

Recovery of Aniline from Aqueous Solution Using the Membrane Aromatic Recovery System (MARS)

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This paper describes a new process for the recovery of aromatic, cyclic, and aliphatic amines from aqueous streams, the membrane aromatic recovery system (MARS). The process comprises a stripping vessel, where the amines are extracted through nonporous membranes and concentrated into an HCl solution as hydrochloride salts, and a two-phase separator in which the solution from the stripping vessel is separated into an aniline-rich phase and an aqueous phase by adjusting the pH to caustic conditions with NaOH. In this study, aniline was recovered from a synthetic wastewater using silicone rubber tubing as the membrane. The stripping-solution temperature was 50 °C, and the HCl concentration was 10.45 wt %. After recovery, an organic-rich product phase containing 96.5 wt % aniline and 3.5 wt % water was obtained. The overall mass-transfer coefficients (OMTCs) for a range of amines were also investigated to demonstrate the wide potential application of MARS technology.

Introduction

Aniline is a chemical that is produced in large quantities (U.S. production of 450 000 tons in 1992¹) and has broad market application. The main use for aniline is the production of isocyanates (specifically diphenylmethane diisocyanate, which is heavily employed in the manufacture of polyurethanes). Aniline is also widely used in the production of pesticides, dyes, rubber, pharmaceuticals, and chemical intermediates. Laboratory studies have shown that the presence of aniline in the diet of animals might cause cancer, adverse effects in the blood, and spleen damage.² Aniline is relatively soluble in water (3.4 wt % at ambient conditions) and is very toxic to aquatic life. It is estimated that a concentration of 10 ppm can kill 50% of exposed aquatic organisms in 96 h.³ Even so, it is estimated that 725 tons of aniline was released during 1992 in the U.S. alone.² Because aniline is such a common and important chemical, it was chosen for investigation as a model compound in this study.

Processes proposed to remove aniline from wastewater are often destructive processes, such as biological treatment,^{4–6} wet air oxidation,⁷ photocatalytic oxidation,⁸ ozonolysis,⁹ and electrochemical oxidation.¹⁰ However, these processes have the drawback of destroying a valuable chemical.

Aniline has a high boiling point (184.4 °C at 1 atm) and a low vapor pressure (0.3 mmHg at 20 °C). Therefore, aniline recovery from wastewater using steam stripping requires large steam flows and creates a need to deal with the condensate flow. Solvent extraction,¹¹ adsorption, and membrane processes have been proposed as less energetically intensive separations for the removal and recovery of aniline from wastewater. Liquid extraction has some drawbacks: when the concentration in the wastewater is very low or an apolar solvent is used, recovery efficiencies are low; if a polar solvent is used, the wastewater becomes contaminated with the solvent because of its high solvent solubility.¹² The tendency to form stable emul-

sions of the two phases is a further problem of liquid extraction.¹³ The use of solid adsorbents,¹⁴ such as activated carbon¹⁵ or organobentonite,¹⁶ avoids the problems of phase separation. However, adsorbent regeneration is required, and this operation often implies destruction of the compound¹⁵ or its dissolution in a liquid, thus requiring further treatment.¹⁷ The stability and loss of the adsorbent phase is also an issue.

Membrane processes reported for aniline recovery include liquid membrane extraction and pervaporation. Emulsion liquid membranes¹⁸ are inherently unstable because of the leakage of the internal phase into the wastewater and the swelling of the liquid membrane by the wastewater phase.¹⁹ This process also requires a demulsification step to recover the final product and reuse the membrane phase.¹⁸ In pervaporation, the use of a nonporous solid membrane avoids problems related to membrane instability.^{20,21} This technique has been heavily explored in academic research over the past 10 years. However, it has not achieved widespread application to the recovery of low-volatility organics from wastewaters. The present authors believe that this is due to the low driving forces and the costs and practicalities associated with producing the very high vacuums required for pervaporation of low-volatility compounds.

Klein et al. reported the use of a dialysis system to extract phenol²² and aniline²³ from a wastewater to a receiving solution. In these studies, the driving force for phenol and aniline extraction was maintained by an acid–base reaction in the receiving solution, using sodium hydroxide or sulfuric acid. These studies showed the possibility of using acid–base dissociation to extract aromatic molecules. However, the molar concentration of acid or base was higher than the molar concentration of anilinium or phenolate, respectively, in the stripping solution, and organic recovery was neither possible nor attempted.

Membrane aromatic recovery system (MARS) is a new process that has been developed for recovery of aromatic

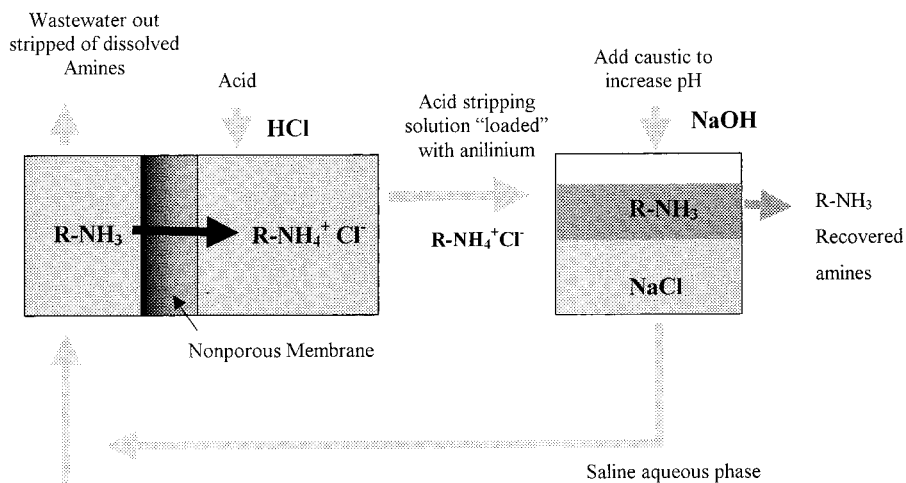


Figure 1. Schematic diagram of MARS process showing the operating principle.

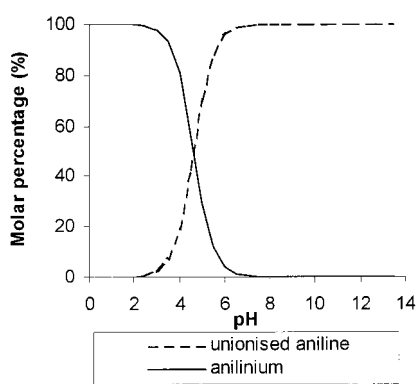


Figure 2. Molar percentages of total aniline present as un-ionized aniline or anilinium as a function of pH.

acids.²⁴ In this paper, we show that the MARS process can also be used to recover aromatic bases, such as aniline, from wastewaters. The MARS process, applied to amine recovery, is shown schematically in Figure 1. Aniline is continuously extracted from a wastewater passing through a tubular membrane into an acidic stripping solution, where pH is controlled by the addition of HCl as required. Under acidic conditions, aniline, a weak base, reacts with HCl to form anilinium chloride salt. Anilinium is a charged ion that cannot cross back through the hydrophobic membrane into the wastewater, so the driving force for mass transfer through the membrane is maintained. Therefore, the concentration of aniline in the stripping solution increases with time until the system reaches a steady state. Aliquots of the stripping solution produced are collected and adjusted to alkaline conditions by the addition of sodium hydroxide. Anilinium chloride reacts back to form un-ionized aniline and NaCl. Because the aniline present in the resulting solution is over its solubility limit in aqueous solution, the solution separates into two phases: an aniline-rich phase and a saline aqueous underlayer phase. The aqueous underlayer phase is returned to the wastewater, and the aniline-rich phase is the final product.

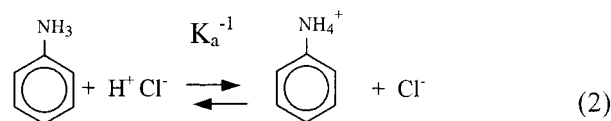
The MARS process will produce 1 g of salt (NaCl) per 1.6 g of aniline recovered. However, (a) NaCl is considerably less toxic on a mass basis than aniline, and (b) many of the waste streams emanating from chemical manufacture already contain sufficient inorganic NaCl that the extra salt produced by MARS is insignificant.

Theoretical Background

Acid–Base Equilibrium. Amines are weak bases. Acid–base reversible reactions in water are proton-transfer reactions, described as Brønsted equilibria expressed by the acid dissociation constant (K_a)

$$K_a = \frac{[\text{R-NH}_3][\text{H}_3\text{O}^+]}{[\text{R-NH}_4^+]} \quad (1)$$

In this study, it is assumed that the acid dissociation constant is independent of temperature and ionic strength. In the stripping solution, aniline reacts with hydrochloric acid to produce anilinium chloride



In the stripping solution, the total aniline concentration comprises the sum of the anilinium and the un-ionized aniline concentrations. Using a K_a of 2.34×10^{-5} for aniline, calculated values of the molar percentages of aniline present in each form as a function of pH are shown in Figure 2. The concentration of the un-ionized aniline is related to the total aniline concentration in the stripping solution by

$$C_s^N = \frac{C_s^T}{1 + 10^{-\text{pH}/K_a}} \quad (3)$$

Overall Mass-Transfer Coefficient (OMTC). The overall mass-transfer coefficient is the reciprocal of the sum of all of the resistances to mass transfer in the system. In this case, we use film theory to describe mass transfer and assume that the resistances are (i) the membrane itself, (ii) the membrane/wastewater liquid-film resistance, and (iii) the membrane/stripping solution liquid-film resistance. In the present system, we further assume that the reaction that occurs in the stripping solution is both instantaneous and reversible. Thus, we can write for the flux of aniline across the membrane

$$J = K_{ov}(C_w - C_s^N) \quad (4)$$

where

$$\frac{1}{K_{ov}} = \frac{1}{k_t} + \frac{r_i \ln \frac{r_o}{r_i}}{DK} + \frac{r_i}{Er_o k_s} \quad (5)$$

E in eq 5 is the enhancement factor, as developed by Hatta²⁵ for gas–liquid adsorption and extended to liquid–liquid systems by Grosjean and Sawistowski²⁶ for instantaneous but irreversible reactions. Olander²⁷ has developed an expression for E in instantaneous reversible reaction systems. Unlike the case for irreversible reactions, this expression does not have a solution for E in terms of readily measurable system variables. In addition, the effects of ion rather than molecule diffusion have not been assessed for reversible reactions. A detailed analysis of mass-transfer phenomena is beyond the scope of the present paper. Rather, these points are noted to caution readers when using the K_{ov} values from this paper: we recognize that a more detailed analysis is required for extrapolation beyond the present system to other concentrations and membrane resistances. However, in the present system, preliminary calculations show that membrane resistance of the relatively thick (500 μm) silicone rubber tube dominates K_{ov} , and eq 5 can be simplified to

$$\frac{1}{K_{ov}} = \frac{r_i \ln \frac{r_o}{r_i}}{DK} = \frac{r_i \ln \frac{r_o}{r_i}}{P} \quad (6)$$

This assumption is borne out for the conditions employed by subsequent experimental data. In the case analyzed, the wastewater flows inside the membrane tubes in plug flow, and a well-mixed stripping solution is present on the outside of the tubes. Using eq 4 at steady state, a differential mass balance can be derived, which, upon integration along the membrane tube, yields

$$\ln \left(\frac{C_{out} - C_s^N}{C_{in} - C_s^N} \right) = - \frac{2\pi r_i}{F_w} K_{ov} L \quad (7)$$

Substituting eq 3 into eq 7 gives

$$K_{ov} = - \frac{F_w}{2\pi r_i L} \ln \left(\frac{C_{out} - \frac{C_s^T}{1 + 10^{-\text{pH}/K_a}}}{C_{in} - \frac{C_s^T}{1 + 10^{-\text{pH}/K_a}}} \right) \quad (8)$$

Materials and Methods

Chemicals and Assays. Organic amines were supplied by Aldrich, U.K., and Lancaster Synthesis, U.K. HCl solution (37 wt %) was supplied by BDH Laboratories, U.K., and NaOH (50 wt %) solution was supplied by Solutia (U.K.) Ltd. K_2HPO_4 , KH_2PO_4 , and NaCl, were supplied by Rose Chemicals, U.K. Deionized water was used in all dilutions and solution preparations. Synthetic wastewaters of most of the amines, including aniline, were prepared by dissolving pure amine in deionized water.

Organic compound concentrations were assayed using gas chromatography (GC) and total organic carbon

Table 1. Experimental Conditions

parameter	value
inlet aniline concentration	5 g L ⁻¹
length of membrane	10.5 m
inner diameter membrane	0.003 m
outer diameter membrane	0.004 m
thickness of membrane wall	0.0005
flow rate	(a) 5.5 L day ⁻¹ (b) 3.5 L day ⁻¹
HCl concentration fed	10.45 wt %
pH of stripping solution	1, 2, 2.4
temperature of stripping solution	50 °C
stripping vessel liquid volume	1.5 L

(TOC) analysis. The TOC machine required sample pH's between 4 and 8. For successful GC, all of the aniline should be in the un-ionized form; at pH 7, Figure 2 shows that 99.4% of aniline is in the un-ionized form. Therefore, the samples were diluted in a buffer of $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ to provide pH 7 prior to extraction.

A gas chromatograph (Perkin-Elmer AutoSystem XL) with a FID detector was fitted with a megabore column 25 m in length with a 0.53-mm internal diameter. Helium was used as carrier gas. Prediluted samples (0.5 mL) were extracted with 1 mL of a solution of dichloromethane containing chlorobenzene as the internal standard. One microliter of this extracted solution was injected onto the GC the column. The program ran for 2 min at 60 °C, followed by an increase of temperature to 240 °C at a rate of 20 °C min⁻¹. The coefficient of variation of this assay (from five independent measurements) was less than 5% at a concentration of 300 mg L⁻¹. TOC was measured using a TOC-5050 analyzer (Shimadzu Corporation, Kyoto, Japan). The coefficient of variation of this assay (from three independent measurements) for each sample was less than 2%. The water concentration in the recovered aniline phase was measured using Karl Fisher titration. Each sample (2.5 μL) was injected in a Mettler DL37 KF Coulometer machine. The coefficient of variation of this assay (from five independent measurements on each sample) was less than 5%.

Membrane Material. The commercially available silicone rubber membrane used in this study is composed of 30 wt % fumed silica and 70 wt % poly(dimethylsiloxane) (PDMS). The membrane was supplied as a tube of 3-mm internal diameter and 0.5-mm wall thickness by Silex Ltd U.K. The addition of the fumed silica to the silicone rubber tubing is necessary to impart mechanical strength to the membrane.

MARS Operation. The process was run with an aniline-containing synthetic wastewater. Figure 3 shows a schematic diagram of the experimental setup. Table 1 summarizes the main parameters of the system. Using a peristaltic pump, the wastewater was pumped in a single pass through the membrane tube at a constant flow rate of either 3.4 or 5.5 L day⁻¹, corresponding to Reynolds numbers of 30 and 50, respectively. The membrane tube was coiled around a support and submerged in the stripping solution. Temperature control and well-mixed conditions in the stripping solution were achieved by connecting a stirred magnetic hot plate to a temperature controller and a temperature probe. The stripping-solution pH was kept constant via a feedback loop. HCl solution was pumped from a measuring cylinder as required to maintain the pH value in the stripping solution. An overflow outlet in the side wall of the stripping vessel kept the volume inside this vessel constant.

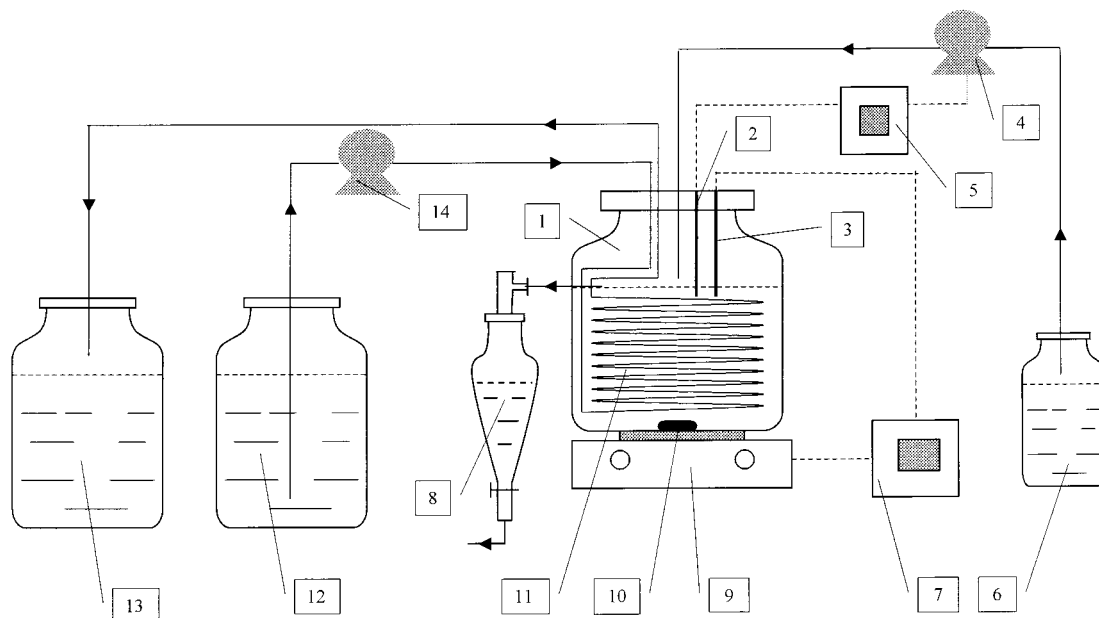


Figure 3. Diagram of experimental setup: 1, stripping vessel; 2, pH probe; 3, temperature probe; 4, peristaltic pump; 5, pH controller; 6, tank for HCl solution; 7, temperature controller; 8, collector; 9, magnetic stirrer hotplate; 10, magnetic bar; 11, membrane tube; 12, tank for wastewater containing dissolved aniline; 13, tank for clean water; 14, peristaltic pump.

The stripping-solution overflow was collected in a measuring cylinder. It was periodically removed to a separating funnel, where the pH was adjusted to alkaline conditions using 50 wt % NaOH, and the resulting two-phase mixture was allowed to stand overnight to separate. The aniline-rich organic phase was recovered, and the aqueous-phase underlayer was recycled in batches to the untreated-wastewater container (number 12 in Figure 3) and passed through the membrane to extract any residual dissolved aniline.

Mass-Transfer Tests. A similar apparatus was built to measure the OMTCs for a range of amines. Three independent noncoiled (randomly spaced) membrane tubes were submerged in a single stripping-solution vessel. The pH was kept below 1 using HCl solution. Under these conditions, the un-ionized amine concentration in the stripping solution was assumed to be zero. In each run, three amines were tested, with a solution of each amine being pumped through one of the three membrane tubes using a multichannel peristaltic pump regulated to a flow of 5 L day⁻¹. This corresponded to a Reynolds number of 45 inside each 18-m-long tube.

Mutual Solubility Tests. To study the effect of ionic strength on the mutual solubility of aniline and water, five flasks of 100 mL of aqueous solutions with different NaCl concentrations and 20 g of aniline each were prepared. The solutions were mixed overnight at 30 °C. Then, each mixture was transferred to a separating funnel, where it was left overnight to phase separate. The water concentration in the organic phase and the aniline concentration in the aqueous phase were then measured, and the Na⁺ and Cl⁻ concentrations in the aqueous phase were measured by ion chromatography.

Results and Discussion

Overview of MARS Performance. Figure 4 shows the inlet and outlet concentrations in the wastewater and the total concentration of aniline in the stripping solution over 107 days of experiment. The total aniline concentration in the stripping solution took 56 days to

reach a steady state at a value 43.6 times higher than that at the wastewater inlet (218.5 vs 5 g L⁻¹), allowing for high recovery efficiencies. The value of 218.5 g L⁻¹ is the average value of the aniline concentrations in the stripping solution at steady state over the last 51 days of experiment (with a coefficient of variation of 2.3% over 47 points). The outlet concentration showed a significant effect of stripping-solution pH on the mass-transfer rate. An aniline mass balance on the stripping process was struck for each sampling period, as expressed below

$$F_w \Delta t (C_{in} - C_{out}) = V_s \Delta C_s^T + C_s^T \Delta V_{out} \quad (9)$$

This mass balance (plotted in Figure 5) compares the mass of aniline removed from the wastewater to the mass of aniline accumulating in the stripping solution and leaving the system via the stripping-solution overflow. The data in Figure 5 show good agreement with a deviation below ±10%. The organic phase obtained after recovery was composed of 96.5 wt % aniline and 3.5 wt % water. No other organic compound was detected by GC analyses of the recovered organic phase.

Effect of pH in the Stripping Solution. The pH in the stripping solution was controlled at value of 1 during the first 88 days of the experiment. After operating at steady state for 32 days, i.e., at a constant concentration of total aniline in the stripping solution, the pH was then controlled at 2.4 and then at 2, and then HCl addition was finally ceased.

The effect of pH on the mass-transfer rate is shown in Figure 4. It can be seen that an increase of pH in the stripping solution clearly corresponds to an increase in outlet aniline concentration. According to Figure 2, the concentrations of un-ionized aniline in the stripping solution at pH 1, 2, and 2.4 are 0.05, 0.51, and 0.59 g L⁻¹, respectively. Therefore, as stripping-solution pH increases, the driving force decreases, and the mass-transfer rate decreases, resulting in the increase in the aniline outlet concentration shown in Figure 4 and predicted by eq 7.

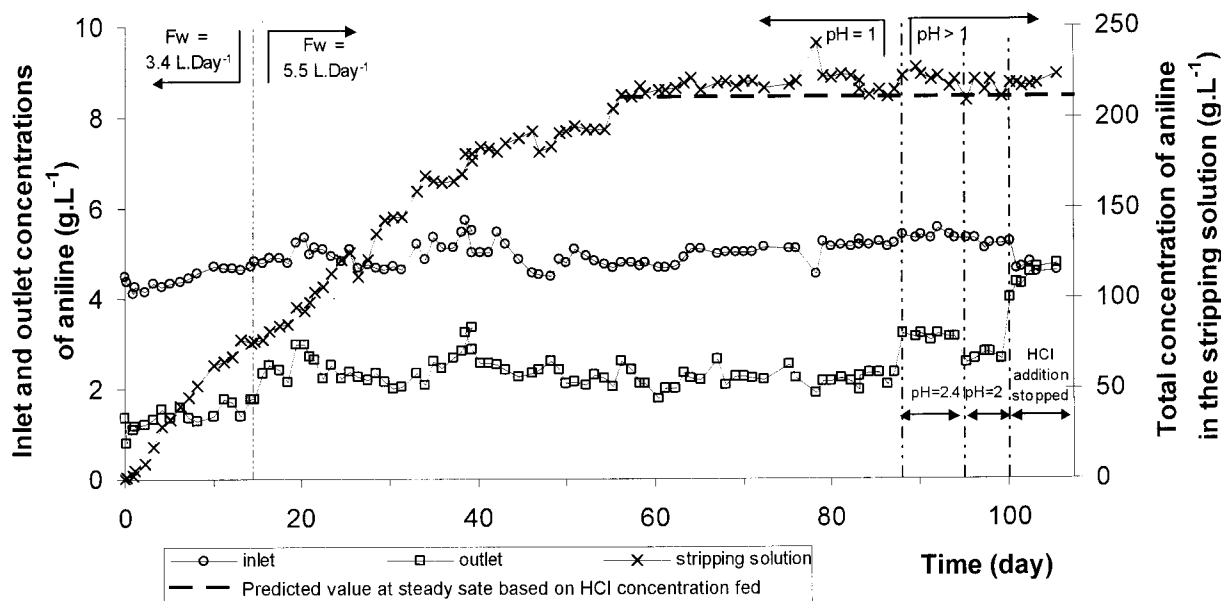


Figure 4. Evolution of aniline concentrations in the inlet, outlet, and stripping solution over time in the MARS process.

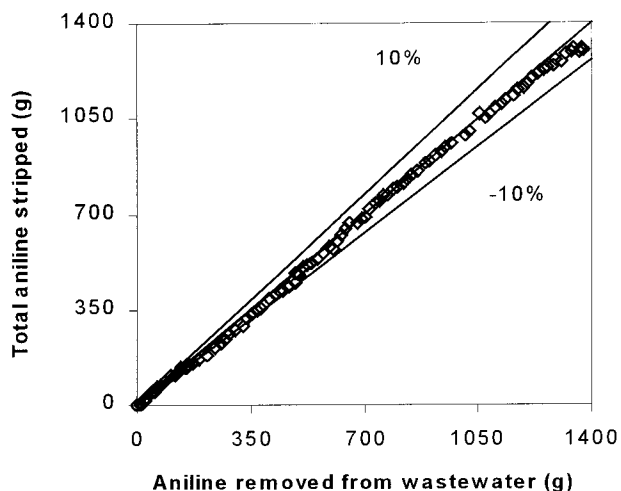


Figure 5. Mass balance between aniline removed from wastewater and aniline appearing in the stripping solution.

After 100 days of experiment, addition of HCl was stopped, and pH was no longer controlled. An increase in pH was then observed because aniline continued to cross the membrane and neutralize the free HCl in the stripping solution. An increase in aniline outlet concentration was also observed until the aniline inlet and outlet concentrations were equal and the experiment was finished. At this stage, the stripping-solution pH was 3.4, with a total aniline concentration of 218 g L^{-1} and a wastewater aniline inlet concentration of 4.6 g L^{-1} . Equation 3 predicts that, for a stripping-solution concentration of 218 g L^{-1} , the concentration of unionized aniline in the stripping solution should be equal to the inlet wastewater aniline concentration of 4.6 g L^{-1} when the pH is 2.96. The slight disparity between the measured value of 3.4 and the predicted value of 2.96 is most probably due to the effects of temperature and ionic strength on the acid dissociation constant or errors in concentration and pH measurements.

Overall Mass-Transfer Coefficient. Using eq 8, OMTCs were calculated, and the data are shown in Figure 6. The OMTC of aniline fluctuated slightly, probably because of oscillations in the flow rate and

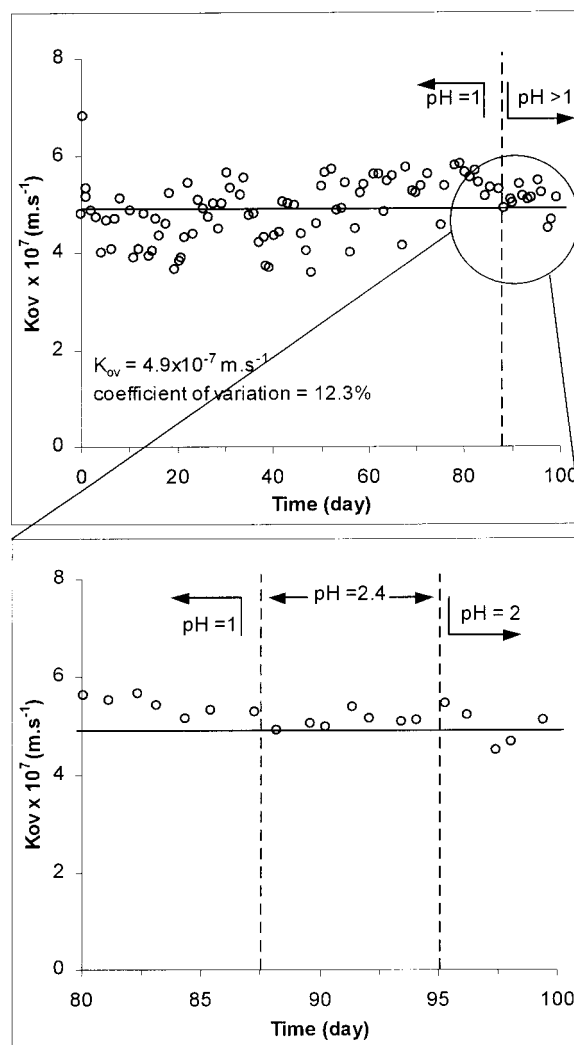


Figure 6. Overall mass-transfer coefficient for aniline over time.

errors in the concentration measurements, but it had an average value of $4.9 \times 10^{-7} \text{ m s}^{-1}$ with a coefficient of variation of 12.3%. It was constant with respect to pH in the range 1–2.4, which gives confidence in the

assumption that the OMTC is dominated by the membrane resistance, as the pH in this range will influence E in eq 5 but this does not affect K_{ov} .

Aniline Removal Efficiency. Removal efficiency is defined as

$$\eta_{Remv} (\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (10)$$

In this work, a short membrane tube of 10.5 m was chosen to quantify the outlet concentration and calculate the OMTC easily. Removal efficiencies of 53 and 68% were achieved, corresponding to flow rates of 5.5 and 3.4 L day⁻¹, respectively, with coefficient of variation of 5 and 4%. The aniline outlet concentration can be predicted by eq 7 for a longer membrane tube. A removal efficiency of 98.6% requires a 50-m membrane tube with a flow rate of 3.4 L day⁻¹ or an 80-m tube with a flow rate of 5.6 L day⁻¹. It is likely that removals of at least 90–95% would be required in an industrial application. At the operating Reynolds numbers, the pressure drop is only about 10⁻⁴ bar per meter of membrane length, or 0.008 bar for an 80-m membrane tube. These values are negligible when compared to the burst pressure value of 2.2 bar for this type of membrane tube.²⁸ Process scale-up can be achieved based on membrane area by using multiple tubes in parallel. MARS can also be operated in batch configuration, in which the wastewater is contained in the membrane tank and the stripping solution is recirculating inside membrane tube.

Stability of Recovered Aniline. To evaluate whether aniline reacts to form side or oxidation products during the MARS process, the concentration of total aniline in the stripping solution measured using GC was compared to the total aniline concentration calculated from TOC concentrations. TOC values were converted to aniline concentrations by assuming aniline is the only organic compound in the stripping solution, i.e., 1 g of TOC corresponds to 1.3 g of aniline. Deviations observed between the two values were within $\pm 15\%$ and were random rather than systematic. Thus, it was concluded that all of the organic constituent in the stripping solution is aniline.

Aniline Recovery. The recovery step was performed in batch mode 20 times. NaOH (50 wt %) was added to batches of stripping solution until the pH reached a value of 13. The mixture was then left overnight in a separating funnel. Figure 7 shows mass balances of aniline before and after the recovery with a deviation of $\pm 8\%$. It can also be seen in Figure 7 that the bulk of the aniline was recovered in the organic phase. Recovery efficiency (η_{Rec}) is defined as

$$\eta_{Rec} (\%) = \frac{\text{aniline recovered in the organic phase (g)}}{\text{aniline in the stripping-solution overflow fed to recovery step (g)}} \times 100 \quad (11)$$

A recovery efficiency of 92% was typically achieved.

No other compounds were detected in the recovered organic phase by GC analyses, and so, the aniline purity in the organic phase was calculated from the total weight of the organic phase minus the weight of dissolved water, divided by the total weight of the organic phase. Recovery efficiency increases with anilinium chloride concentration fed to neutralization. After the stripping solution reached a steady state, recovery

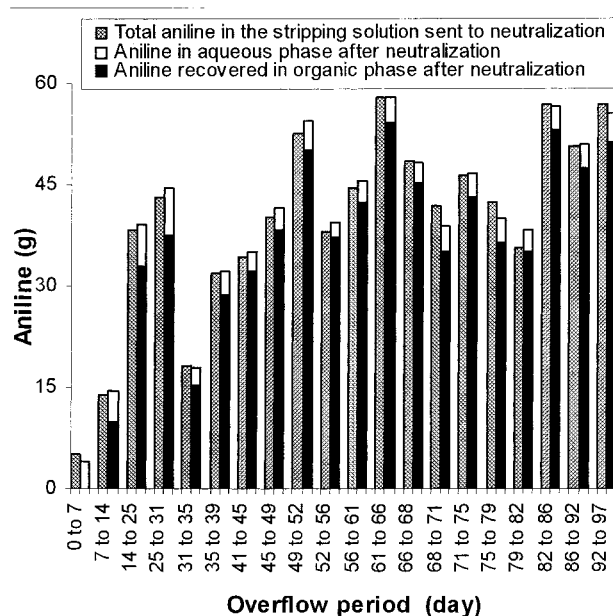


Figure 7. Mass balances for batch recoveries. Each mass balance is shown for one batch recovery.

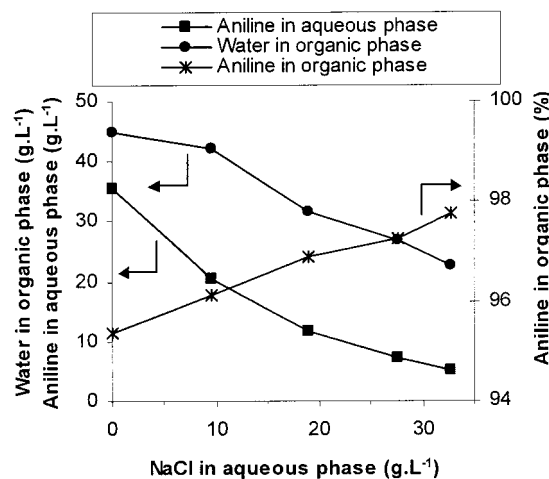


Figure 8. Aniline concentration in the aqueous phase and water and aniline concentrations in the aniline-rich phase as a function of NaCl concentration in the aqueous phase.

efficiencies were always over 90%, and a typical value of 3.5 wt % of water in the organic phase was measured, i.e., 96.5 wt % aniline purity.

The stoichiometry of the acid–base reaction requires 1 mol of NaOH for the neutralization of 1 mol of anilinium. Hence, for each batch recovery, the ratio of the number of moles of NaOH added to the number of moles of aniline in solution should be 1.0. However, to ensure that the system was driven well beyond the neutralization point, a molar ratio of around 1.1 was employed, resulting in a final aqueous pH of 11–13.

Effect of Ionic Strength on Aniline Recovery. The effect of ionic strength on the mutual solubility of water and aniline was investigated. The NaCl concentration after neutralization in the solution has a “salt-ing-out” effect on the aniline solubility in the aqueous phase. Figure 8 shows the changes in the aniline solubility in the water phase and the water solubility in the aniline phase with increasing NaCl concentration. As the NaCl concentration increases from 0 to 30%, aniline concentration in the aqueous phase decreases

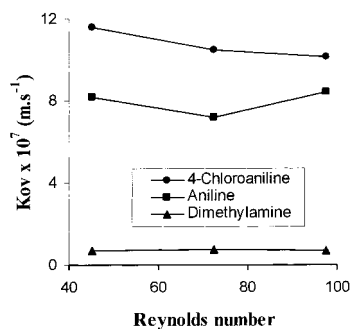


Figure 9. Overall mass-transfer coefficients as a function of Reynolds numbers.

by 6-fold, and the water concentration in the organic phase decreases to one-half of the value for NaCl-free water.

In the MARS, the stripping solution sent to recovery is composed of anilinium chloride and a small amount of HCl. NaCl is formed when NaOH is added to neutralize this acid solution. Hence, the higher the anilinium chloride concentration in the stripping solution sent to recovery, the higher the NaCl concentration after recovery.

Effect of HCl Concentration. Acid–base reaction stoichiometry requires 1 mol of HCl for each mole of aniline removed from the wastewater. On the basis of mass balances for aniline and HCl the following equation can be obtained at steady state

$$C_s^T (\text{g L}^{-1}) = \frac{1000}{\frac{1}{\rho_{\text{Aniline}}} + \frac{100}{C_{\text{HCl}} (\%) \text{MW}_{\text{Aniline}}}} \text{MW}_{\text{HCl}} \quad (12)$$

where ρ_{Aniline} is 1.02 kg L⁻¹, MW_{HCl} is 36.45 g mol⁻¹, and $\text{MW}_{\text{Aniline}}$ is 93.13 g mol⁻¹.

A HCl solution of 10.45 wt % was added into the stripping vessel in this study. The total aniline concentration of 211.5 g L⁻¹ at steady state was calculated from eq 12 and showed a good agreement with the average observed value of 218.5 g L⁻¹, as shown in Figure 4.

As shown in eq 12, the higher the HCl concentration (C_{HCl}), the higher the total aniline concentration in the stripping solution (C_s^T) at steady state. However, as shown in eq 3, for a given pH, the higher the total aniline concentration (C_s^T), the higher the un-ionized aniline concentration (C_s^N). A higher un-ionized aniline concentration in the stripping solution (C_s^N) reduces the driving force for mass transfer. On the other hand, the higher the total aniline concentration in the stripping solution, the higher the recovery efficiency in the next stage because of the increased NaCl concentration and enhanced salting-out after neutralization. Therefore, the HCl concentration in the HCl solution is a key parameter for the removal and recovery of aniline, and there is an optimum HCl concentration for use in this process.

Effect of Hydrodynamic Conditions on Mass Transfer. In overall mass-transfer tests, the stripping-solution pH was kept below 1, and the solution was regularly replaced by fresh HCl solution, so that un-ionized amine concentration in the stripping solution was effectively zero. Three compounds were selected to investigate the effect of film resistance on the wastewater side, as shown in Figure 9. It can be seen that

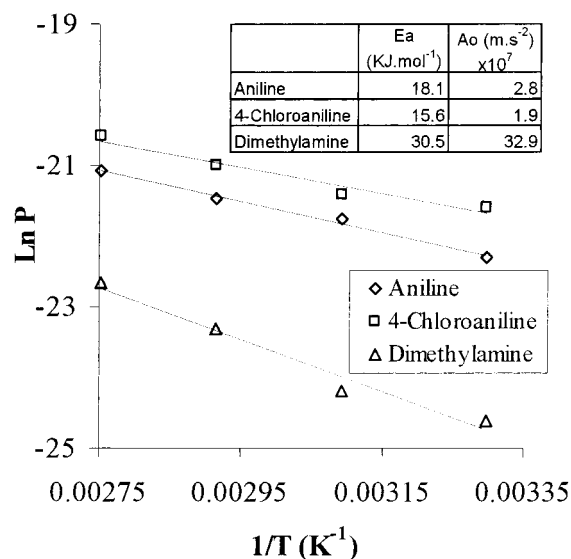


Figure 10. Arrhenius linear relationship between OMTCs and temperature.

the changes in flow rate on the tube side had little effect on the OMTCs in the range studied. This is further evidence that the OMTC is dominated by membrane resistance. This high membrane resistance for amines is mainly due to the use of a thick membrane (500 μm) and to the fact that hydrophilic amines have relatively low partition coefficients between the hydrophobic silicone rubber membrane and aqueous solution,²⁹ e.g., aniline has a value of 1.8.

Effect of Temperature on Permeability. Aniline, 4-chloroaniline, and dimethylamine were selected to investigate the effect of temperature on the OMTC. The OMTCs for these three amines across a 500 μm thickness silicone membrane were measured at 30, 50, 70, and 90 °C, and the permeabilities were calculated using eq 6. For rubbery polymers above their glass transition temperatures, the effect of temperature on permeability can be described by the van't Hoff–Arrhenius relationship³⁰

$$P = A_0 \exp\left(\frac{-E_a}{RT}\right) \quad (13)$$

It was observed that permeability increases with temperature, which can lead to significant reductions in membrane area. This is mainly due to the effect of temperature on the polymer chains, increasing their movement and membrane-free volume and promoting the diffusion of the molecules in the polymer. The activation energy and preexponential factor were estimated as shown in Figure 10.

The activation energy for dimethylamine is twice those for aniline and chloroaniline. The penetration of a penetrant molecule in the membrane depends on several factors such as the size and shape of the molecule and the interaction between the membrane material and the molecule. Although dimethylamine is a smaller molecule than the aromatic amines, its permeability is lower than those of aromatic amines because dimethylamine is more polar (see its water solubility in Table 2). Although the size of the molecule is one of the important factors, in this case, it seems that the polymer–penetrant interaction plays the decisive role.³⁰

Table 2. Properties of Amines^{31–33}

compound ^a	MW (g mol ⁻¹)	ρ (g mL ⁻¹)	pK _a	S (g L ⁻¹)	K _{ov} × 10 ⁷ (m s ⁻¹) ^b	P × 10 ¹⁰ (m s ⁻¹) ^b	C _{in} (g L ⁻¹)
aniline ^L	93.13	1.02 ²⁰	4.63 ²⁵	34 ²⁰	8.20	3.53	2
4-chloroaniline ^L	127.57	1.43 ²⁰	4.15 ²⁵	2.6 ²⁰	11.6	5.00	2.2
2,4-dichloroaniline ^L	163.02	1.57 ²⁰	2.05 ²⁵	0.62 ²⁵	6.36	2.73	0.55
4-nitroaniline	138.02	1.44 ²⁰	1 ²⁵	0.724 ²⁰	4.34	1.87	0.55
4-fluoroaniline ^L	111.12	1.58 ²⁰	4.65 ²⁵	slight	10.27	4.42	2
2,4-difluoroaniline ^L	129.11	1.28 ²⁰		slight	9.33	4.01	2
benzildimethylamine ^A	135.23	0.96 ²⁰		slight	18.00	7.74	2
triethylamine ^L	101.19	0.726 ²⁰		soluble	20.00	8.6	4
dimethylamine ^A	45.06	0.68 ⁰	10.5 ⁴⁰	soluble	0.72	0.31	1
2,4,6-tris(dimethylaminomethyl)phenol ^A	265.4	0.969			0.64	0.28	2
dicyclohexylamine ^L	181.32	0.91 ²⁰		1 ²⁰	16.5	7.10	1

^a A, Chemical supplied by Aldrich, U.K.; L, Chemical supplied by Lancaster Synthesis, U.K. ^b At 50 °C.

Applicability of MARS to Other Amines. To verify the application of MARS to the recovery of other amines, OMTCs were measured for aniline, 4-chloroaniline, 2,4-dichloroaniline, 4-nitroaniline, 4-fluoroaniline, 2,4-difluoroaniline, benzylidimethylamine, triethylamine, dimethylamine, 2,4,6-tris(dimethylaminomethyl)phenol, and dicyclohexylamine. The OMTCs, solubilities, and acid dissociation constants of these amines in water are shown in Table 2. Permeability values in silicone membrane were calculated using eq 6 and are also shown in Table 2.

The OMTC of aniline in Table 2 is 1.7 times higher than the average value obtained by MARS. This is probably because, in the mass-transfer test, the membrane was loosely arranged to ensure good contact with the stripping solution, whereas the membrane in the MARS process was tightly rolled around a support, reducing the effective membrane–stripping solution interfacial area. Judging from the difference between the two values, the effective membrane area in the MARS runs was 59% of the total. Note that other differences in the experimental conditions could also be the reason for the differences observed, such as ionic strength, stripping-solution concentration (200 g L⁻¹ vs nearly zero anilinium chloride concentrations), and aniline concentration in the wastewater (5 vs 2 g L⁻¹). A more detailed analysis of the mass transfer across the film layer at the stripping solution–membrane interface and of the effect of the reversible and instantaneous reaction is the subject of ongoing work.

It can be seen that benzylidimethylamine, dicyclohexylamine, and triethylamine have high OMTCs, so they can be relatively easily removed from wastewaters using MARS. Although aniline and all of the halogenated anilines have intermediate mass-transfer rates, it could be difficult to recover 4-nitroaniline as it has low permeability, and almost impossible to recover dimethylamine and 2,4,6-tris(dimethylaminomethyl)phenol.

To maintain a high mass-transfer driving force, it is necessary to keep the stripping solution at a pH significantly lower than the pK_a. For compounds with low pK_a's, such as 2,4-dichloroaniline and 4-nitroaniline, it might be hard to maintain this condition using silicone rubber membranes because of their susceptibility to acid attack.

Conclusions

MARS has proven to be a successful process for the removal and recovery of aniline, with a recovered aniline purity of 96.5 wt %. pH is an important parameter, as it controls the driving force across the membrane and

consequently the removal efficiency of aniline from the wastewater. Anilinium in the stripping solution was accumulated to a high concentration without back-extraction to the wastewater side. At steady state, the total aniline concentration in the stripping solution was 6 times higher than the aniline solubility in water and 43.6 times higher than the aniline concentration in the wastewater used in this study. These values illustrate the potential of MARS as a concentrating process.

The HCl concentration is the key parameter that links the two steps of the process. In the removal step, it controls the concentration of total aniline in the stripping solution. In the recovery step, the higher the concentrations of anilinium submitted to neutralization, the higher the recovery efficiency. However, the higher the total aniline in the stripping solution, the higher the concentration of un-ionized aniline in the stripping solution, and consequently, the lower the driving force for extraction. This is a parameter that we hope to optimize in future work.

Ionic strength, resulting from high concentrations of NaCl in the aqueous phase after neutralization, has a positive effect on the phase separation, decreasing the water concentration in the organic phase and the aniline concentration in the aqueous phase. As the ionic strength increases, a recovered aniline phase with a higher purity and an aqueous phase containing less dissolved aniline are obtained.

The MARS process couples detoxification and recovery. It is capable of achieving high recovery efficiencies, and producing a relatively pure stream of recovered organics. It is simple, stable, and easily operated in a continuous configuration because of the use of non-porous membranes. It has low energy requirements because it exploits the basicity of amines to produce a driving force based on the chemical energy contained in HCl and can be carried out under conditions of pressure and temperature that are near ambient throughout all items of equipment. MARS has been shown to be promising for industrial application to the recovery of a wide range of amines beyond aniline.

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Nomenclature

A₀ = pre-exponential factor (m s⁻¹)
C = concentration of amine (g L⁻¹)

dx = short length of membrane tube (m)
 D = diffusion coefficient for amine in the membrane ($\text{m}^2 \text{s}^{-1}$)
 E_a = apparent activation energy (J mol^{-1})
 F_w = wastewater flow rate inside tube ($\text{m}^3 \text{s}^{-1}$)
 J = total mass-transfer rate across tube wall (g s^{-1})
 K = partition coefficient for amine between membrane and aqueous phase
 K_a = acid constant of dissociation
 k_t = mass-transfer coefficient in liquid film in tube lumen side (m s^{-1})
 K_{ov} = overall mass-transfer coefficient (OMTC) (m s^{-1})
 k_s = mass-transfer coefficient in liquid film in shell side (m s^{-1})
 L = length of the membrane tube (m)
 MW = molecular weight (g mol^{-1})
 P = permeability of amine ($\text{m}^2 \text{s}^{-1}$)
 $pK_a = -\log K_a$
 $pH = -\log \text{H}_3\text{O}^+$
 R = molar gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)
 Re = Reynolds number
 r_i = inner radius of the membrane tube (m)
 r_o = outer radius of the membrane tube (m)
 S = solubility (g L^{-1})
 T = absolute temperature (K)
 V_s = volume of the stripping vessel (L)
 $\pi = 3.14$
 η_{Remv} = removal efficiency (%)
 η_{Rec} = recovery efficiency (%)
 ρ = density (kg L^{-1})

Superscripts and Subscripts to Concentrations

in = wastewater inlet of the tube
 out = wastewater outlet of the tube
 s = shell side
 w = wastewater in tube lumen side
 N = un-ionized amine in the solution
 T = total amine in solution

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