A Vegetable Oil-based Green Process for the Membrane Extraction of Ionic Solutes

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Abstract: Extraction or removal of the polluting components can be accomplished by a variety of physical, chemical and biological methods. Solvent extraction has demonstrated as one of the promising methods to accomplish the extraction or removal of ions more or less selectively from the source streams. The processes, especially when operated in membrane modules, have been successful and effective in reducing the pollutant concentration. In the development of these processes in to industrial operations the solvents (or the extracting phase) used or recommended in the literature are from non-sustainable source, they have undesirable properties (toxic, corrosive and health and safety issues). In recent years there have been research work to examine the feasibility of other solvents from sustainable sources and with good characteristics to overcome or minimize some of the above adverse effects. In this paper, the effectiveness of sunflower oil (as a model for vegetable oil), is described in extraction (or removal) of a polluting component in a small-scale membrane contactor. The components are: chromate ion and ammonium ion and the process is developed using a carrier molecule (di-2-ethylhexyl phosphate for ammonium and Aliquat 336 for chromate) in sunflower oil. The removal percentages are very good (in the range of 43-99%) and obtained at their natural conditions (with no chemical added for the adjustment of pH) of the aqueous feed. The main attraction of the process is the good performance of sunflower oil, which can be considered a "green" solvent system as it has the benefit of being environmentally friendly, less costly, non-toxic and sustainable.

Keywords: Ammonium, chromium, Extraction, Hollow-fibre contactor, Seawater, Sunflower oil.

INTRODUCTION

Seawater, ground water and wastewaters from many industrial processes contain molecules (ionic at their natural conditions), which are considered as polluting sources even at low concentrations. The removal of these compounds are necessary to solve the environmental pollution problems and to meet the limits of the regulatory authorities. On the other hand, the recovery of some of these compounds may help generate additional sources of supply for applications in the industry where they are utilized making the entire process sustainable.

In this work two ionic pollutants are considered: (A) chromate (as anionic solute) and (B) ammonium (as cationic solute) for their removal from the polluted source (normally an aqueous solution). The developed process for ammonium removal also allows some reduction of carbon dioxide (the concentration in the atmosphere is very high and considered responsible for global warming). Ammonia/ammonium ion exists in the industrial wastewaters (fertilizer, oil and gas exploration, petroleum refining) and ground waters (through the discharges from domestic and agricultural activities). Ammonia in the 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 these compounds is desirable for many reasons:(i) to minimize its toxic effects on human operators, (ii) to generate a source of useful waters and (iii) to recover this in less toxic form that have application in agriculture, chemical and medical industries.

High concentrations of ammonia (system B) are discharged from coal-conversion processes, petroleum refining, tannery, textiles and fertilizer wastewaters [1, 2]. In some cases, ammonia coexists with gases like CO_2 (fertilizer industry) and H_2S (petroleum sour water); the natural pH of these wastewaters are in the range 7- 8.5 [3]. At the natural condition (pH being less than 8.5) 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 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 substantial removal of ammonia. In order to circumvent this disadvantage methods of removal in the ammonium form at its natural pH have been investigated [4-6].

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 [7-17].

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The results of most of these methods except for membrane-based methods were obtained at low concentrations and the efficiency was moderate (ca. 60%). In addition they suffer from regeneration difficulties requiring high temperatures.

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_2 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.

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 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). In the literature the methods such as precipitation [18], ion exchange [19], adsorption [20] and reverse osmosis [21] have also been studied for the removal of ionic compounds. These processes are able to remove the pollutants from wastewaters, but may produce concentrated stream of many components and thus may be uneconomic for selective removal and recovery of a particular component. Liquid-liquid extraction method, especially in combination with membrane separation processes, has shown to be more efficient and selective with potential for easy scale-up as an industrial separation technology [22-25]. 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.

Chromate (system A) can be treated by applying the reactive liquid-liquid extraction process with an appropriate carrier-diluent system [26-30]. Effluents from tannery, electroplating and timber treatment processes are the major sources of chromate form contaminating the aquatic and industrial environments. Chromium can also be used in chemical and refractory industry and the use has increased considerably [31]. A significant proportion of this chromium is released to the environment [32]. As a result, the ground water sources may also contain chromium and at the natural pH of the polluted sources Cr(VI) exists as chromate (an anion). The toxicity of these source waters can be reduced by their complete or partial removal from the streams and economic benefit can be gained by recovering them in the recyclable form. This may add to the sustainable development by applying these pollution control measures and creating additional sources of the depleting primary resources [31, 32].

Recently, there has been increased interest in developing green extraction processes for recovering high-value component from natural sources and removing polluting compounds from waste sources [33-38]. The recovery of hexavalent chromium from a simulated effluent using Alamine 336 in refined palm oil was reported [36]. 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 these processes depends on many factors including the selection of environmentally benign solvent with operator-friendly characteristics, compatibility to the 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-based liquid membranes for removal of chromium and ammonium ions from solutions at their natural pH (without any pH adjustment). This will include the determination of the partition behavior of the aqueous phase in these systems and evaluation of the performance of the process in a bench-scale membrane contactor for removing chromate and ammonium ions from groundwater and industrial wastewater samples (at their natural pH).

2. MASS TRANSFER MODELLING

In the derivation of the mathematical model the procedure followed is similar to that presented earlier [39]. 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. The liquid membrane is composed of an ionic carrier (either Aliquat336 for chromate ion or

D2EHPA for ammonium ion) 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, is filled with the liquid membrane. First, the ion being investigated (either chromate, anion or ammonium, a cation) diffuses from the bulk solution to the feed–membrane interface (tube side mass transfer), reacts with the carrier to form a complex (shown in Eqn. 1) that dissolves in the diluent phase. This ionic complex diffuses through the membrane pores (membrane mass transfer) and finally diffuses into the bulk liquid membrane phase in the shell side and thus removed from the feed. In the overall mass transfer process chromate or ammonium molecules from an aqueous feed side are transported to the organic side through the hollow-fibre wall as shown in Figure **1**. Substantial or total removal of ions could be theoretically possible under this configuration, since the driving force for this liquid membrane contactor operation is the difference in the specific ion concentration between the bulk feed phase and the receiving diluent phase.

For chromate system (A), the chemical equilibrium can be described by any of following equations (depending on the solution pH) [24, 40, 41]

$$CrO_4^{-2}\,(aq) + 2ACl\ (org) \Leftrightarrow A_2CrO_4\,(org) + 2Cl^-(aq) \tag{1}$$

$$Cr_2O_7^{-2}(aq) + 2ACl\ (org) \Leftrightarrow A_2Cr_2O_7\ (org) + 2Cl^-(aq) \tag{2}$$

where ACl represents the carrier Aliquat 336, $A_2Cr_2O_7$ and A_2CrO4 represent the chromium-carrier complexes with dichromate and chromate ions, respectively. It is noted that at higher pH (more than pH 6.5) the dominating ion is the chromate ion, not the dichromate ion [42]. The carrier concentrations are expressed in whole volume (carrier + solvent).

For ammonium system (B), the chemical equilibrium can be represented by the reaction between the ammonium ion with the carrier molecules (D2EHPA) in the solvent phase:

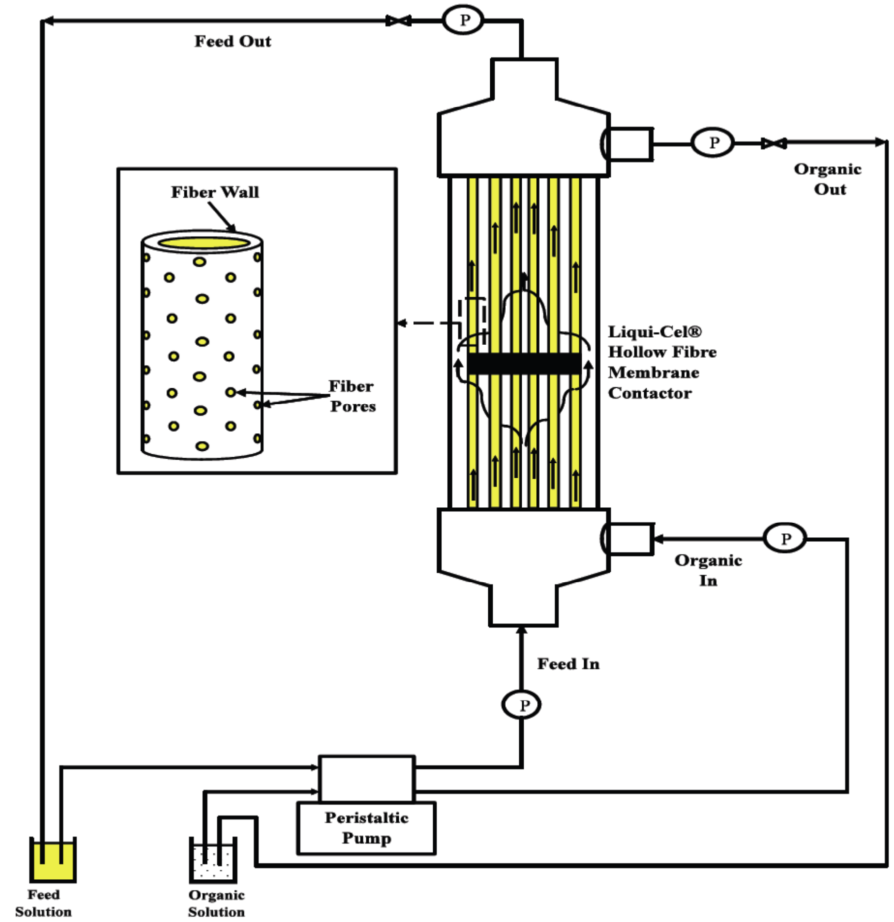


Figure 1: A schematic of the experimental set-up with the hollow-fibre membrane contactor.

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

The overall mass transfer for the 'target' ion, *i.e.* the mass flux of chromate-carrier complex (or ammonium-carrier complex) can be determined from the following equation:

$$N_{Chromatf} = K_{OF}\left(C_{Cromatf} - C_{ChromatO} / D_{E}\right) \tag{4}$$

where K_{OF} is the overall mass transfer coefficient of the process, the concentrations $C_{Chromatf}$ and $C_{ChromatO}$ are the concentration of the chromate ion in the bulk aqueous phase and in the bulk organic phase, respectively and D_E is the apparent distribution constant.

The apparent distribution coefficient for extraction, DE, is concentration-based and can be defined as the ratio of the concentration of chromate$^-$ ion in the organic phase over that in the aqueous phase at equilibrium:

$$\mathrm{DE} = \frac{\mathrm{C}_{\mathrm{Chromat*(org)}} * V_{org}}{\mathrm{C}_{\mathrm{Chromat*(aq)}} * V_{aq}} \tag{5}$$

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

The complete model is simplified based on the following assumptions:

- The steady-state condition applies
- The fluid flow is of plug flow pattern
- Isothermal operation of the system
- The properties such as density and viscosity are constant
- The fluid is Newtonian
- The reactions are instantaneous

The simplified model equations are shown in Table **1**. The solution of the model requires the calculation of the overall mass transfer coefficient from their individual values. The theoretical overall mass transfer coefficient is calculated by resistance-in-series model with the individual mass transfer coefficients estimated from many different theoretical equations, correlations, and analogies [17].

First, the mass transfer coefficient in the fibre-side or the tube-side, $k_{a,}$ is calculated using the following equation:

$$\frac{2r_i k_a}{D} = 1.62\left(\frac{4r_i^2 u_{tube}}{DL}\right)^{\frac{1}{3}} \tag{6}$$

Second, the mass transfer coefficient on the shell-side, $k_{o,}$ is calculated using the following equation:

$$\frac{d_h k_o}{D} = 0.56\left(\frac{4d_h u_{she;;}}{v}\right)^{0.62}\left(\frac{v}{D}\right)^{0.33} \tag{7}$$

The hydraulic diameter is calculated by the equation below:

$$d_h = \frac{2\left(R_i^2 - Nr_o^2\right)}{Nr_o} \tag{8}$$

The velocity in the shell side by the equation below:

$$u_{shell} = \frac{Q}{\pi\left(R_i^2 - Nr_o^2\right)} \tag{9}$$

Third, the mass transfer coefficient of the membrane, $k_{m,}$ is calculated using the following equation:

$$k_m = \frac{\varepsilon D}{\delta\pi}\frac{r_o}{r_i} \tag{10}$$

Table 1: Simplified Model Equation for Mass Transfer in Hollow-Fibre Membrane Contactor

Mass Balance	Model Equation	Boundary Condition	Solution
Feed Tank	$V\frac{dC_{\tan k}}{dt} = QC_{Z=L} - QC_{\tan k}$	$t = 0, C_{\tan k} = C_O$	$\frac{C_t}{C_i} = e^{-Ft}$
Lumen of membrane	$\frac{dC}{dz} = \frac{k_o \pi d}{Q_L}\left(C - C_O / DE\right)$	$z=0$, $C = C_t$ $z=L$, $C = C_L$	$\frac{C}{C_t} = \frac{(V_{OD} + e^{-EVz})}{\left[1 + V_{OD}\right]}$

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

$$\frac{1}{k_{OV}} = \frac{1}{k_a} + \frac{1}{D_E k_m} + \frac{1}{D_E k_o} \tag{11}$$

The model equations for ammonium are similar to the above equations with the values for the concentrations, the apparent distribution coefficient and the mass transfer parameters are replaced by those for ammonium ion.

An approximate solution of the model is derived to determine the concentration of the solutes:

$$\frac{C_t}{C_i} = e^{-Ft} \tag{12}$$

Where:

$$F = \frac{Q}{V}\left[\frac{1-e^{-(EV)L}}{\left(1+V_{OD}\right)}\right] \tag{13}$$

$$V_{OD} = \frac{V_f}{V_O D_E} \tag{14}$$

$$E = \frac{4K_{OV}}{uf\ d_i} \tag{15}$$

$$EV = E\left(1+V_{OD}\right) \tag{16}$$

From the estimate of the overall mass transfer coefficient (designated as K_{OV}), and using the experimental data obtained in the membrane contactor the exit concentration of the ionic compound can be determined.

3. MATERIALS AND METHODS

(A) For chromate removal process

Potassium chloride and potassium carbonate Anala R grade were purchased from BDH Chemicals Ltd, Poole, England. Potassium dichromate ($K_2Cr_2O_7$) was from Riedel-deHaen, Germany. To study the effect of pH, solutions were pH adjusted using reagent grade HCl or NaOH (BDH Chemicals, England). The metal concentrations were determined by ICP spectrophotometer (Varian 710-ES 03, Australia). The temperature was maintained using a water bath (Grant Industry, Cambridge Ltd, England) and a magnetic stirrer hotplate (Stuart Co., England).

(B) For ammonium removal process

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%, 100g, by Gohanson Matthey Company, UK). Aliquat 336 (tricaprylyl-methylammonium chloride), $CH_3N((CH_2)_7CH_3)_3Cl$) and hexan-1-ol ($CH_3(CH_2)_4CHOH$) were obtained from Aldrich, New Jersey, USA 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. 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). The pH was measured using a pH meter (Thermo Orion pH meter, USA) calibrated at pH 4 and 10.

3.1. Procedure for Equilibrium Measurements of Solutes

(A) Chromium (VI) feed solution – the standard solution of potassium dichromate was prepared by dissolving a known amount of this chemical in distilled water.

All the removal and recovery experiments were conducted at room temperature of 25 ^{0}C. A feed solution containing Cr (VI) with adjusted pH to a desired value contacted with the organic phase containing Aliquat-336-organic solvent-hexanol at a volume ratio of 1:1 in the 25 ml centrifuge tubes. The addition of hexanol as modifier was required to keep Aliquat 336 in solution and maintain a clear interface after the equilibrium, about 10% (v/v) hexanol were required. The aqueous feed concentration was varied in the range: 20 - 500 ppm (except for the ground water samples) and initial feed pH range was within 6-12. The solution in the tubes was mixed for a period of 2 hours using magnetic stirrer. After mixing the solutions were allowed to settle for 60 minutes to separate the two phases and obtain a clear bottom aqueous phase. The bottom aqueous layer was removed using a Pasteur pipette and analysed for its chromium (VI) content. The initial and final pHs of the aqueous phase were also measured.

(B) 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 decanolor kerosene) was measured and added to di-(2-ethylhexyl) phosphate as desired. The procedure (time of contact and sampling) is similar to that of (A) with the same volumes for both the aqueous and organic phases.

All the concentrations after the equilibrium experiments were measured and the values of the distribution coefficient were determined. A large value of DE suggests good extraction.

3.2. Hollow-Fibre Membrane Module

The experiments were carried out in a hollow fiber membrane contractor, 5PCM-218, purchased from Membrana, 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 **2** below.

Table 2: Characteristics of the Hollow Fiber Membrane Contactor

Characteristics of the Module	
Fibre Type	Microporous Polypropylene Hollow Fiber
Effective Pore Size	0.05 μm
Pore tortuosity Porosity	2.25 40%
Operating Chracteristics	
Cartridge Length	16 cm
Shell Inner Diameter	6.3 cm
Effective Mass Transfer Area	1.4 m^2
Effective Area/Volume	29.3 cm^2/cm^3
Priming Volumes:	
Tubeside (include endcaps)	145 cm^3
Shellside	195 cm^3

3.3. 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 ammonium chloride solution was fed inside the hollow fibres and the organic phase was pumped through the shell side. A little pressure of 20 kPa was applied on the feed side to stabilize the interface in the pores. The experiment was run in a recycle mode, *i.e.* both the phases were recycled. The samples were taken a regular intervals and were 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.

3.4. Analytical Methods

3.4.1. Analytical Method for Cr (VI) Content using a Spectrophotometric Method

The values of concentration for the initial feed solution and the aqueous phases produced after the extraction experiments, were measured using the atomic absorption spectrophotometer, fuelled by argon. The industrial samples had to be diluted (usually 10 x dilution) to be less than the maximum value that can be measured by the instrument. The concentration values were measured at a wavelength of 267.7 nm. The values of organic phase concentration were calculated from differences of initial and final aqueous phase concentrations. The distribution coefficient for extraction (DE) was calculated by using equation 2.

3.4.2. Measurement of NH_4^+ Concentration using a Spectrophotometric Method

To measure the ammonium concentration of the aqueous phase a photometric method was used. A high range concentration reagent was used which is Vario Ammonia test reagent and the samples were diluted in the range of the reagent (0-50 ppm NH_3-N). This reagent contains test tubes and is filled with 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 analysis, 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. 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_3 and this reading was changed to mille-molar of NH_4Cl.

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, R(%) (or E(%)), was calculated from the following equation

$$R(\%) = \left(1 - \frac{C_{fo(aq)}}{C_{fi(aq)}} \right) x100 \qquad (17)$$

where C_{fo} (aq) and C_{fi} (aq) are the concentrations of NH_4Cl at various time intervals and in the initial feed solutions, respectively.

4. RESULTS AND DISCUSSION

All the extraction experiments were repeated and the results are within 5% of error.

4.1. Chromate Removal Process

4.3.1. Effect of Initial Cr (VI) Concentration

The effect of the initial Cr (VI) concentration on DE (the distribution coefficient) and %E (extraction/removal) is shown in Figure **2**. The organic phase containing 5% Aliquat-336, 10% 1-hexanol and 85% sunflower oil was used. It is clearly observed that both DE and E% decrease with the increase in the initial feed concentration. At lower feed concentration of up to 25 ppm, the value of the distribution coefficient is more than 100 and %E is approx. 99%. Beyond this feed concentration, both the distribution coefficient and the E% decrease considerably up to 100 ppm and then the decrease is gradual. At very high concentrations (approx. about 500 ppm), the distribution coefficient is less than 10 with E% being approx. 87%. This observations suggest that the removal process at higher initial Cr(VI) concentration may require longer contact time and may demand higher Aliquat 336 concentration.

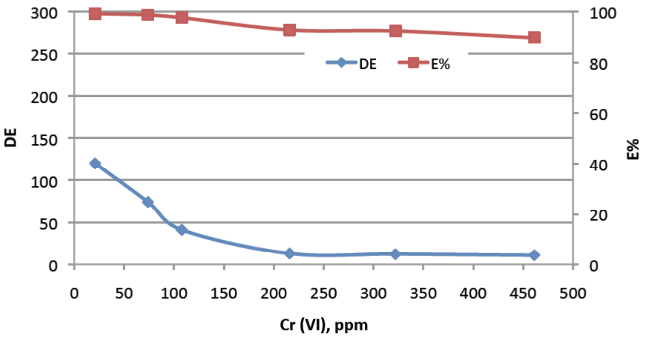


Figure 2: Distribution coefficient (D_E) and extraction (%) versus chromium concentration (ppm or mg/L) in equilibrium experiments, using the organic phase: 5% Aliquat 336, 10% n-hexanol and 85% diluent (sunflower oil).

4.3.2. Effect of Feed pH on Extraction in Various Solvents

The effect of initial feed pH on the extraction of chromium (VI) using 5% Aliquat-336 and 10% 1-hexanol in two diluent able oil (sunflower oil and kerosene) is presented in Figure **3**. It can be seen that the trends for both the solvents are similar. With the increase in feed pH within 6-10 the percentage extraction decreased, from approx. 95% (at pH 7) to 83% (at pH 9). The performance of the new diluent, sunflower oil, is as good as kerosene (the solvent being tried by many investigators) except at higher pH of 10. The gradual decrease in the percentage extraction could be due to the changes of ionic form of Cr(VI) in this pH range. The percentage removal is still good within the pH range 7-9 which is the natural pH of many ‘real’ water samples. It is observed that sunflower oil performs well and has the potential to replace kerosene as a renewable and biodegradable solvent. It is noted that kerosene has been trialed in many industrial extractions and treatment of environmental polluting sources [23, 40-43]. It has been effective as an

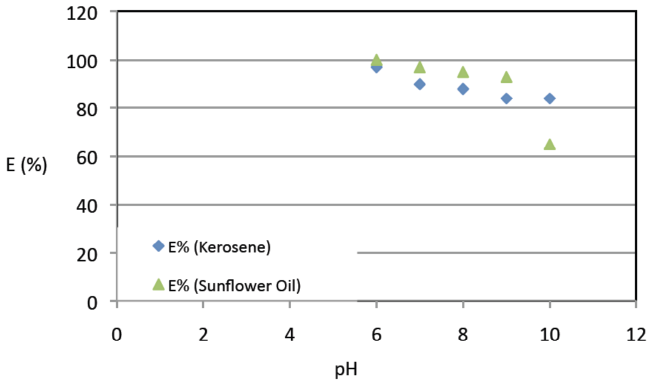


Figure 3: Effect of pH with two diluents on extraction of Cr(VI) (400 ppm at pH 7), and with the organic phase: 5% Aliquat 336, 10% n-hexanol and 85% diluent (sunflower oil/kerosene).

extracting solvent but it is toxic, environmentally harmful, and unpleasant to the operators. It has been found to be incompatible with many industrial membrane separation modules, caused swelling of the polymeric membranes and created difficulties during long-term operation.

In long-term, the sunflower oil-based phase can be considered stable because the operating temperature is around ambient temperature and 1-hexanol is a nonreactive component [44, 45]. Therefore it is expected that this new solvent phase could retain its stable performance in the long-term treatment of aqueous Cr(VI) containing wastewaters.

4.3.3. Effect of Carrier Concentration

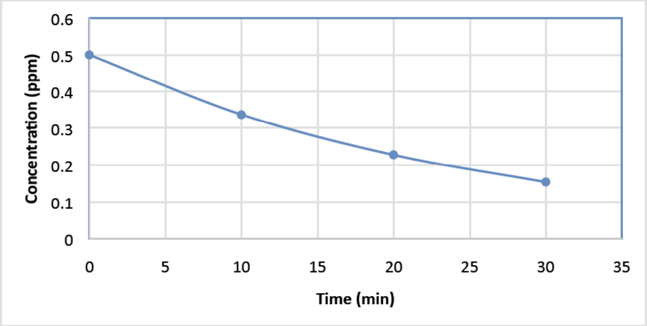
Experimental results on the effect of carrier concentration (Aliquat 336 in the range 1% v/v to 20% v/v in fresh sunflower oil) for extraction of Cr (VI) at pH 7 are listed in Table **3**. The effect of increasing the concentration of Aliquat 336 was evident by the increase in both DE and E (%). This increase was significant as the percentage removal increased from approx. 50 % (at 2 % v/v Aliquat 336) to 88% (at 10% v/v Aliquat 336). This suggests that Aliquat 336 concentrations required for the separation process is much more than the stoichiometric proportion, *i.e*. approx. 40 times in the molar ratio. The addition of the carrier might have allowed faster diffusion of concentrated chromate ions (as the contact time was the same for low/high concentrations of Aliquat 336) in the oil phase.

Table 3: Values of the Distribution Coefficient Chromate in Sunflower Oil

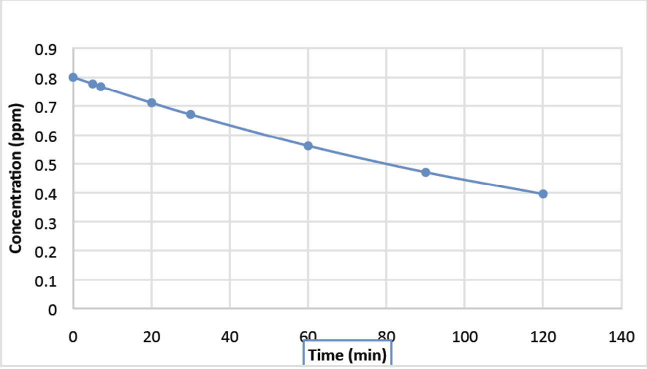
Aliquat-336 % (v/v)	Cr (VI) conc (mg/L)		%E	DE
	Initial	Final		
2	466.57	232.48	50.2	1.00
5	466.57	153.24	67.2	2.05
10	466.57	55.58	88.1	7.40
20	466.57	16.73	96.4	26.89

4.3.4. Removal of Cr (VI) from Groundwater Sample using Hollow-FIbre Membrane Contactor

The removal of Cr(VI) from a local ground water source [46] was examined using the sunflower oil-Aliquat 336 system. The existing concentration of Cr(VI) was low (0.09 ppm, pH 6.3) and Cr(VI) was added to examine its effect at the required concentrations (*i.e* 0.5 ppm and 0.8 ppm). It is observed that the percentage extraction (or removal) was 68% (0.5 ppm feed) and decreased to 50% at 0.8 ppm feed (Figure **4** (**a**) and (**b**)). These results were obtained with only 2% Aliquat 336-10% 1-hexanol-88% sunflower oil in a single stage. Using higher Aliquat 336 concentration and multiple stages more removal of Cr(VI) can be achieved. The values of the exit concentrations at various times were calculated using the simplified equation (Eqn. 12) and are also shown in these figures. The overall mass transfer coefficient required for Eqn. (12) was calculated from the Eqns. (6) – (11) and are listed in Table **4**. The predictions of the simplified solution are good at these low concentrations. More tests and comparison at higher Cr(VI) concentrations in a wider range of experimental conditions are required to show the validity and superiority of the equations.



4(a)



4(b)

Figure 4: Concentration of Cr(VI) (ppm in the groundwater sample) versus time from using the organic phase: 2% Aliquat 336, 10% n-hexanol and 88% diluent in a hollow-fibre membrane contactor; initial Cr(VI) concentrations are: (a) 0.5 ppm and (b) 0.8 ppm. The solid line represents the prediction from the simplified model solution.

4.4. Ammonium Removal Process- Equilibrium Experiments

The results are presented for equilibrium experiments with the carrier D2HEPA dissolved in sunflower oil/decanol. In Table **5** the effects of initial feed NH_4Cl concentration in distilled water and seawater 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_4Cl, 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 [3] 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 the results in the literature the values obtained in this work look encouraging as these were obtained with smaller amounts of sunflower oil which has better characteristics in terms of economics, environment and operation.

4.5. Ammonium Removal Process- Experiments in Hollow-Fibre Membrane Contactor

The ammonia removal process was upgraded and the performance was studied in the membrane contactor at the natural pH of the feed phase. The experimental conditions of the ammonia removal run is listed in Table **6**. In Table **7** the experimental results of removal of ammonium ion, both from feed of distilled water and sea water, are shown. In both cases the carrier used was di-(2-ethylhexyl) phosphate and the diluent was sunflower oil.

Table 4: Values of the Parameters used in the Calculation of Solute Concentration (Chromate and Ammonium) using the Simplified Model Solution

Parameter	Ammonium Removal Process	Chromate Removal Process
Dt (m^2/s)	1.95×10^{-9}	3.32×10^{-10}
Ds (m^2/s)	2.64×10^{-10}	5.54×10^{-10}
Dm (m^2/s)	2.92×10^{-10}	2.92×10^{-10}
Ri (m)	0.25	0.25
V (m^3)	$(0.5)\times10^{-3}$	0.5×10^{-3}
ε	0.4	0.4
VOD	1	1
τ	2.6	2.6
DE	0.2	4.5 (0.5 ppm), 2.8 (0.8 ppm)
K_{OV} (m/s)	1.1×10^{-7}	1.4×10^{-6} and 1.1×10^{-6}

The percentage ammonia 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 percentage can be considered a good result as it was achieved at a very high concentration (approx. 25120 ppm of NH_4Cl) and obtained with use of less than stoichiometric proportion of carrier in a cheap solvent. The results from other investigators are also 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). Considering all these benefits of the new system, the results are encouraging as initial efforts towards the development of a sustainable process for removal of

Table 5: Extraction of Ammonium Chloride from Distilled Water and Seawater

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

ammonium and for production of water from seawater to be used for irrigation purposes.

Table 6: Experimental Conditions of HFMC Experiments for Ammonium Ion

Feed Solution	
Concentration of ammonium chloride (mg/L):	25000
Volume (L)	0.5
pH (-):	7.2-7.8
Flow rate (L/h):	12-13
Temperature (K):	293 K
Organic Solution	
Concentration of carrier in the solvent (mM):	200
Volume (L):	0.5
Flow rate (L/h):	9-10
Temperature (K):	293

The results were achieved in a single module (easy-to-scale-up type) within a contact time of approximately 4 hours. The values of the exit ammonia concentrations were calculated using the simplified analytical solution (Eqn. 12) and the experimental parameter values. The overall mass transfer coefficient was calculated using the correlations (Eqns. (6) – (11)) and are listed in Table **4**. The calculated values are very close to those of the experimental data points (Figure **5**). This suggests that the prediction of the simplified model can be useful for determining the exit concentration at various contact time. Obviously more comparisons are required with a wide range of conditions to recommend this simplified solution for predictive purposes.

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 for removal of both anionic and cationic pollutants. It is noted that kerosene has been used commercially in the treatment of environmental polluting sources [23, 25]. It has been effective as an extracting solvent but it is considered toxic, environmentally harmful, and unpleasant to the operators. It has also been found to be incompatible with industrial membrane modules, caused swelling of the polymeric membranes and created difficulties during long-term operation.

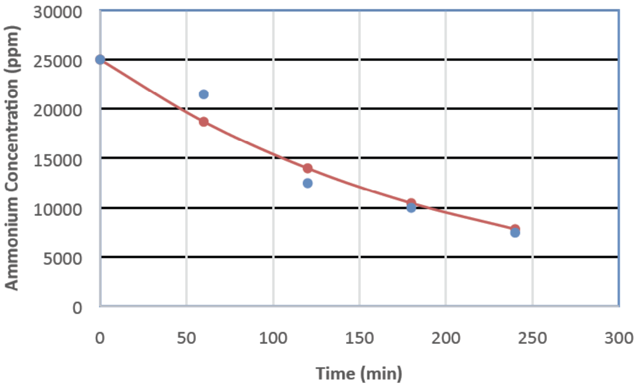


Figure 5: Concentration of ammonium (ppm in the feed sample) versus time using the organic phase: 200 mM D2EHPA in sunflower oil (diluent) in a hollow-fibre membrane contactor. The solid line is the prediction from the simplified model solution.

CONCLUSIONS

In both the examples the percentage removal was moderate, within contact times of 1- 4 h and these were obtained at the natural pH of the polluting streams using sunflower oil as diluent. The remarks for the two processes are:

- The values of the percentage removal of chromium with Aliquat 336 and that of ammonium with di(2-ethyhexyl) phosphate are good using sunflower oil as a diluent.
- The performance of the systemis significantly affected by the feed solution pH, its initial concentration and the composition of the oil

Table 7: Percentage Removal of Ammonium using the Hollow-Fibre Membrane Contactor

Condition of Feed Solution	Aqueous NH_4Cl Feed (mM)	Organic phase /Removal solution	Removal %	Reference
Seawater at pH 7	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 (pH not indicated)		0.2-0.4 M sulphuric acid	60-78%	Hou, S.-W. (2011)
Aqueous solution at pH 7	60.0-95.0	D2EHPA in 50%(v/v) decanol-toluene	Less than 15%	Qin & Cabral (1996)

1mM (NH_4Cl) =53.49 ppm (mg/L), 200 mM = 10,700 ppm, 500 mM = 26,750 ppm.

phase (Aliquat 336 or di(2-ethylhexyl) phosphate concentration).

- At low concentration (less than 1ppm of Cr(VI)) in the ground water, the removal percentage is good using a hollow-fibre membrane contactor with an area of 1.4 m^2.
- For removal of ammonia in the upgraded process a good percentage removal was achieved (in the range 43-73%) and from a concentrated feed solution (25,200 ppm), much higher than the reported values.
- The other diluents kerosene/ n-decanol (used in the literature) worked well but is less recommended because of cost, health and safety issues and unsustainability.

The new solvent system, sunflower-based, has several merits including less toxicity, less corrosiveness, low environmental impact and good health and safety benefits and compatibility with the large-scale membrane contactors and have been successful both for anions and cations.

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SYMBOLS

Nomenclature

d_h	hydraulic diameter, used in Eqn. (8)
D	diffusivity, used in Eqn. (7)
DE	apparent distribution coefficient defined in Eqn. (5)
E	percentage extraction defined in Eqn. (17)
k_a	mass transfer coefficient on the fibre-side, used in Eqn. (6)
k_m	mass transfer coefficient in the membrane pore, used in Eqn. (10)
k_o	mass transfer coefficient on the shell-side, used in Eqn. (7)
K_{OF}	overall mass transfer coefficient, used in Eqn. (1)
K_{OV}	overall mass transfer coefficient, used in Eqn. (15)
L	length of the tubes
N	number of fibres
C_{NH4f}	ammonium concentration in the aqueous bulk phase
C_{NH4o}	ammonium concentration in the organic bulk phase
C_{NH4fi} (aq)	ammonium concentration in the tank at the initial stage
C_{NH4fo} (aq)	ammonium concentration in the tank at various times
q_f	feed flow rate, used in Eqn. (10)
Q	volumetric flow rate on the shell side
r_i	inner radius of the fibre, used in Eqn. (3)
r_o	outer radius of the fibre, used in Eqn. (6)
R_i	inner radius of the shell, used in Eqn. (8)
t	time
u_f	linear velocity in the fibre-side, used in Eqn. (15)
u_{tube}	velocity in the fibre-side, used in Eqn. (6)
u_{shell}	velocity in the shell side,used in Eqn. (7)
V_{aq}	volume of aqueous solution, used in Eqn. (5)
V_{org}	volume of diluent phase (organic solution), used in Eqn. (5)

Greek Symbols

v	kinematic viscosity, used in Eqn. (4)
ε	porosity, used in Eqn. (10)
τ	tortuosity, used in Eqn. (10)
δ	thickness of the membrane, used in Eqn. (10)
ACI	Aliquat-336 in the organic phase
C	Concentration of the ion (either ammonium ion or chromate ion)

Cl	Chloride ion in the aqueous phase
C_0, C_L	Solute concentration at the initial stage and after extraction
DE	Distribution coefficient or distribution ratio of the solute ion (ammonium or chromate ion) for extraction
V	Volume of the solution

Subscripts

Aq	Aqueous phase
fi(aq)	The aqueous phase initial concentration
fo(aq)	The aqueous phase concentration at various times
NH_4	Ammonium concentration
NH_4A	Concentration of the ammonium ion complex
Org	Organic phase
E	Extraction process

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