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Liquid–liquid separation of aqueous ammonia using a hollow-fibre membrane contactor

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ABSTRACT

Ammonia in the form of gas or ammonium ion is toxic to the environment. Removal of this compound in either form is important in order to meet the limits set by regulatory authorities. The treatment of the polluted waters can be accomplished by a variety of physical, chemical, and biological methods. Liquid–liquid separation is one of the promising methods that has been developed and demonstrated success for removing ions selectively. In many industrial operations, the solvents used are fossil fuel-based (a non-sustainable source), they have undesirable properties (toxic, corrosive, and health and safety issues). In recent years, there has been research work to examine the feasibility of other solvents from sustainable source and with good characteristics to minimize some of the above adverse effects. In this study, the effectiveness of a new solvent, sunflower oil, is described in the removal of ammonium in a small-scale pilot process at their natural pH. High percentage removal was achieved (in the range 43–73%) from a high feed of concentrated ammonia solution (25,600 ppm). It would require 1,000 L of sunflower oil with 100 L of D2EHPA to treat 1 m^3 of ammoniated seawater to reduce the concentration to 3,750 ppm from such high concentration. With this reduced concentration, the treated water is suitable for irrigation purposes. The main attraction of the process is the performance of sunflower oil, which offers the benefit of being environmentally friendly, less costly, non-toxic, and from a sustainable source.

Keywords: Sunflower oil; Polluted water; Ammonium ion; Nontoxic solvent; Sustainable source

1. Introduction

Ammonia or ammonium ion is a common pollutant which is considered toxic even at low concentrations. Effluents are from a wide range of industries such as coal gasification, fertilizers, plastics, explosives, and petroleum refining in the range of 5–1,000 mg/L. The wastewaters from food and pharmaceutical contain ammonium in the range of 2,000–7,000 mg/L. In the municipal waste, the concentration is in the range of 0–200 mg/L and the landfill leachate is 1,000–4,000 mg/L. Complete or partial removal of this either in the form of ammonium or in the form of non-ionic ammonia is required in order to

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meet the limits set by regulatory authorities. This will also create treated water sources for their recycle and reuse in many activities including irrigation. On the other hand, its recovery may help generate additional sources of supply for applications in the industry where they are utilized making the entire process sustainable.

In this work, ammonium (an ionic pollutant) is considered for its removal from the polluted source (normally an aqueous solution). A mathematical model, developed previously [1], is applied to its validity for the ammonium removal process. Ammonia/ammonium ion exists in the industrial wastewaters (fertilizer, oil and gas exploration, petroleum refining) and groundwaters (through the discharges from domestic and agricultural activities). Ammonia gas (as nonionic form) is extremely toxic (even at concentrations of 1 ppm) and can cause damaging effect to the working and aqueous environment. A complete or partial removal of this compound is required 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 this in less toxic form that have application in agriculture, chemical, food, and medical industries.

High concentrations of ammonia are discharged from coal conversion processes, petroleum refining, tannery, textiles, and fertilizer wastewaters [2,3]. In some cases, ammonia coexists with gases such as CO_2 (fertilizer industry) and H_2S (petroleum sour water); the natural pH of these wastewaters are in the range of 6.5–8 [4]. At the natural condition (pH being less than 8), ammonia exists predominantly in the form of ammonium ion. Therefore, methods applied for separating ammonia (in the gas form) will leave a lot of ammonium ion in the wastewaters to make them unsuitable for secondary 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 the substantial removal of ammonia. In order to circumvent this disadvantage, previous studies adjust natural pH and remove ammonia in the gaseous form [4–6].

Traditional methods for the removal of ammonia and other similar solute gases include air stripping, adsorption, ion exchange, precipitation, advanced oxidation, microwave technology, biological treatments, and gas and liquid membrane processes [7–19]. The important results of a few recent papers are summarized in the next paragraph with some details of the systems.

Methods based on adsorption using adsorbents in the removal of ammonium have recently been reported [19–22]. The results show that the efficiency was in the range of 60–80% and it decreased with the increase in initial concentration in the range of 2.5–6,000 mg/L. The adsorbent was used with frequent regeneration, and the overall contact time was long approx. 25–30 h. All these reports treat waters containing small concentration of ammonium that is prevalent in domestic wastewaters. The results suggest a number of disadvantages including regeneration and long processing time even at smaller concentrations.

Compared to the above-mentioned methods, processes based on membrane contactors have shown their advantages in large-scale development [23–30]. 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_2 is also present and may demand intensive post-treatments before it can be used for agricultural purposes [2]. 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, with less safety, operation, and operational issues than those by various researchers.

A few studies have been reported (a list is presented in Table 1) 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 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 [30] 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 pH (6.5–8 pH range). The industrial applicability of the above-mentioned processes depends on many factors including the selection of environmentally benign solvent with operator-friendly characteristics, compatibility to the

Table 1
Removal of ammonia from aqueous solution using hollow fiber membrane contactors

Membrane surface area (m^2)	Initial concentration of ammonia/ammonium (mg/L)	Recovery/Extraction/Absorption solution	Recovery (%) (initial pH)	Refs.
Not mentioned	Not mentioned	1% (w/w) sulfuric acid	25 (pH 9) 100 (pH 11.5)	[7]
0.17, 0.13	50–10,000	5% (w/w) sulfuric acid	25 (pH 9) 99 (pH 13)	[14]
Small area	Not mentioned	Ozonation and natural hot spring water	91 (pH 11)	[24]
0.58	250–500	0.1–0.3 M sulfuric acid	99 (pH 7)	[8]
Small area	126–754	0.05 M sulfuric acid	25 (pH 8) 95 (pH 12)	[6]
1.4	5–25	0.02 M sulfuric acid	15 (pH 8) 40 (pH 9) 65 (pH 10)	[26]
Not mentioned	800	0.1–0.4 M sulfuric acid and phosphoric acid	12 (pH 8) 100 (pH 11)	[25]
1.4	50–800	Dilute sulfuric acid	100 (9–11 pH)	[32]

commercially available equipment, and potential for reuse/recycle of the organic phase. The aim of this study was to examine the potential of sunflower oil (is considered to be operator-friendly solvent and from a sustainable source) for the removal of ammonium ion from solutions at the natural pH (without pH adjustment).

Therefore, the removal of ammonium ion from aqueous sources was examined using D2EPHA in sunflower oil. The plan includes the following stages:

(1) Determine the partition behavior of ammonium ion in the sunflower oil-based phase and determine the partition coefficient for a wide range of feed concentrations.
(2) Evaluate the performance of the process in a bench-scale membrane contactor for removing ammonium using a feed prepared in distilled water and seawater (at their natural pHs).

2. Mass transfer calculations

In the derivation of the mathematical model, the procedure followed is similar to that presented earlier [1]. The hydrophobic hollow fiber separates two circulating phases; the feed that is an aqueous phase containing ammonium ions on the lumen side and the receiving solution is a liquid membrane solution flowing in the shell side. This liquid membrane is composed of an ionic carrier (D2EHPA) dissolved in a diluent (an organic solvent or a vegetable oil in this case). The pores of the hydrophobic membrane, which is not wetted by the aqueous solution, are filled with the liquid membrane. First, ammonium ion (NH_4^+) diffuses from the bulk solution to the feed–membrane interface (tube side mass transfer) and reacts with the carrier to form a complex (shown in Eq. (3)) that dissolves in the diluent phase. This ammonium complex diffuses through the membrane pores (membrane mass transfer) and finally diffuses into the bulk liquid membrane phase in the shell side, where the concentration of ammonium is initially zero. Substantial removal of ammonium could be theoretically possible under this configuration, since the driving force for this liquid membrane contactor operation is the difference in ammonium concentrations between the bulk feed phase and the receiving diluent phase.

The mass transfer for the overall process under steady state condition, i.e. the mass flux of ammonium can be obtained as:

$$N_{\mathrm{NH_4f}} = K_{\mathrm{OF}}(C_{\mathrm{NH_4f}} - C_{\mathrm{NH_4O}}/D_E) \tag{1}$$

where K_{OF} is the overall mass transfer coefficient of the process, the concentrations $C_{\mathrm{NH_4f}}$ and $C_{\mathrm{NH_4O}}$ are the concentration of ammonium in the bulk aqueous phase and in bulk organic phase, respectively, and D_{E} is the apparent distribution coefficient.

The apparent distribution coefficient for extraction, D_{E}, is assumed concentration-based and can be defined as the ratio of the concentration of NH_4^+ ion in the organic phase over that in the aqueous phase at equilibrium:

$$D_{\mathrm{E}} = \frac{C_{\mathrm{NH_4*(org)}} * V_{\mathrm{org}}}{C_{\mathrm{NH_4*(aq)}} * V_{\mathrm{aq}}} \tag{2}$$

where $C_{\mathrm{NH_4*(org)}}$ and $C_{\mathrm{NH_4*(aq)}}$ represent the concentrations of NH_4^+ ion in the organic and aqueous phases, respectively, and V_{aq} (or V_{org}) represents volume of the respective phases.

The overall mass transfer coefficient (K_{OF}) relates the mass transfer rate to the mass transfer area and the concentration gradient across the membrane wall. Its value is a measure of the efficiency of the mass transfer process, i.e. how efficiently the ammonium is removed from the source system. The theoretical overall mass transfer coefficient K_{theo} is calculated by resistance-in-series model [26]. Individual mass transfer coefficients can be estimated from many different theoretical equations, correlations, and analogies [23] and are listed in Appendix A.

The reaction between the ammonium ion with the carrier molecules (D2EHPA) in the solvent phase can be represented by:

$$\mathrm{NH_4^+\ (aq) + HA\ (org) \Leftrightarrow NH_4A\ (org) + H^+\ (aq)} \tag{3}$$

From the analysis of the simplified model equations [1], an estimate of the overall mass transfer coefficient, designated as K_{OF}, has been calculated from Eq. (4) using the experimental data obtained in the membrane contactor. The following equation shows the relationship between the concentration time data, flow rate, solution volumes, and other physical parameters—all related to and obtained in the membrane contactor.

$$\ln\left(\frac{C_{\mathrm{NH_3\,fi(aq)}}}{\left(1+\frac{1}{D_E}\right)C_{\mathrm{NH_3\,fo(aq)}}-\frac{C_{\mathrm{NH_4\,fi(aq)}}}{D_E}}\right)=\frac{q_f}{v^t}\left(1-\exp(-BK_{\mathrm{OF}})\right)t \tag{4}$$

$$B=\frac{\left(1+\frac{1}{D_E}\right)L}{\left(\frac{V}{A}\right)_{\mathrm{in}}u_f} \tag{5}$$

3. Materials and methods

3.1. Chemicals and reagents

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 di-(2-ethylhexyl) phosphate, D2EHPA (99%, 100 g, by Gohanson Matthey Company, UK). Distilled and seawater were also used without any treatment. 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. After each experiment, samples were put in a 22-mL vile (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). The pH was measured using a pH meter (Thermo Orion pH meter, USA) calibrated at pH 4 and 10.

Sunflower oil is very high in monounsaturated fatty acids. General composition of sunflower oil includes the following: stearic acid (50–55%), palmitic acid (4–7%), oleic acid (27–30%), and linoleic acid (0–1%) [31]. Sunflower oil brand (Noor brand) used in this investigation has no trans-fatty acid, and due to its higher stearic acid, contents provide good physical and chemical properties for industrial applications. The flash point of this product is in the range of 160–170˚C.

3.2. Procedure for equilibrium measurements

The feed was prepared by weighing different amounts of ammonium chloride, expressed as ammonia concentration (340–16,014 mg/L) and volume of distilled water or seawater. The pH of the feed was measured. In order to prepare the organic phase, measured volumes of sunflower oil (or decanol) and di-(2-ethylhexyl) phosphate were mixed to the required concentration.

Feed and organic phase were then added together in a 100-mL beaker and put on the shaker for three 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. For all experiments, same volumes for both the aqueous and organic phases were used.

3.3. Hollow fiber membrane contactor

The experiments were carried out in a hollow fiber membrane contractor, 5PCM-218, purchased from Membrana 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. A schematic diagram of the experimental apparatus is shown in Fig. 1.

3.4. Mass transfer experiments in the membrane contactor

This liquid–liquid extraction technique was carried out in the hollow fiber membrane contractor. 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 contractor, the feed, which is the ammonia solution, was fed inside the hollow fibers and the organic phase was pumped to the shell side. A pressure of about 20–30 kPa was applied on the aqueous phase to prevent the organic from flowing out of the pores. pH of the feed solution was measured before and after each experiment. The samples from the exit solution were taken after each interval and were measured by a photometric system (by PC multi-direct). The contact time was four hours, and a sample was taken every hour.

3.5. Measurement of 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_3-N). 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 deionized water. Each reaction in the photometer takes a certain period of time; the reaction time of ammonia solutions is 20 min. After adjusting the system and preparing the samples, the photometer was turned to the on mode and waited for 20 min 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_3, and this reading can be changed to millimolar of NH_4Cl.

The values of concentration for the initial feed solution and the aqueous phase samples were used to calculate the removal percentage, R (%), which was calculated from the following equation:

$$R(\%) = \left(1 - \frac{C_{\mathrm{NH_3fo(aq)}}}{C_{\mathrm{NH_3fi(aq)}}}\right) \times 100 \tag{6}$$

where $C_{\mathrm{NH_3fo(aq)}}$ and $C_{\mathrm{NH_3fi(aq)}}$ are the concentrations of NH_3 in the aqueous phase at various time intervals and in the initial feed solutions, respectively.

4. Results and discussion

The results are presented for equilibrium experiments with the carrier D2EHPA dissolved in either sunflower oil or decanol. The experimental data from the hollow fiber contactor have been analyzed using the simplified model equations described in the previous section. All the extraction experiments were repeated, and the results are within 5% of error.

4.1. Removal of ammonium: comparison of sunflower oil and decanol

In Table 2, the effects of initial feed NH_3 concentration on the distribution coefficient are shown. The pH was kept at the natural pH (5.1 for the distilled water and 7 for seawater) 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 values of the distribution coefficient (D_E) depend largely on the initial concentration of NH_3, being high (approx. 1.9) for smaller concentration and low (approx. 0.60) for medium and very small (approx. 0.2) for high concentration of NH_3 (approx. 16,000 mg/L). For constant initial concentration of NH_3, the values of D_E can be increased by increasing the carrier concentration (shown in the last 3 rows of Table 2). The values were similar for both the solvents—sunflower oil and decanol. The D_E value reported earlier [3] was 6.1. They used 8% (v/v) D2EHPA in 50% (v/v) decanol–toluene mixture for NH_3 feed concentration of 4,800 mg/L. The volumetric phase ratio of the solvent-to-feed was 5, compared to 1 in this work, and the initial NH_3 concentration was low compared to the concentrations used in Table 2. The value of the distribution coefficient (D_E) would have been different if the phase ratio was unity. Compared to the results in the literature, the values obtained in

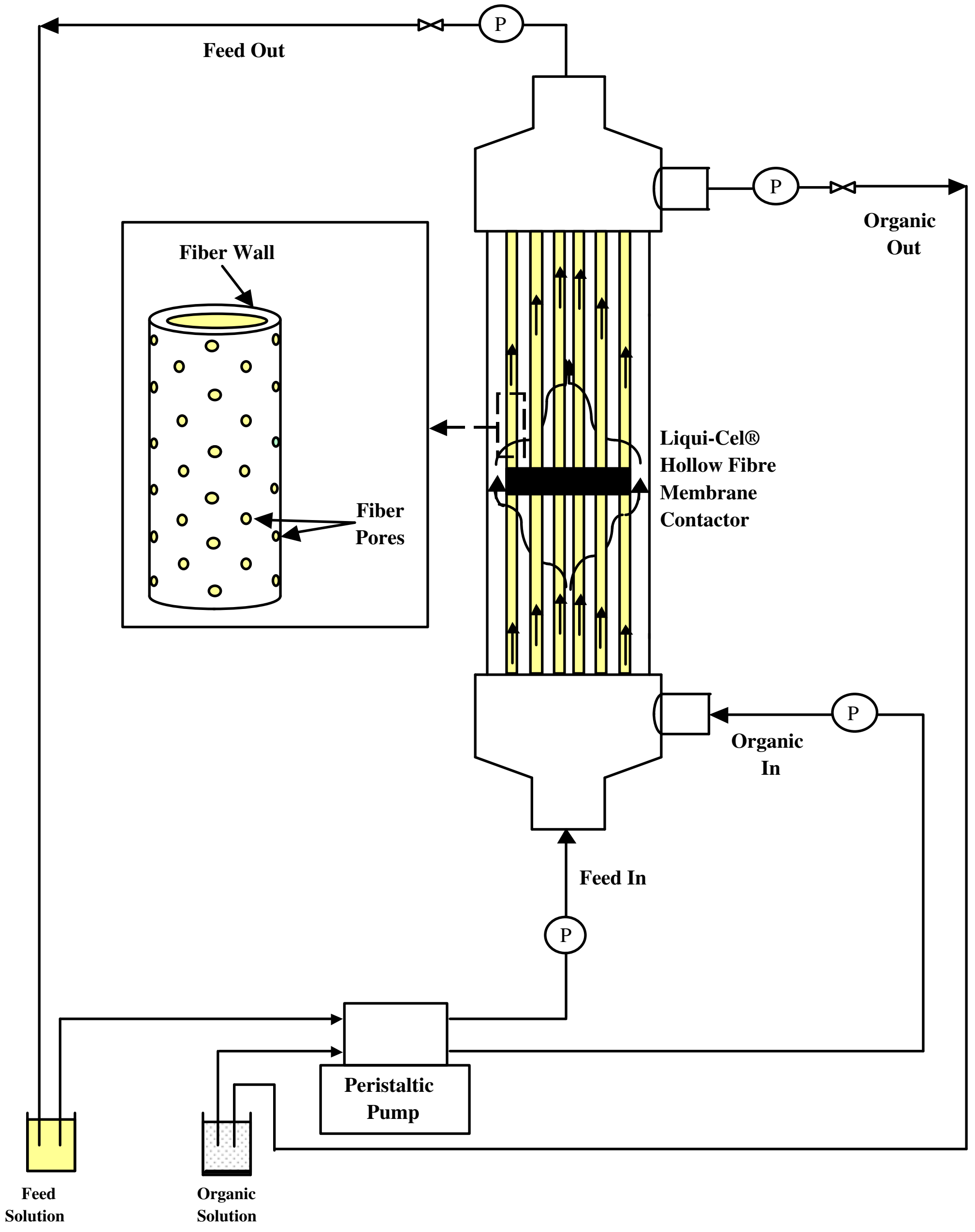

Fig. 1. A schematic diagram of the experimental setup with the hollow fiber membrane contactor for the removal (or extraction) of ammonia from the aqueous phase.

this work look encouraging as these were obtained with smaller amounts of sunflower oil which has advantages in terms of economics, environment, and operation.

4.2. Mass transfer experiment in the membrane contactor

The process was upgraded, and the performance was studied in a small-scale membrane contactor without any adjustment of aqueous phase pH. The initial volumetric ratio of the flow rates of the two phases was approximately one. Table 3 shows the experimental results of ammonium removal after 4 h of treatment of distilled water and seawater. In both the examples, the carrier used was di-(2-ethylhexyl) phosphate and the diluent was sunflower oil.

As observed in Table 3, the removal of ammonia was lower (approx. 42.7%) when seawater was used.

Table 2
Values of the distribution coefficient in the liquid membrane of D2EHPA in sunflower oil and in decanol for ammonia removal from distilled water and seawater

	Aqueous phase			Organic phase		
Initial NH_3 concentration (mg/L)	Initial pH	Final pH	Final NH_3 concentration (mg/L)	Carrier concentration in oil, % (v/v)	Solvent	Distribution coefficient (DE)
342.7	5.4	2.4	120.3	0.82	Sunflower oil	1.86
3,427.3	5.6	2.7	2,086.8	8	Sunflower oil	0.64
3,427.3	7.0	3.2	2,554.8	8	Sunflower oil	0.34[a]
3,427.3	5.6	2.7	1,620.9	8	Decanol	1.11
8,567.3	5.8	2.6	6,999.6	20	Decanol	0.22
8,567.3	5.8	2.6	7,059.6	20	Sunflower oil	0.21
16,014	6.5	2.6	13,674	15	Sunflower oil	0.17
16,014	6.5	2.5	11,094	30	Sunflower oil	0.44
16,014	6.5	2.2	8,385	60	Sunflower oil	0.90

[a] Seawater at pH 7.

This could be due to (i) the presence of other components in seawater competing with ammonia during the process and (ii) the higher value of feed pH for seawater which reduces available ammonium concentration. This removal percentage can be enhanced using higher concentration of the carrier (as shown in Table 2). This result was achieved using only 10% (v/v) of the carrier in sunflower oil for a very high feed concentration (approx. 25,600 mg/L of NH_3). The results from other investigators are also presented in Table 3. The differences between this work and those in the literature are to be recognized first: The results herein are for very concentrated aqueous ammonia solution (many times larger than those reported) and at the natural pH (i.e. no chemicals added for pH adjustments) and with sunflower oil (is obtained from a sustainable source). Considering all the benefits of the new system, the results are encouraging as initial efforts toward the development of a sustainable process for the removal of ammonia and for the production of treated water that can be suitable for secondary purposes.

Also, all results were achieved in a single module (easy-to-scale-up type) within a contact time of 4 h at an aqueous flow rate of 12–14 L/h. The concentration of ammonia vs. time is presented in Fig. 2 for both seawater and distilled water. It is expected that the percentage removal can be increased using carrier concentration of higher proportions and adding more modules. It is estimated from this data that it would require 1,000 L of sunflower oil with 100 L of D2EHPA to treat 1 m^3 of seawater to reduce high concentration of ammonia from 25, 600 to 3,750 ppm in two stages. With this reduced ammonia concentration, the treated water is suitable for irrigation purposes. More work is underway to recover ammonium from the oil phase and recycle oil, making the overall process more economically attractive.

The stability of the organic phase results from the fact that this sunflower-based system is not expected to undergo alcoholysis, because the operating temperature is around ambient temperature Therefore, it is expected that the sunflower-based extraction phase could retain its stable performance over a long period

Table 3
Removal (%) of ammonia from aqueous feed solutions in hollow fiber contactor: comparison of results of this work with other similar methods

Feed solution (initial pH)	Aqueous NH_3 feed (mg/L)	Organic phase/removal solution	Removal % (contactor area, m^2)	Refs.
Seawater (pH 7)	19,123	5% (v/v) D2EHPA in sunflower oil	42.7 (1.4)	This work
Distilled water at (pH 5.1)	25,612	5% (v/v) D2EHPA in sunflower oil	72.5 (1.4)	This work
Aqueous feed (pH 7)	250–500	0.1–0.3 M sulfuric acid	98 (0.014)	[8]
Aqueous feed (pH 7)	5,083	4.5% (v/v) D2EHPA in 50%(v/v) decanol-50% toluene mixture	Less than 15% (0.01)	[3]

for the treatment of wastewaters containing ammonium ion.

4.3. Overall mass transfer coefficient: approximate solution vs. correlation

The overall transfer coefficient (K_{OF}) was calculated from the slope of the plot of the left-hand side (LHS) of Eq. (4) vs. time. A plot of the LHS of Eq. (4) using the concentration of ammonia (Fig. 3) at various time of the experiment is shown in Fig. 3. The concentration data over the first 45 min were analyzed as these data give a good correlation. From the slope of the plot and using the value of B in Eq. (5), the overall mass transfer coefficient for the removal process has been calculated. The value of the overall mass transfer coefficient, K_{OF}, is obtained as 0.9×10^{-7} m/s for the ammonia removal process in the membrane contactor. This value is similar to the values 1.2×10^{-7} m/s reported in the literature [6,14]. The value has been found to depend on the concentration of the carrier, initial concentration of ammonia, and initial pH of the feed solution. The value of the overall mass transfer coefficient obtained in this work can be taken as reasonable considering the fact that the initial concentration of ammonia is many times higher and process conditions (with pH lower than those of the literature) are unchanged from the existing sources of samples, and more importantly, a diluent from sustainable source has been utilized.

For comparative purposes, the overall mass transfer coefficient (K_{theo}) was also evaluated using the correlations (Eqs. (A1)–(A6) in Appendix A). The value of K_{theo} obtained by the use of correlations with the values of parameters in the literature [26] is in the similar range, (1.1×10^{-7} m/s), as determined from our experimental data. These data are directly used, whereas the correlations were derived from experiments in different devices, not at the conditions in the membrane contactor. It is also noted that the correlation takes into account the effect of the flow rate and resistances in the individual diffusional processes, so as to provide more insight into the steps. However, it does not include the effect of the initial ammonium concentration for a fixed concentration of the carrier (the D2EHPA concentration). The initial concentration (especially at such high value considered in our experiments) would have affected the overall mass transfer process [14,26]. Because of its inclusion in Eq. (4) this solution might have represented the process better.

The values of the overall mass transfer coefficient have been reported in the literature for the removal (or extraction) of ammonia from aqueous phase using hollow fiber contactors [8,26]. In their studies, feed concentrations were lower, the initial pH was higher, and the contactor was smaller in terms of mass transfer area. Because of the effects of these variables the overall mass transfer coefficient values were greater than those calculated here. More work need to be done and more tests have to be made in a wider range of operating variables to confirm these findings. Nevertheless, it can be emphasized that the values in the present report are for higher ammonium concentrations at their natural pH and was obtained using an inexpensive solvent in a hollow fiber membrane contactor.

It is encouraging to observe that sunflower oil, a non-traditional solvent, can be used as an extracting phase and it allows greater extraction when combined with a carrier; it is noted that sunflower oil is

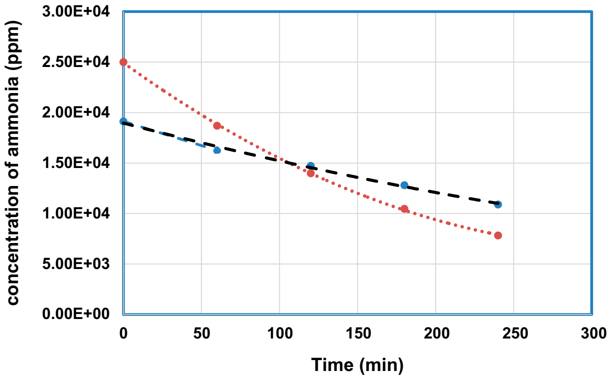

Fig. 2. Concentration of ammonia (ppm) in the aqueous phase vs. time (min) in the removal process using a hollow fiber membrane contactor. The liquid membrane phase consisted of fresh sunflower oil (diluent) with 5% (v/v) DEHPA (carrier). (—) for seawater and (……) for distilled water.

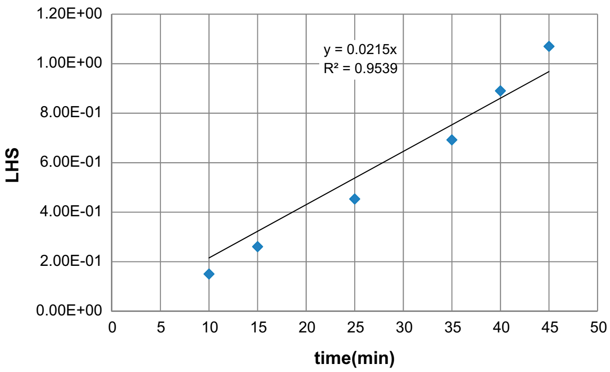

Fig. 3. A plot of the LHS of Eq. (4) vs. time (min) to determine the overall mass transfer coefficient for the liquid membrane process, the parameters are listed in the nomenclature.

compatible with large-scale contactors and it is environmentally friendly, and less harmful to the operators. The other solvents (or mixtures of solvent) although more effective, but are harmful, possess undesirable characteristics, have also been found to be incompatible with industrial membrane contactors, caused swelling of the polymeric membranes, and created difficulties during long-term operation.

5. Conclusions

From the study of the removal of ammonia from aqueous feed at its natural pH from two samples (distilled water as well as seawater), the following remarks are made:

(1) Removal was successful with D2EHPA (di(2-ethyhexyl) phosphate) used as a carrier in sunflower oil (as a diluent) and from a wide range of ammonia concentrations.
(2) In a bench-scale hollow fiber membrane contactor with an area of 1.4 m^2, moderate degrees of removal was achieved (in the range of 43–73%) within a contact time of 4 h.
(3) This result was obtained from a high feed of concentrated ammonia (25,600 ppm), much higher than the values reported in the literature.
(4) It was estimated that it would require 1,000 L of sunflower oil with 100 L of D2EHPA to treat 1 m^3 of seawater to reduce ammonia concentration from high value to 3,750 ppm. With this concentration, the treated water is suitable for irrigation purposes.
(5) The overall mass transfer coefficient values for the sunflower oil system are comparable to those reported in the literature for similar extraction situations.
(6) The diluents from fossil fuel sources, *n*-decanol and toluene (used in the literature), are effective but are less recommended because of the issues of cost, safety, and unsustainability.
(7) Finally, the results were obtained at the natural pH (no chemicals added for pH adjustments) using sunflower oil, an environmentally friendly, cheap, and benign solvent, which can be considered as a "green" solvent.

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Symbols

B — defined in Eq. (5), 2.243×10^5 s/m
d_h — hydraulic diameter, used in Eq. (A3)
D — diffusivity in water, used in Eq. (A1), 1.76×10^{-9} m^2/s
D_o — diffusivity in oil, used in Eq. (A2), 2.64×10^{-10} m^2/s
D_m — diffusivity in membrane pores, used in Eq. (A5), 2.92×10^{-10} m^2/s
D_E — apparent distribution coefficient defined in Eq. (2) (–)
E — percentage extraction defined in Eq. (6)
k_a — mass transfer coefficient on the fiber side, calculated in Eq. (A1) (m/s)
k_m — mass transfer coefficient in the membrane pore, calculated in Eq. (A5) (m/s)
k_o — mass transfer coefficient on the shell side, calculated in Eq. (A2) (m/s)
K_{OF} — overall mass transfer coefficient, obtained from the plot of Eq. (4) (m/s)
K_{theo} — overall mass transfer coefficient, calculated in Eq. (A6) (m/s)
L — length of the fibers, used in Eq. (A1), 15 cm
N — number of fibers, used in Eq. (A3) 9,950 (–)
$C_{\mathrm{NH_4f}}$ — ammonium concentration in the aqueous bulk phase (mg/L)
$C_{\mathrm{NH_4O}}$ — ammonium concentration in the organic bulk phase (mg/L)
$C_{\mathrm{NH_4fi(aq)}}$ — ammonium concentration in the tank at the initial stage (mg/L)
$C_{\mathrm{NH_4fo(aq)}}$ — ammonium concentration in the tank at various times (mg/L)
q_f — feed flow rate, used in Eq. (4), 12,000 cm^3/h
Q — flow rate on the shell side, used in Eq. (A4), 9,000 cm^3/h
r_i — inner radius of the fiber, used in Eq. (A1), 120 μm
r_o — outer radius of the fiber, used in Eq. (A3), 150 μm
R_i — inner radius of the shell, used in Eq. (A3), 3.15 cm
t — time (s and min)
u_f — linear velocity in the fiber side, used in Eq. (5), 0.74 cm/s
u_{tube} — velocity in the fiber side, used in Eq. (A1), 0.74 cm/s
u_{shell} — velocity in the shell side, used in Eq. (A2), 0.08 cm/s
V_{aq} — volume of aqueous solution, used in Eq. (2), 500 cm^3
V_{org} — volume of diluent phase (organic solution), used in Eq. (2), 500 cm^3
$\left(\frac{V}{A}\right)_{\mathrm{in}}$ — volume per unit mass transfer in the fibers, used in Eq. (A5)), 1.4×10^{-4} m

Greek symbols

ν — kinematic viscosity (for water), used in Eq. (A2), 10^{-6} m^2/s
ν — kinematic viscosity (for oil), used in Eq. (A2), 6.63×10^{-5} m^2/s
ε — porosity, used in Eq. (A5), 0.4 (–)
τ — tortuosity, used in Eq. (A5), 2.25 (–)
δ — thickness of the membrane, used in Eq. (A5), 30 μm

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Appendix A

Mass transfer correlations

First, the mass transfer coefficient in the fiber side or the tube side, k_a, is calculated using the following equation:

$$\left(\frac{2r_i k_a}{D}\right) = 1.62\left(\frac{4r_i^2 u_{\text{tube}}}{DL}\right)^{1/3} \tag{A1}$$

Second, the mass transfer coefficient on the shell side, k_o, is calculated using the following equation:

$$\frac{d_h k_o}{D_o} = 0.56\left(\frac{4d_h u_{\text{shell}}}{v}\right)^{0.62}\left(\frac{v}{D_o}\right)^{0.33} \tag{A2}$$

The hydraulic diameter is calculated by the equation below:

$$d_h = \frac{2(R_i^2 - Nr_o^2)}{Nr_o} \tag{A3}$$

The velocity in the shell side by the equation below:

$$u_{\text{shell}} = \frac{Q}{\pi(R_i^2 - Nr_o^2)} \tag{A4}$$

Third, the mass transfer coefficient of the membrane, k_m, is calculated using the following equation:

$$k_m = \frac{\varepsilon D_m}{\delta\tau}\frac{r_o}{r_i} \tag{A5}$$

Finally, K_{theo} is calculated using the following equation:

$$\frac{1}{K_{\text{theo}}} = \frac{1}{k_a} + \frac{1}{D_E k_m} + \frac{1}{D_E k_o} \tag{A6}$$