

## **Solvent extraction of ammonium ions from seawater using sunflower oil**

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### **ABSTRACT**

Wastewaters from industrial processes including fertilizer production, petroleum refining, oil and gas exploration contain ammonia or ammonium chloride, which is considered as a pollutant in higher concentrations. The removal of these components is required to meet the statutory regulations. In this paper, results on the removal of ammonium chloride from aqueous solutions are reported. The experiments were conducted at two different levels- laboratory-scale (equilibrium data) and pilot-plant scale (hollow-fibre membrane module). Reactive solvent extraction with carrier dissolved in sunflower oil was studied. The carrier based on phosphoric acid dissolved in sunflower oil gave 43-70% removal of ammonium chloride from aqueous solutions. This was achieved in a single-stage contact at the natural pH (no addition of chemicals required to adjust the pH).

### **1. INTRODUCTION**

Ammonia/ammonium ion is one of the major pollutants in the natural waters and it is introduced through the discharges from domestic, industrial and agricultural activities. A complete or partial removal of this compound is desirable for many reasons: (i) to minimize its toxic effects on human and aquatic species, (ii) to generate a source of useful waters and (iii) to recover these important elements that have application in agriculture, chemical and medical industry. High concentrations of this compound are discharged from coal-conversion processes, petroleum refining, tannery, textiles and fertilizer wastewaters (Marr 1993, Qin 1996). In some cases, ammonia coexists with gases like CO<sub>2</sub> (fertilizer industry) and H<sub>2</sub>S (petroleum sour water); the natural pH of these wastewaters are in the range 7-9 (Mackenzie 1985). At this condition the compound is predominantly an ammonium ion. Therefore, methods applied for separating ammonia (in the gas form) will leave a lot of ammonium in the wastewaters to make them unsuitable even for irrigation purposes. However, by increasing the natural pH (i.e., converting to gaseous form by the addition of chemicals) beyond pH 11 the processes can be used for substantial removal of ammonia. In order to circumvent this disadvantage methods of removal in the ammonium form at its natural pH are

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being investigated (Tan 2006, Norddahl 2006, Hasanoglu 2010).

Traditional methods for removal of ammonia include air stripping, adsorption, ion exchange, precipitation, advanced oxidation, micro-wave technology, biological treatments, gas and liquid membrane processes (Moazed 2008,; Jorgensen 2003, Liu 2008, Miladinovic 2008, Uludag-Demirer 2005, Vassileva 2008, Zheng 2009, Lin 2009, Hung 2003, Klassen 2005, Bringas 2006, Hasanoglu 2010).

The important results of a few recent papers are summarized in the next paragraph with some details of the system are presented in Table 1.

Huang *et al.* (2010) used adsorption in removal of ammonium using natural Chinese Zeolite as adsorbent. The results show that as the particle size increased, adsorption decreased and the efficiency decreased with the increase in initial concentration. The initial concentration was 80 ppm at a pH of 8. After a contact time of 3 hours, the maximum removal percentage reached 85%. Ma *et al.* (2011) used adsorbent prepared from wheatstraw and found that the amount of adsorbed ammonium decreased as the adsorbent concentration increased (from 0.2-6 g/L). The amount adsorbed increased with the increase in initial concentration being in the range of 250 ppm. Bao-hua *et al.* (2007) used synthesized zeolite as adsorbent that was treated first with an acid. The highest efficiency of approx. 60% was obtained in the feed concentration range of 2.5-1200 ppm at pH 9. Li *et al.* (2011) developed a regeneration process to increase the removal efficiency and prolong the adsorbent use. The process was regenerated by NaCl, acidic solution or heating method. The “NaCl regeneration” method was superior to other methods and the adsorption capacity of the adsorbent was 0.1117 mg/L after “NaCl regeneration” and was closest to that of fresh adsorbent which was 0.1155 mg/L. The contact time was long (25-30 hours) and the feed concentration was in the range 3 -1200 ppm at pH 9. All these reports treat waters containing small concentration of ammonium chloride that is prevalent in domestic wastewaters. The results suggest a number of disadvantages including regeneration and long time for treatment even at smaller concentration. More details of the organic system and their performances are available in a recent literature (Li 2011).

Compared to the above-mentioned methods, processes based on membrane contactors have shown their advantages in large-scale development. There are a number of studies in recent years for ammonia removal by gas absorption and through a chemical reaction in membrane contactors. They have been effective but require the pH of wastewaters to be raised beyond pH 11 in order to convert most of the compound in the gaseous form. This may require large quantities of chemicals especially if CO<sub>2</sub> is also present and may demand intensive post-treatments before it can be used for agricultural purposes. The process proposed in this report is similar to the above-mentioned membrane processes, the difference being the use of an “ammonium” selective carrier and a diluent that shows a good solubility for the ammonium-carrier complex, less toxic and cheaper than those examined by various researchers.

A few studies have been reported (a list is presented in the Table 2) and they show the potential of the membrane-based removal processes. The processes based on liquid-liquid extraction, especially reactive extraction using ammonium-selective carrier molecules, such as di(2-ethylhexyl) phosphate [D2EHPA) in the organic phase, have been being actively considered as the potential candidate. In most of these studies the solvent or diluent used were of hydrocarbon-based (e.g. toluene, hexane, kerosene,

decanol), halogenated organics (chloroform, dichloromethane). These solvents work effectively in small-scale processes, but are considered unsuitable due to the impact on the environment, non-renewable sources of supply, occupational, health and safety point of view. Recently, a feasibility study is reported (Bachmann 2010) on the recovery of hexavalent chromium from a simulated effluent using Alamine 336 in refined palm oil. The results are encouraging and applicable to wastewaters at acidic pH. Most of the wastewaters containing ammonia from various industries, especially if they contain dissolved carbon dioxide exist at near neutral and alkaline pH (6.5 -8 pH range).

The aim of this study was to investigate the removal of ammonium ion from solutions containing it using the reactive system of D2EHPA in sunflower oil (is considered to be a non-toxic solvent and from a sustainable source). This study is intended to initiate the research in this direction and present the preliminary results. More specifically the aims were to:

- (a) Determine the partition behavior of ammonium in the above-mentioned organic phase and determine the partition coefficient for a wide range of feed concentrations.
- (b) Evaluate the performance of the process in a bench-scale membrane contactor using a feed prepared in distilled water and seawater (at their natural pHs).

Table 1 Removal of ammonium chloride by adsorption method

Initial ammonia concentration (ppm)	Adsorbent/Solvent	pH	Contact time (hour)	Reference
80	Natural Chinese Zeolite	8	3	Huang <i>et al.</i> 2010
250	Fertilized controlled release agent prepared from wheat straw	8	2-4	Ma <i>et al.</i> 2011
2.5-1200	Zeolite synthesized from coal fly ash influenced by acid treatment	9	24	Bao-hua <i>et al.</i> 2007
3-1200	Silicate carbon modified Zeolite	9	25-30	Li <i>et al.</i> 2011
-	Natural mordenite	10	-	Noda 1997

Table 2 Removal of ammonia solution through Membrane contactors

Membrane surface area (m <sup>2</sup> )	Initial concentration of ammonia in ppm	Recovery /Extraction solution	Feed pH	Reference
0.58	250-300	Sulphuric acid	7.0	Hasanoglu <i>et al.</i> 2010
0.01	4118.7	D2EHPA/DTPA in decanol	7.0	Qin & Cabral 1996
0.171, 0.128	50-10,000	Sulphuric acid	9-12	Zhu <i>et al.</i> 2005
Not mentioned	Not mentioned	Sulphuric acid	9-11.5	Norddahl <i>et al.</i> 2006
Small area	100-120	Sulphuric acid	8-12	Tan <i>et al.</i> 2006

## 2. MATERIALS AND METHODS

Ammonium chloride compound (MW=53.49 g/mol, by BDH Laboratory supplies) was used as the source of ammonium chloride. The sunflower oil used in all experiments was Noor brand, a trans fat free oil (by Emirates Refining Co., UAE). The decanol used is Alcohol C10\*n-Decylalcohol (99%, SIGMA ALDRICH-Germany). The carrier used was Bis (2-ethylhexyl) phosphate (99%, 100g, by Gohanson Matthey Company). Salicylic acid, Aliquat336 and ethanol were also used. Distilled and sea water were also used. A Blau brand pipette, 100 mL beakers, spatula and 100 mL measuring cylinders (by ILDAM) were used for measurements. Moreover, a balance (by Citizen Scale) was used for weighing different masses of ammonium chloride. An Orbital shaker (Japan Corporation Centre) was used in the equilibrium technique. pH measurements ( by HANNA) were taken for the feed before and after each experiment. After each experiment samples were put in a 22 mL (by SUPLECO, USA) for analytical analysis. A high range concentration reagent was used in order to analyze the samples ( Vario AM tube test reagent set by Tintometer GmbH, Bereich Aqua Lytic- Germany).

### 2.1 Procedure for equilibrium measurements of solutes

The feed was prepared by weighing different amounts of ammonium chloride based on the desired concentration (20-500mM) and volume in distilled or sea water. The pH of the feed was measured. In order to prepare the organic phase, known volume of sunflower oil or decanol was measured and added to either salicylic acid or Bis (2-ethylhexyl) phosphate as desired. When salicylic acid was used as carrier, the organic phase contained sunflower oil and ethanol.

Feed and organic phase was then added together in a 100 mL beaker and put on the shaker for four hours in order to allow the equilibrium process to proceed. After that, the solution was left to settle down for an hour so the aqueous and organic phases are clearly separated. A sample of the aqueous phase was taken by a Blau Brand pipette. This technique was applied to proof if the experiment succeeds or fails. On the other hand, the working volume of all experiments carried out with the same volumes for both the aqueous and organic phases.

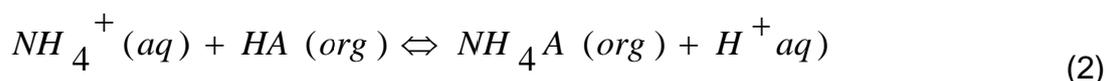
The apparent distribution coefficient for extraction, DE, is assumed concentration-based and can be defined as the ratio of the concentration of  $\text{NH}_4^+$  ion in the organic phase over that in the aqueous phase at equilibrium:

$$DE = \frac{C_{\text{NH}_4^+(\text{org})} * V_{\text{org}}}{C_{\text{NH}_4^+(\text{aq})} * V_{\text{aq}}} \quad (1)$$

where  $C_{\text{NH}_4^+(\text{org})}$  and  $C_{\text{NH}_4^+(\text{aq})}$  represent the concentrations of  $\text{NH}_4^+$  ion in the organic and aqueous phases, respectively and  $V_{\text{aq}}$  (or  $V_{\text{org}}$ ) represents volume of the respective phases.

All the concentrations in the above equations can be measured and the distribution

coefficient can be determined. A large value of DE suggests good extraction. The reaction between  $NH_4^+$  ion and the carrier can be expressed by the simplified equation as in Eqn. (2). The exact equation may depend on the form of the carrier (could be dimeric or any other form). The equilibrium constant, KE, can be calculated from the Eqn (3) based on the following equation for reactive extraction



$$KE = \frac{C_{H^+(aq)} C_{NH_4A^*(org)}}{C_{HA(org)} C_{NH_4^+(aq)}} \quad (3)$$

where  $C_{H^+}$  and  $C_{HA}$  represents the concentrations of hydrogen ion and D2EHPA in the aqueous and organic phases, respectively.

## 2.2 Hollow-fibre membrane module

The experiments were carried out in a hollow fiber membrane contractor, 5PCM-218, purchased from Hoechst Celanese Corporation, Charlotte, NC, USA. The contractor had a shell and tube configuration with hollow fibers (Celgard X-30 type) potted with polyethylene. This type of contactor allows flow of two phases without being dispersed and provides large surface area per unit volume, compared to the conventional contactor. These are also available with very large area for mass transfer and can be used for both liquid and gas phase separation processes. The main characteristics of this contactor are shown in Table 3 below. A schematic diagram of the experimental apparatus is shown in Figure 1.

Table 3 Characteristics of the hollow fiber contactor

Provider:	Celgard
Contactor type:	Liqui-Cel extra-flow 2.5 in. × 8 in. (64 mm × 203 mm)
Shell diameter	$d_S = 6.3$ cm
Fiber bundle diameter	$d_a = 4.7$ cm
Distribution tube diameter	$d_i = 2.2$ cm
Overall contact area (based on outer fiber diameter)	$A_S = 1.4$ m <sup>2</sup>
Overall contact area (based on inner fiber diameter)	$A_F = 1.13$ m <sup>2</sup>
Fiber material/type	Polypropylene (X-30)
Number of fibers	9,950
Outer fiber diameter	$d_o = 300$ μm
Inner fiber diameter	$d_F = 240$ μm
Fiber wall thickness	$e = 30$ μm
Fiber porosity	$\epsilon = 0.4$
Pore tortuosity	$\tau = 2.25$
Pore diameter	0.03 μm

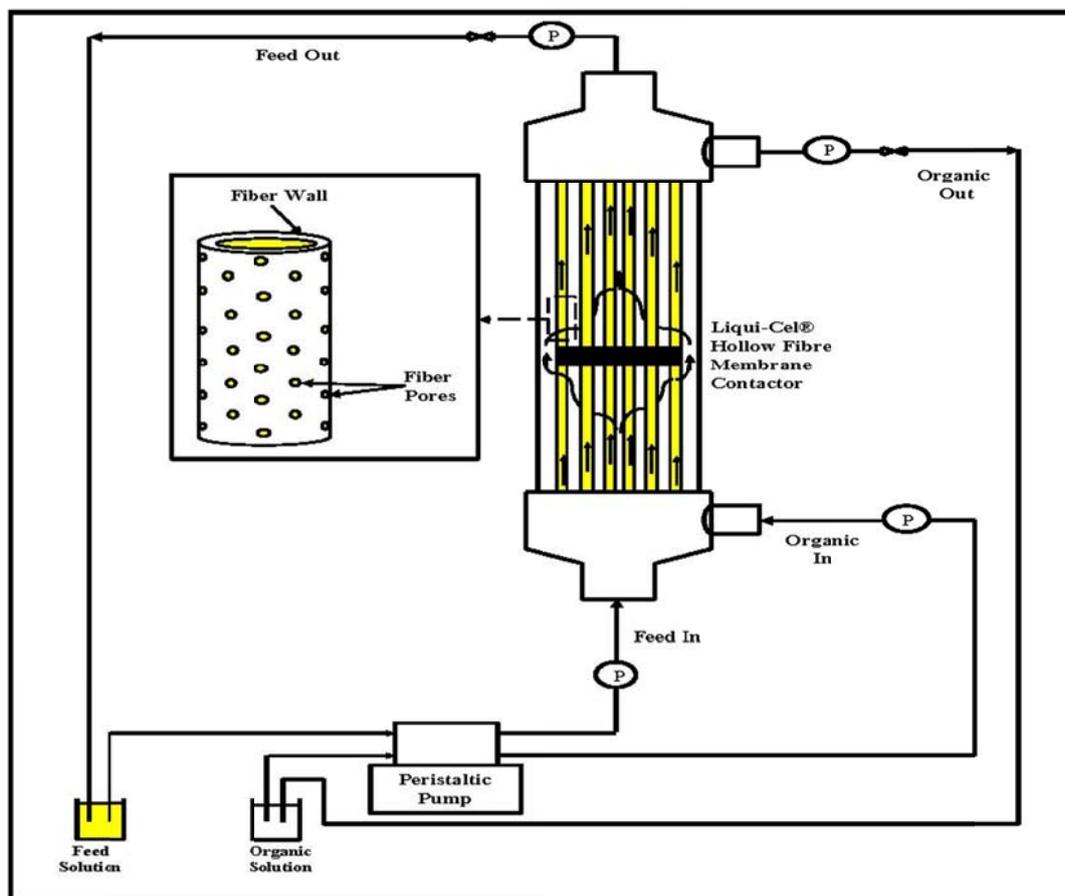


Figure 1 Characteristics of the hollow fiber contactor

### 2.3 Mass transfer experiments in the membrane contactor

This liquid-liquid extraction technique was carried out in the hollow fiber membrane contactor. Before conducting each experiment, the hollow fiber membrane contactor was washed with a 20% ethanol solution to get rid of any remaining oils in the system. In the hollow fiber membrane contactor, the feed which is the ammonium chloride solution was fed inside the hollow fibres and the organic phase to the shell side. pH measurements were taken for the feed before and after each experiment. The final concentration of the samples taken after each experiment was measured by a photometric system (by PC multi-direct) in conjunction with the high range concentration reagent. The membrane allows large working volumes (in litres). The contact time was four hours and a sample every 1 hour was taken. pH measurements were taken initially and every hour within each sample. The system was cleaned after each experiment with a 20% ethanol solution as well.

### 2.4 Measurement of $\text{NH}_4^+$ concentration using a spectrophotometric method

To measure the ammonium concentration of the aqueous phase a photometric method was used. Because the photometer system is not capable of analyzing high

concentrations of ammonium chloride solutions; a high range concentration reagent was used which is Vario Ammonia test reagent. Before the analysis was carried out, samples were diluted to the concentration range of the reagent (0-50 ppm NH<sub>3</sub>-N). This reagent contains test tubes that have a diluent reagent filled inside each tube. Along with the filled test tubes are two powdered chemicals which are ammonia silicate and ammonia cyanurate. After diluting all samples with distilled water, 0.1 mL of each sample was put in the test tubes filled with the reagent. Then ammonia silicate and cyanurate were added to each test tube in series.

In the photometer system, ammonium solutions have the code of 66. The system was adjusted to that code in order to carry out the analysis. First of all, a blank sample was done exactly the same as all other samples, but the 0.1 mL was taken from de-ionized water. Each reaction in the photometer takes a certain period of time; the ammonium solutions reaction time is 20 minutes. After adjusting the system and preparing the samples, the photometer was turned to the on mode and waited for 20 minutes till the reaction took place. After that, the blank was put first and then the rest of the samples were examined in series. Each sample gave a reading in mg/L of NH<sub>3</sub> and this reading was changed to mille-molar of NH<sub>4</sub>Cl.

The values of concentration for the initial feed solution and the aqueous phases produced after the extraction experiments, were used to calculate the removal or extraction percentage. The removal percentage, E(%), was calculated from the following equation

$$R(\%) = \left( 1 - \frac{C_{fo(aq)}}{C_{fi(aq)}} \right) \times 100 \quad (4)$$

where  $C_{fo}$  (aq) and  $C_{fi}$  (aq) are the concentrations of NH<sub>4</sub>Cl at various time intervals and in the initial feed solutions, respectively.

### 3. RESULTS AND DISCUSSION

The results are presented in terms of DE for equilibrium experiments and R(%) for mass transfer experiments in hollow-fiber contactor. The experiment carried out using salicylic acid and Aliquat 336 as carriers did not work well only achieving only 11.5% of ammonium chloride from 2mM feed solution. Therefore, only results with the carrier D2HEPA dissolved in sunflower oil and decanol is presented.

In Table 4, the effects of initial feed NH<sub>4</sub>Cl concentration are shown. The pH was the natural pH of the aqueous solution and the volume ratio of the organic phase to feed solution was kept 1. The diluents tested were sunflower oil and decanol. The distribution ratio for both the organic phases depend largely on the initial concentration of NH<sub>4</sub>Cl, being high (approx. 1.9) for smaller concentration and low (approx. 0.60) for medium and very small (approx. 0.2) at high concentration of 500 mM (which is equivalent to 26,750 ppm). This trend was similar for both the solvents- sunflower oil and decanol. The DE value reported earlier (Mackenzie and King, 1985) was 6.1. They used 210 mM D2EHPA in 50% (v/v) decanol-toluene mixture for a feed concentration of 600 mM. But the volumetric phase ratio of the solvent-to-water was 5, compared to 1 in

our case. The value would have been considerably less if the ratio was unity. Compared to their results our values look encouraging as these were obtained with smaller amounts of sunflower oil which has better characteristics in terms of economics, environment and operation.

Table 4 Values of the distribution coefficient in sunflower oil and decanol experiment in

Aqueous Phase			Organic Phase		
Initial Concentration (mM)	Initial pH	Final Concentration (mM)	Carrier Concentration (mM)	Solvent	Distribution coefficient (DE)
20	5.4	7.0	20	Sunflower oil	1.86
200	5.4	121.9	200	Sunflower oil	0.64
200	5.5	94.6	200	Decanol	1.11
500	5.3	408.5	500	Decanol	0.22
500	5.5	412.0	500	Sunflower oil	0.21

a small-scale membrane contactor

1mM=53.49 ppm (mg/L), 200 mM = 10,700 ppm, 500 mM = 26,750 ppm

The process was upgraded and the performance was studied in a small-scale membrane contactor. It is noted that the aqueous phase pH was not adjusted with extra chemicals. The volumetric ratio of the flow rates was similar, approximately one, was maintained for the aqueous-to-organic phases. Tables 5 and 6 show the experiment results of removal of ammonium chloride achieved after 4 hours of experiment. Table 4 shows the experiment carried out using distilled water in the aqueous phase where Table 5 shows the results of extraction using seawater as feed sample. In both cases the carrier used was Di-(2-ethylhexyl) phosphate and the diluents were sunflower oil.

Table 5 Removal of ammonium chloride from distilled water

Aqueous Phase			Organic Phase	
<i>Initial Conditions</i>		<i>Final Concentration</i>	<i>Carrier Concentration (mM) in sunflower oil</i>	<i>Removal %</i>
mM	pH	mM		
478.7	5.1	131.9	200	72.5

Table 6 Extraction of ammonium chloride from sea water

Aqueous Phase			Organic Phase	
<i>Initial Concentration</i>		<i>Final Concentration</i>	<i>Carrier Concentration (mM) in sunflower oil</i>	<i>Removal %</i>
mM	pH	mM		
357.44	7.02	204.97	200	42.7

As observed in Tables 5 and 6, the removal was lower (approx 42.7%) in the case of seawater. This could be due to (i) the presence of other components in seawater competing during the process and (ii) the higher value of feed pH for seawater. This removal can be considered a good result as it was achieved at a very high concentration (approx. 19120 ppm of NH<sub>4</sub>Cl) and obtained with use of less than stoichiometric proportion of carrier in a cheap solvent. The results from other investigators are presented in Table 7. The differences between this work and the literature are to be recognized first: the results herein are for very concentrated aqueous ammonia solution (many times than those reported) at the natural pH (i.e. no chemicals added for pH adjustments) and the use of sunflower oil (a non-toxic and cheap solvent) with many process benefits. Considering all these the results are encouraging as initial efforts towards the development of a sustainable process for conversion of seawater to irrigation purposes.

Also, all results were achieved in a single module (easy-to-scale-up type) within a contact time of 4 hours at a flow rate of 12-14 L/h. It is expected that the percentage removal can be increased by using carrier concentration of higher proportions and use of solvent such as decanol (or a mixture of sunflower oil and decanol) instead of sunflower oil only.

A simplified model (Hossain 2008) was applied to predict the results of the hollow-fibre experiments. The values of the parameters were obtained from the experiment except for diffusivity which was taken from the literature (Quin 1996). The model can predict the concentration of ammonia well during the initial stage of 1 hour after that the predictions are higher than the experimental values.

The steady state model of the process is presented below:

$$\ln \left[ \frac{CA_0}{\left(1 + \frac{1}{DE}\right)CA - \frac{CA_0}{DE}} \right] = \frac{Qa}{Va} \{1 - \exp(-BK_{of})\}t \quad (5a)$$

where CA<sub>0</sub> and CA are the initial and final concentrations of ammonium ion, respectively, Qa is the flow rate through the membrane, Va is the volume of the solution in the reservoir, K<sub>of</sub> is the overall mass transfer coefficient and DE is the apparent distribution coefficient. The parameter B has been defined by the following equation

$$B = \frac{\left(1 + \frac{1}{DE}\right)L}{\left(\frac{V}{A}\right)_{in} u_{tube}} \quad (5b)$$

where L is the length of each fibre, u<sub>tube</sub> is the velocity inside the fibre, and (V/A)<sub>in</sub> is the ratio of the volume to area based on inside diameter of the fibre.

Table 7 Comparison of removal processes for various feed solutions

Condition of Feed Solution	Aqueous NH <sub>4</sub> Cl Feed (mM)	Organic phase/Removal solution	Removal %	Reference
Seawater at pH 7.01	357.44	D2EHPA in sunflower oil	42.7	This work
Distilled water at pH 5.1	478.73	D2EHPA in sunflower oil	72.5	This work
Aqueous solution (pH not indicated)		0.2-0.4 M sulphuric acid	60.01-78.03%	Hou and Shou-Wei 2011
Aqueous solution at pH 7	2.5-2.0	D2EHPA in 50%(v/v) decanol-toluene	More than 90%	Qin and Cabral 1996
Aqueous solution at pH 7	60.0-95.0	D2EHPA in 50%(v/v) decanol-toluene	Less than 15%	Qin and Cabral 1996

It is evident that sunflower oil, with all the benefits of health and safety and being environmentally benign, has the potential to replace toluene or kerosene as a renewable and sustainable solvent. It is noted that kerosene has been used commercially in the treatment of environmental polluting sources (Alonso 1997 and Ho 2001). It has been effective as an extracting solvent but it is toxic, environmentally harmful, and unpleasant to the operators. It has also been found to be incompatible with many industrial membrane separation modules, caused swelling of the polymeric membranes and created difficulties during long-term operation.

More investigations are underway to explore the effects of the variables such as the high concentration of NH<sub>4</sub>Cl in feed, ratio of the concentration of carrier, addition of any modifier, flow rate of the two phases and recovery from the ammonia in a desirable from the organic phase.

## CONCLUSIONS

It is shown from the experimental investigation that removal of ammonium chloride from pure water as well as seawater is possible. The experiments were conducted at two different levels- laboratory-scale (equilibrium data) and bench-scale (hollow-fibre membrane module). The following remarks can be made:

- In the equilibrium technique, results show that the removal of ammonium was successful when Di(2-ethylhexyl) phosphate was used as a carrier in sunflower oil (as a diluent). The contact time for all experiments was 4 hours which is much less than or similar to the time mentioned in the literature (up to 30 hours). Moreover, experiments were carried out at the natural pH (no chemicals were added for pH adjustments) and using sunflower oil, an environmentally friendly, cheap and non-

toxic solvent.

- The process when operated to a bench-scale membrane contactor with an area of 1.4 m<sup>2</sup>, good percentage removal was achieved (in the range 43-73%).
- This result was obtained from a feed of concentrated ammonium chloride solution (19,200 ppm), much higher than the reported values. Also a short contact time of 4 hrs was needed at a flow rate of 12-14 L/h of feed.
- The other diluent n-decanol worked well but is not recommended (when used in high percentage or used as single diluent) because of cost, health and safety issues and unsustainable source of supply.
- The experimental results can be predicted from a simple model of the process.

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