is 1.357 mm. For a 12% emulsion fraction, the inter-droplet distance shrinks to 0.634 mm, thus contributing to the increase in initial removal rates.

These experiments were repeated for higher aniline concentrations with the same acid fraction and concentration. Figs. 4 and 5 show the results for concentrations of 1% and 2%, respectively. The percentage of aniline removed decreases with increasing aniline percentage for equal amounts of emulsion. Most of the separation in 1% and 2% aniline solutions occurred in the first 2 min, whereas for the 0.5% aniline solution (Fig. 3), aniline removal levels off after about 2 to 4 min. The absolute removal rate in the first
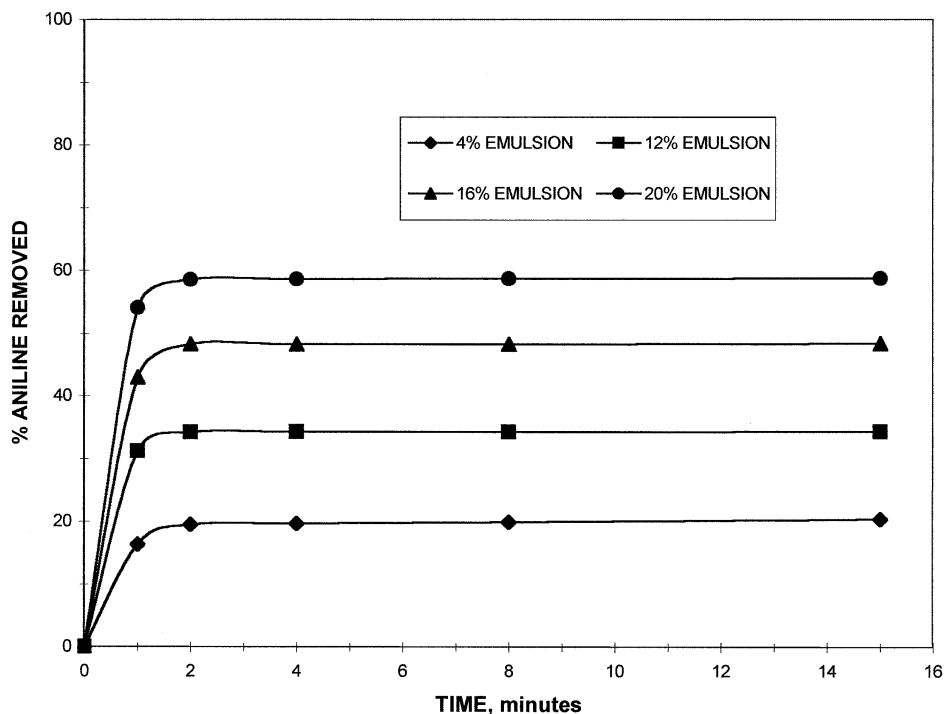

Fig. 5. The effect of emulsion fraction on aniline removal. External phase = 2% aniline in water; acid (3.0 M) fraction in emulsion = 0.25.

minute, however, increases with aniline percent. For example, with 0.5% aniline and 12% emulsion, 67% or 3350 ppm of 5000 ppm available is removed in the first minute. For the 2% aniline solution with 12% emulsion, only 32% is removed in the first minute but this corresponds to 6400 ppm of 20,000 ppm. This increase in initial removal rate is due to the higher concentration driving forces with higher concentrations of aniline.

Acid concentration was increased from 3.0 to 6.0 M and acid fraction in the emulsion was decreased from 0.25 to 0.125. The number of moles of acid remained the same as in previous experiments, but the emulsion quality was physically different (fewer interior phase globules, therefore less transfer area). Figs. 6 and 7 show the results for 0.5% and 1% aniline concentration, respectively. For 0.5% aniline concentration, separation increases with time throughout the 15-min experimentation period, rather than leveling off after only 2 to 4 min, as in previous experiments (Figs. 3–5). The generally slower removal rates are due to the lesser transfer area in the internal phase. Also, the more gradual behavior may be due to an emulsion made with an acid fraction of 0.125 having a relatively lower density and a tendency to float somewhat in the external phase. The emulsion density in this case is 852.9 kg/m^3 compared with 870.6 kg/m^3 when the acid fraction is 0.25 at 3.0 M concentration. A close look at the 1% aniline removal rates shows that although they do not level off, the increase is more subtle than for the 0.5%
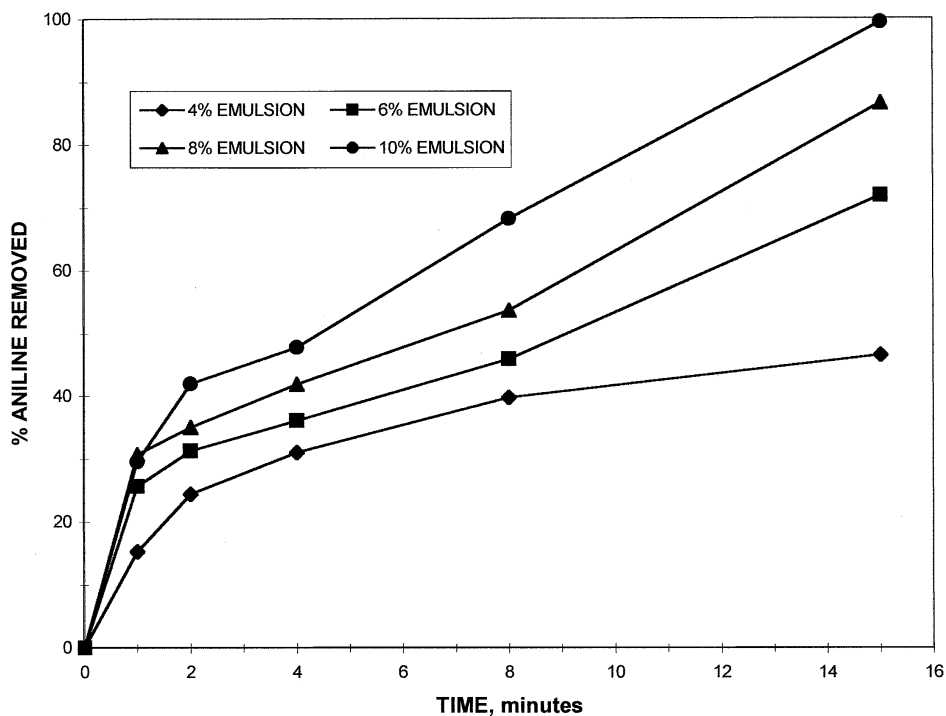

Fig. 6. The effect of emulsion fraction on aniline removal. External phase = 0.5% aniline in water; acid (6.0 M) fraction = 0.125.
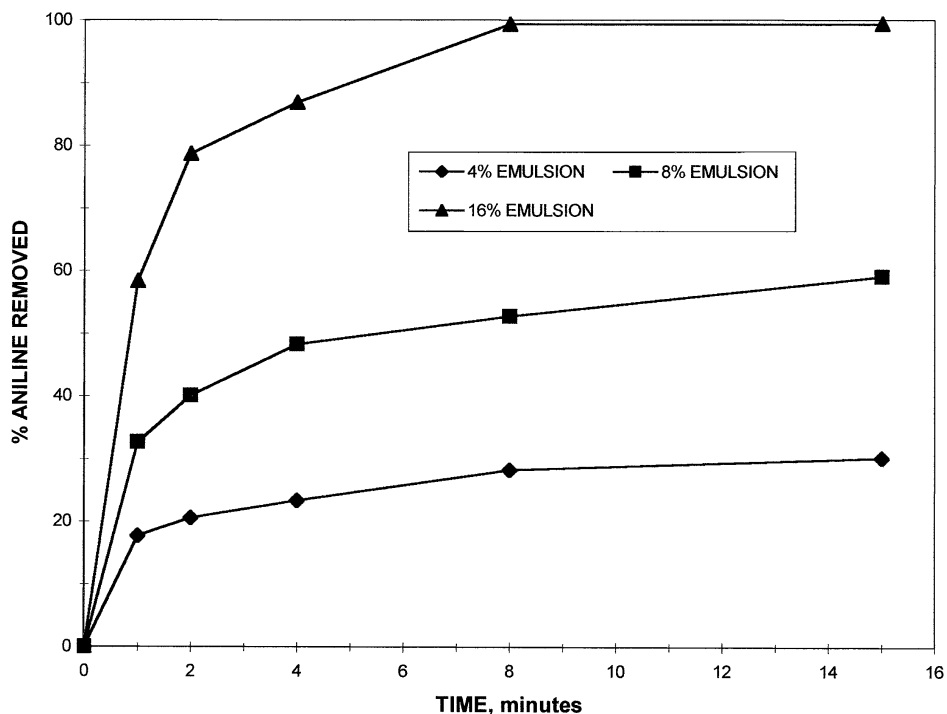
Fig. 7. The effect of emulsion fraction on aniline removal. External phase = 1% aniline in water; acid (6.0 M) fraction = 0.125.

removal rates. This may be due to a damping effect of the higher aniline concentration, which is previously shown to produce higher initial removal rates and lower rates thereafter.

Although the initial rates are lower, ultimately, the systems containing 6.0 M acid and a 0.125 fraction have superior removal rates to more dense equal-acid equivalent systems. For 1% aniline concentrations (Fig. 7) and a 16% emulsion fraction, after 8 min, this system removes 99.44% of the aniline, whereas the equal acid (3.0 M/0.25, Fig. 4) system removes only 67.1%. The 6.0 M/0.125 system manages to consume the available acid to a greater extent, although it requires significantly more processing time to do so.

A lower density emulsion may be an advantage for separations carried out in a continuous Oldshue-type device. Here, the dispersed phase floats through a descending external phase in a column with multiple impellers centered along the column axis [10].

To observe the effect of acid quantity, the acid fraction in the emulsion was increased to 0.5. The concentration of acid was 3.0 M and the aniline concentration was 0.5%. Earlier acid fractions of 0.125 and 0.25 resulted in emulsions with lower density and had minor problems with floating and therefore complete dispersion in the external phase. The 0.5 acid fraction has a density of 918.4 kg/m^3. Dispersion in this case was excellent. Using only 8% emulsion (notice this is the same amount of acid as 0.25

fraction and 16% emulsion, but uses less kerosene and span 80), a separation of 98.31% is achieved after 2 min and a separation of 99.44% is achieved after 4 min. See Fig. 8.

Fig. 8 also contains comparisons of systems with equal amounts of acid, but different acid distributions, used to process a 0.5% aniline solution. The aniline removal in a system with an 8% emulsion and a 0.25 acid fraction has a very slightly superior performance when compared to an equal acid system with a 4% emulsion and a 0.50 acid fraction. Although these experimental comparisons are of systems with equal amounts of acid, the higher amounts of emulsion together with the lower fraction of acid presents more transfer surface area and less external transfer distance for the aniline molecule. However, the higher acid percentage has a greater density and therefore better emulsion dispersion, possibly accounting for the better initial removal rates of the 6% emulsion/0.50 acid fraction system over the equal-acid 12% emulsion/0.25 acid fraction system. In general, the lower acid fraction systems eventually have a more complete consumption of available acid (therefore a better total aniline removal), and a slower removal rate.

Fig. 8 also includes an 8% emulsion, 0.5 acid fraction system for which there are no equal-acid data. This system achieved the best aniline removal performance in this study. 92.75% of the aniline is removed in the first minute and 99.44% is removed in only 4 min.
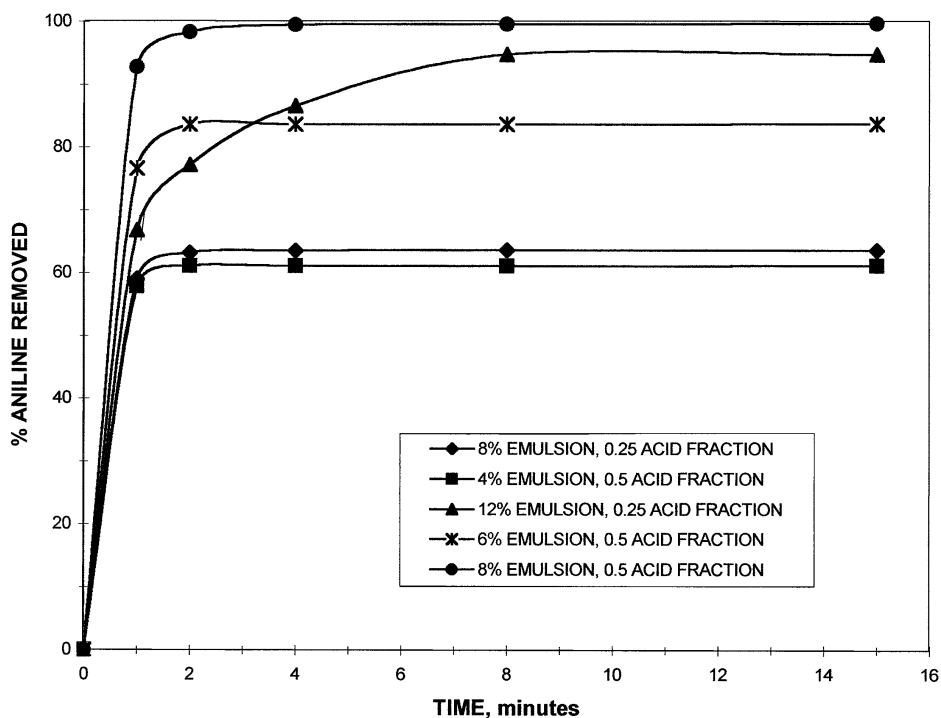

Fig. 8. The effect of acid distribution on aniline removal. External phase = 0.5% aniline in water.
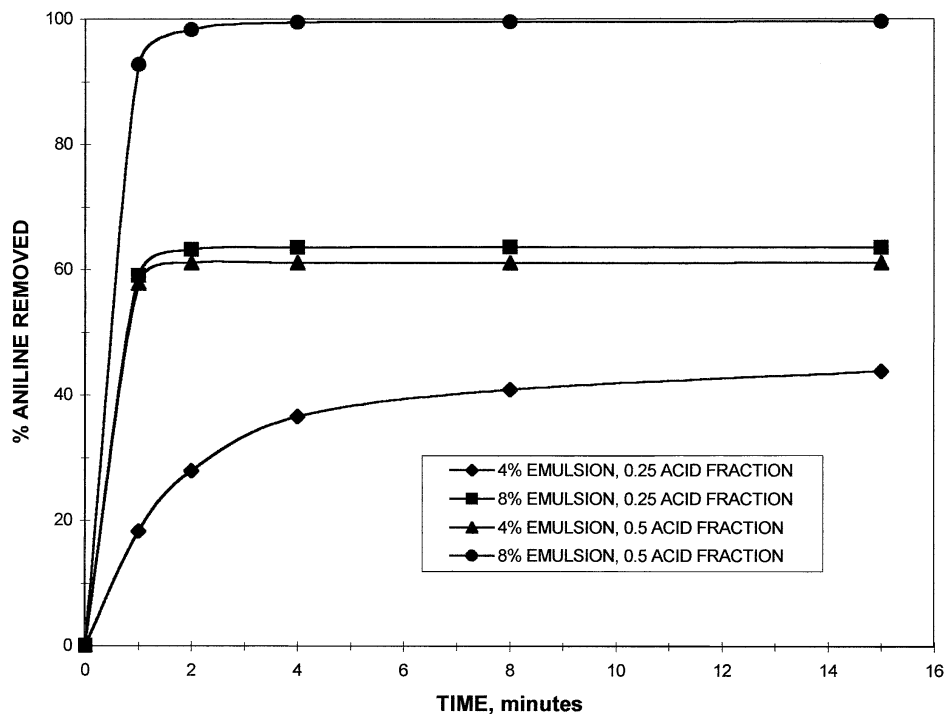
Fig. 9. The effect of doubling the acid fraction to 0.5 (3.0 M) on aniline removal. External phase = 0.5% aniline in water.

The effect of simply doubling the acid fraction is shown in Fig. 9. For an aniline concentration of 0.5%, 3.0 M acid, and 4% emulsion, doubling the acid fraction from 0.25 to 0.5 resulted in about 50% more aniline removed after 8 min. For an 8% emulsion, doubling the acid fraction increased aniline removal from 62% to 99.44% after 4 min. Although the removal performances are clearly superior for the double-acid systems, the available acid is used less efficiently.

3.2. Leakage and swelling

Acid leakage and swelling studies are summarized in Table 1. All experimental systems used acid fractions of 0.5 with 3.0 M. All data were taken after 5 min of processing at 200 rpm. As emulsion fraction increased from 4% to 10%, the amount of acid leaked increased from 8.7 to 13.0 mg/l. The membrane phase swells just over 3% with external phase material (0.5% aniline–water solution) for all systems.

Swelling is low compared with values of found in the literature, which are often 10%, or above [14]. Although comparison data could not be found, leakage seems minimal. This may be due to the relatively low stirring speed of 200 rpm vs. 400 to 600 rpm of other studies. Also kerosene about has a low viscosity (1.09 cp) compared to the paraffin oils (about 20 cp) often used as a membrane phase. Since a higher viscosity liquid

Table 1
Membrane swelling and leakage

Hydrochloric acid fraction = 0.50; hydrochloric acid concentration = 3.0; stirring speed = 200; processing time = 5 min.

Percent emulsion in system	Molarity of acid leaked (moles/l)	Amount of acid leaked (mg/l or ppm)	Water transport to emulsion (kg/m^3)	Percent swelling of membrane
4	0.000238	8.7	29.93	3.16
6	0.000258	9.4	29.50	3.11
8	0.000318	11.6	30.06	3.17
10	0.000357	13.0	29.05	3.07

carries shear better, both smaller droplets and more swelling and leakage should be created with a paraffin or other relatively high viscosity membrane phase [17].

3.3. Demulsification

There are three established methods of demulsification: heating, applying a high voltage electrostatic field, and chemical additives. For all systems in this study, it was found that demulsification proceeds rapidly when the temperature was raised to 180°F. It was also found that adding 2-propanol immediately dissolved the spent emulsion. The required amount of alcohol is about 25% of spent emulsion by volume for complete phase separation. When the recovered kerosene was mixed with fresh hydrochloric acid, a stable emulsion was formed without the addition of the surfactant span 80. This recovered membrane phase was then used in subsequent experiments. The recovery of the membrane phase was about 98% by this process.

4. Conclusions

An emulsion liquid membrane separation system has been successfully developed to remove dilute aniline from aqueous solution. As much as 99.5% of the aniline is removed in as little as 4 min in a standard Rushton stirred tank using kerosene and span 80 as the membrane phase and hydrochloric acid as the internal phase. Total aniline removal and removal rates are strongly influenced by the emulsion fraction of the separation system and the acid fraction in the emulsion globules. Leakage and swelling are minimal.

Demulsification is accomplished by heating to 180°F. Also, it was discovered that 2-propanol is an excellent demulsifying agent for this system. Use of 2-propanol allowed for the recycling of 98% of the membrane phase.

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