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Reactive separation of boron using a liquid membrane of diol in vegetable oil

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Abstract. Boron exists in dilute concentrations in sea water, ground water and waste waters. Reactive liquid extraction can be used for removing boron to make the treated water suitable for drinking and irrigation, with its final concentration less than 0.5 ppm. The results of equilibrium experiments are reported on the removal of boron using 2-butyl-2-ethyl-1, 3-propanediol (BEPD as a nonionic carrier) in sunflower oil, a non-traditional solvent. The results of removal of boron from aqueous solutions in the concentration range 0.5-20 ppm are presented. It is shown that this new liquid membrane system, is able to remove boron from ground waters at their natural pH of 6-8 (without any chemical addition for pH adjustments). The removal efficiency is good when the process is upgraded to a hollow-fibre membrane contactor and approximately 45% boron can be removed in a single-stage contact. There are additional advantages of this new approach that includes reduced operational health and safety and environmental issues. The results reported here provide guidelines to the development of boron removal process using renewable, biodegradable, safe and cheap solvent system such as sunflower oil.

Keywords: boron removal; sunflower oil; organic phase; seawater; hollow-fibre membrane contactor

1. Introduction

Boron is widely distributed in seawater, in rocks and in wastewaters as a form of boric oxide $B(OH)_3$ or borate ion $B(OH)^{-4}$. The boron concentration in seawater is around 4.5 ppm (Nitzan *et al*. 2006) and requires removal in high percentage for its use in agriculture. World Health Organization (WHO) recommends the value of boron concentration in drinking water to be below 0.5 ppm and for irrigation should not exceed 0.2 ppm (Xu and Jiang 2007). Boron has harmful effects on human health depending on the exposure time and frequency (Bryjak, Wolska *et al*. 2008). Consequently, the boron removal is very important to be within the recommended limit. The recovery of boron is expected to create additional sources of this raw material for the production of boric oxide that has use in industry such as: ceramics, glass, enamels, cosmetics, textile, paint wood processing, detergents and insecticides (Xu and Jiang 2007).

In last two decades the reactive extraction systems have received increasing attention for removal of metals from aqueous solutions because of their selectivity, efficiency, compatibility

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with commercially available modules and production of minimal wastes. They are formed by dissolving a carrier in an organic solvent and loading the resulting solution on a polymeric membrane support (Gameiro, Ismael *et al*. 2008, Samaniego, San Roman *et al*. 2007, Carrera, Bringas *et al*. 2009, Bringas, San Roman *et al*. 2006, Ortiz, Bringas *et al*. 2004, Yang, Fane *et al*. 2003). The efficiency of the systems is determined by the ability of the “target” molecules to form complex with the carrier, partition in the solvent phase and the effective diffusivity of the solute-carrier complex in the organic solvent (Yang, Fane *et al*. 2003, Huang, Huang *et al*. 1998, Cerna 1995). A few research groups have been engaged in various stages of development of this technology that includes the determination of thermodynamic and kinetic properties of the systems Gameiro, Ismael *et al*. 2008, Samaniego, San Roman *et al*. 2007, Carrera, Bringas *et al*. 2009, Bringas, San Roman *et al*. 2006, Ortiz, Bringas *et al*. 2004, Klassen and Jansen 2001, Ho and Poddar 2001, Malkoc and Nuhoglu 2006). Despite the increase in number of research in this field, there is lack of published experimental data for the partitioning of model solutes onto potentially useful extraction systems with consideration of environmental impact and occupational health and safety. Recently, a feasibility study is reported (Bachmann, Wiemken *et al*. 2010) on the recovery of metal ions from a simulated effluent using Alamine 336 in refined palm oil. The results are encouraging and applicable to wastewaters at acidic pH. However, most of the wastewaters from various industries and ground waters, especially from the Middle East region (Murad and AlRashdei 2010) exist at near neutral and alkaline pH (6-8 pH range). Therefore, these methods are required to be examined for the removal of ions from these sources, preferably without adjusting their natural pH (i.e., without adding any extra chemicals).

For removal of boron and other metal ions, the methods such as precipitation-coagulation, ion exchange resins, solvent extraction, electrodialysis, reverse osmosis (RO) and hybrid of any of these techniques (Bryjak, Wolska *et al*. 2008, Papp 1994, Simmonot, Castel *et al*. 2008, Jacob 2007, Oren, Linder *et al*. 2006, Polat, Vengosh *et al*. 2004, Badruk, Kabay *et al*. 1999, Kabay, Yilmaz *et al*. 2004, Yilmaz, Kabay *et al*. 2006, Matsumoto, Kondo *et al*. 1999) are available. The processes based on RO have been studied by a number of researchers (Pastor, Ruiz FerrandizL Bartl *et al*. 2001, Cengeloglu, Arslan *et al*. 2008, Rovel 2003, Franks, Bartels *et al*. 2009, Ozturk, Kavak *et al*. 2008, Kalbay, Yilmaz *et al*. 2006). The processes are effective but suffering from the disadvantage of removing the other ions (potassium, calcium and magnesium) in significant proportions. These ions are considered essential for drinking and irrigation waters and are to be added in sufficient amounts at the end of the treatment. The other methods have the disadvantages that include the production of concentrated waste, uneconomic at low effluent concentrations, difficulties in scaling up and not adaptable to continuous processing options (Pasto, ., Ruiz FerrandizL Bartl *et al*. 2001). Liquid-liquid extraction method, especially in combination with membrane separation processes, has shown to be more efficient and economic by overcoming some of the above-mentioned disadvantages (Carrera, Bringas *et al*. 2009, Bringas, San Roman *et al*. 2006, Ortiz, Bringas *et al*. 2004, Yang, Fane *et al*. 2003, Bryjak, Wolska *et al*. 2008, Papp 1994, Simmonot, Castel *et al*. 2008, Jacob 2007, Oren, Linder *et al*. 2006, Polat, Vengosh *et al*. 2004, Badruk, Kabay *et al*. 1999, Kabay, Yilmaz *et al*. 2004, Yilmaz, Kabay *et al*. 2006, Matsumoto, Kondo *et al*. 1999, Criscuoli, Rossi *et al*. 2010, Drioli, Criscuoli *et al*. 2008).

The processes based on liquid-liquid extraction, especially reactive extraction using ionic or non-ionic molecules, have shown some success in selective removal of boron (Kwon *et al*. 2005, Matsumoto, Kondo *et al*. 1997, Criscuoli, Rossi *et al*. 2010, Hosgoren, Tural *et al*. 1997, Karakaplan, Tural *et al*. 2004). In most cases of metal ion removal, the solvent or diluent used were of hydrocarbon-based (e.g., hexane, kerosene, toluene), halogenated organics (chloroform,

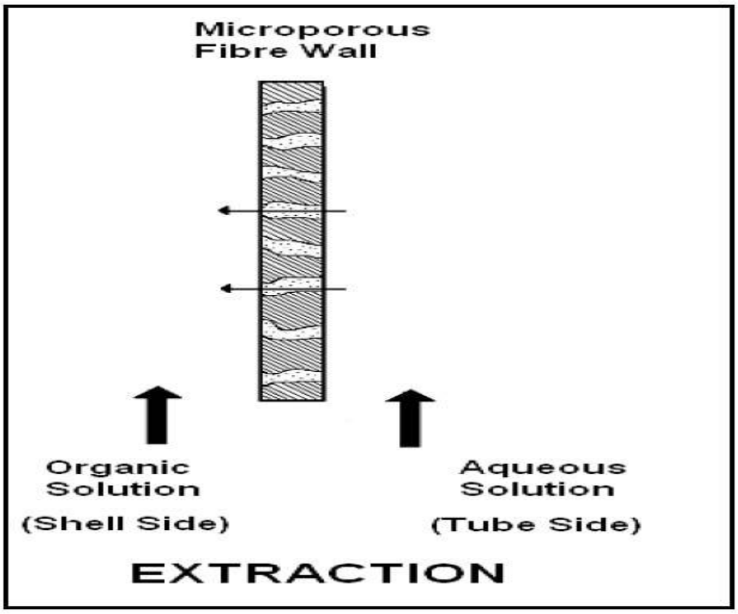

Fig. 1 A schematic of the micro-porous fiber wall

dichloromethane) and alcohols (2-octanol, n-amyl alcohol). Most of 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 in the industrial operations. Therefore, research continues to examine reactive solvent extraction-based membrane processes with environmentally benign solvent systems. This sets the main goal of this report to identify and select such a process with consideration of environmental and operator-friendly characteristics, compatibility to the commercially available equipment and reuse/recycle of the organic phase.

The experimental plan includes the following stages

(a) Evaluate the suitability of sunflower oil (considered as nontoxic, cheap and environmentally benign) as a potential solvent/diluent with/without any any carrier

(b) Determine of partition/distribution constant of boron and the favourable conditions such as pH and the concentration of the carrier in the diluent

(c) Examine the performance of the solvent extraction approach to treat a “real” sample in a commercially available hollow-fiber membrane contactor.

2. Mass transfer of boron

In the derivation of the mathematical model the procedure followed is similar to that presented earlier (Hossain and Dean 2008). In the overall extraction process boron molecules from an aqueous feed side are transported to the organic side through the hollow-fibre wall is shown in Fig. 1. The boron molecules are transported from the bulk feed solution to the feed-membrane interface, reacts to form a boron-diol complex and then transported to the organic side.

Combining the mass transfer processes under steady state condition the mass flux of boron can be obtained as

$$N_{Brf} = K_{of}\left(C_{Brf} - C_{BrO} / D_E\right) \tag{1}$$

where K_{of} is the overall mass transfer coefficient of the process, the concentrations C_{Brf} and C_{BrO} are the concentration of boron in the bulk aqueous phase and in bulk organic phase, respectively and D_E is the apparent distribution constant.

The apparent distribution constant, D_E, is defined as the ratio of the concentration of boron in the organic phase over that in the aqueous phase at equilibrium and can be described by the following expression

$$\mathrm{D_E} = \frac{\mathrm{C_{Br*(org)}}}{\mathrm{C_{Br*(aq)}}} \tag{2}$$

Where * are the concentrations of boron in the organic and aqueous phases, respectively.

In the section below the mathematical model is derived for the mass transfer occurring in a hollow-fibre membrane module. An approximate solution of the model equations is presented to evaluate the overall mass transfer coefficient from a simple analysis of the experimental concentration versus time data in conjunction with the operating conditions (feed flow rate, processing volume and distribution ratio) and the module characteristics (fiber dimensions and volume/area ratio).

2.1 Mathematical model of the process in the contactor

The membrane contactors can be operated in either a once-through mode or a recycling mode. In the recycling mode, the feed and the organic solutions are circulated through the fiber side and shell side of the module, respectively (Fig. 2) and the samples are taken from the feed/organic solution tank. The mathematical model are built by considering the following assumptions:

i. Isothermal process
ii. Feed and extraction solution volumes are large compared to that of the hollow fibre module
iii. Plug flow for the flow in the contactor
iv. The solutions are considered to be at the perfect mixing mode

The mathematical model consists of two main equations describing (i) the change in boron concentration in the contactor and (ii) the change in boron concentration in the feed reservoir. These equations are presented below:

Mass balance in the hollow-fibre contactor

$$\left(\frac{1}{L}\right)\left(\frac{V}{A}\right)_{in}\frac{\partial C_{Brc}}{\partial t} = -\left(\frac{1}{L}\right)u_f\left(\frac{V}{A}\right)_{in}\frac{\partial C_{Brc}}{\partial Z} - K_{of}\left(\frac{1}{L}\right)\left(C_{Brc} - \frac{C_{BrO}}{D_E}\right) \tag{3}$$

Mass balance in the reservoir

$$\frac{dC_{Brt}}{dt} = \frac{q_f}{v}\left(C_{Brc}\Big|_{z=L} - C_{Brc}\Big|_{z=0}\right) \tag{4}$$

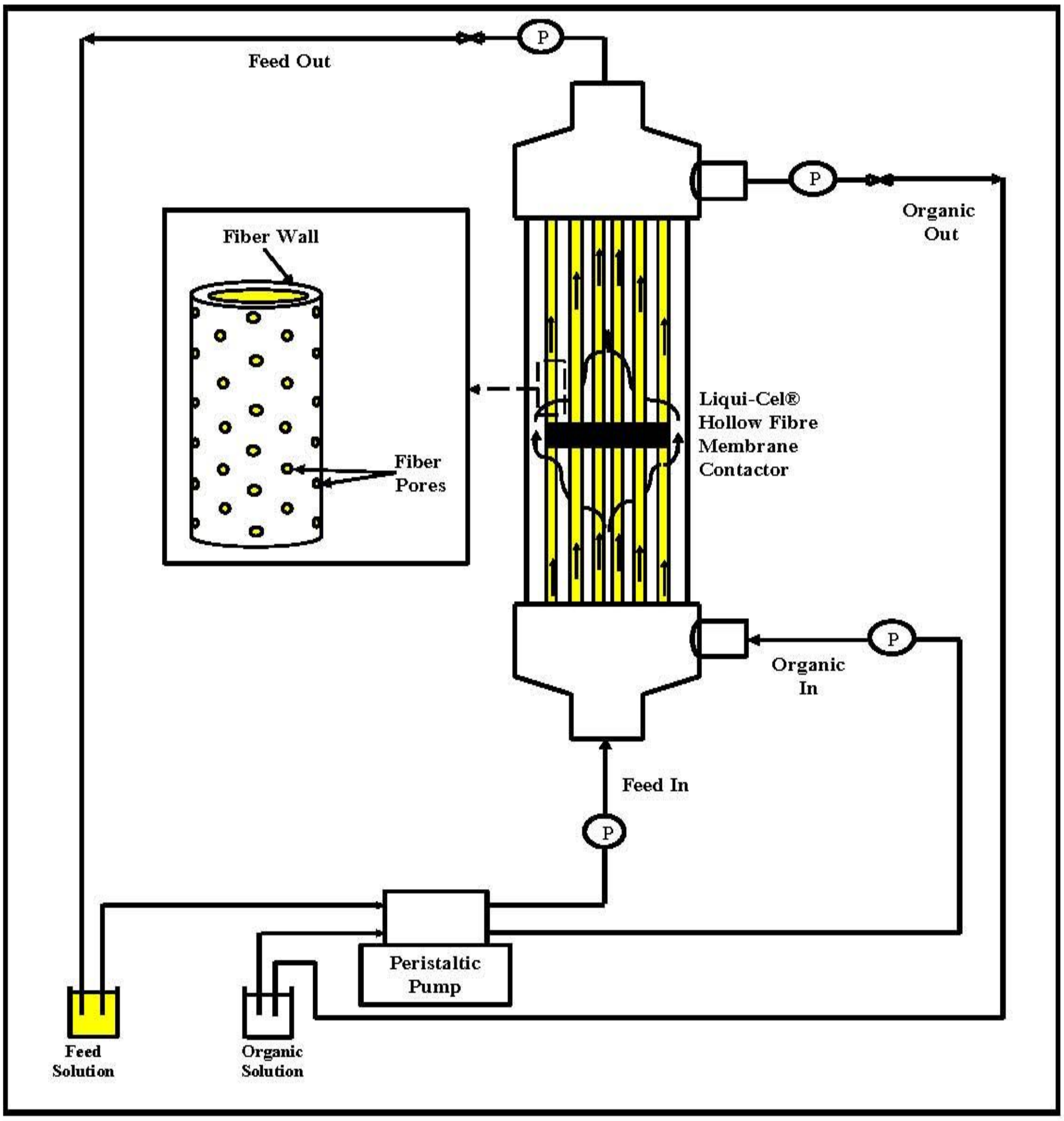

Fig. 2 A schematic diagram of the experimental set-up for the hollow-fiber membrane contactor

where $\left(\frac{V}{A}\right)_{in}$ is the ratio of the volume to inner area of mass transfer in the fibers, L is the length of the fiber, u_f is the linear velocity, q_f is the feed flow rate and v^t is the tank volume. The superscripts m and t refer to the membrane module and tank, respectively.

The factor, $\left(\frac{V}{A}\right)_{in}\frac{1}{L}$, is a small number for this type of contactor, i.e., 4×10^{-4}. Using this and assuming a slow rate of change of concentration in the contactor, Eq. (3) can be simplified and integrated to

$$\mathrm{Ln}\left\{\frac{C_{Bri}}{(1+1/D_E)\,C_{Brt}-\dfrac{C_{Bri}}{D_E}}\right\}=\frac{q}{v}\left\{1-\exp\left(-B\,K_{of}\right)\right\}t \tag{5}$$

where *B* has been defined by the following equation

$$B=\frac{\left(1+\dfrac{1}{D_E}\right)L}{\left(\dfrac{V}{A}\right)_{in}u} \tag{6}$$

An approximate value of the overall mass transfer coefficient (K_{of}) can be determined from the value of the slope of the linear plots of the left hand side (LHS) of Eq. (5) versus t (time). The LHS of Eq. (5) requires (i) the experimental values of the concentrations and (ii) the distribution coefficient of the solute. We also need to calculate B from Eq. (6) which requires the velocity inside the fibre, module characteristics (volume, mass transfer area) and the partition coefficient.

It is noted that the model requires the existence of measurable concentration difference with time of contact, i.e., it is more accurate for the concentration data during the initial stage rather than the time when the process is approaching equilibrium or saturation.

3. Materials and methods

3.1 Chemicals and reagents

Boric acid (99.5-100% pure) and 2-butyl-2-ethyl-1,3-propanediol (BEPD, also known as ‘diol’) (99% pure) and decanol were purchased from Sigma-Aldrich (USA). The “real” sample (the groundwater sample) was supplied by a local company in Al Ain, Abu Dhabi, UAE. Sunflower oil (Noor brand) was purchased from Emirates Refining Co., UAE.

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%) [38]. Sunflower oil brand (Noor brand) used in this investigation has no trans-fatty acid and due to its higher stearic acid contents provide desirable physical and chemical properties for industrial applications. The flash point of this product is in the range 160-170°C and boiling temperature is not applicable (manufacturer’s information).

The experiments in a small pilot-scale membrane module were conducted using the Hoechst Celanese Liqui-Cel hollow-fibre membrane contactor. The contactor had a shell-and-tube configuration with a total of 10,000 microporous polypropylene hollow fibres potted in a polypropylene case of 2.5 cm internal diameter. A schematic diagram of the experimental set-up is shown in Fig. 2. The characteristics of the contactor are listed in Table 1.

3.2 Preparation of solutions

Boron feed solution-the standard solution of boric acid was prepared by dissolving a known amount of this chemical in distilled water. The pH of this feed solution was adjusted (when

Table 1 Hollow-fiber membrane contactor (PCM218)

Fiber Type	Microporous polypropylene hollow fiber
Effective pore size (μm)	0.05
Porosity	40%
Operating Characteristics	
Cartridge length (cm)	16
Shell inner diameter (cm)	6.3
Effective mass transfer area(m^2)	1.4
Effective area/volume (cm^2/cm^3)	29.3
Priming Volumes	
Tube side (cm^3)	145
Shell side (cm^3)	195

required) with the following reagents either by 1M HCl or 0.1M NaOH.

Thermo Orion pH meter (USA) was used for measuring pH. The ICP spectrophotometer was of 710-ES 03 from Varian (Australia) was used for measuring boron concentration. Water bath used was from Grant Industry (Cambridge Ltd, England) and Magnetic Stirrer hotplate was from Stuart Co., England.

3.3 Procedure for equilibrium measurements of solutes at ambient temperature

All the removal and recovery experiments were conducted at room temperature of 25°C. A feed solution containing boron without or with adjusted pH to a desired value was contacted with the organic phase i.e., diol in sunflower oil at a volume ratio of 1:1 in the 25 ml centrifuge tubes. 5% (v/v) decanol was added in the liquid membrane phase to maintain a clear interface after the equilibrium. Aqueous feed concentration was varied in the range: 0.5-20 ppm (except for the groundwater sample which was around 1 ppm) and the organic phase concentrations were varied from 0-10% v/v of BEPD in sunflower oil. 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 boron content. The initial and final pHs of the aqueous phase were also measured.

3.4 Procedure for mass transfer experiments in the hollow-fibre contactor

In these experiments the aqueous feed solution was passed through the tube side and the organic phase containing the carrier was passed through the shell side of the membrane using peristaltic pumps controlled by a variable speed drive unit. The operation mode was concurrent. A positive pressure difference of 20-25 KPa was maintained on the aqueous side of the membrane to prevent the displacement of organic phase into the aqueous side. Experiments were carried out by recycling the feed and solvent solutions. Prior to the extraction experiment, the organic phase was pumped at a slow rate (10 ml/min) on the shell side for 2-3 hours to allow full saturation of pores in the module. Upon the end of organic loading, deionised water was passed through the aqueous side to rinse out any organic phase that may have leaked through to the tube side, and to achieve a steady flow. The deionised water was replaced by the feed containing boron at the desired concentration. The flow rates of the aqueous and organic phase were at 50±10 ml/min. A schematic diagram is shown in Fig. 2 that represents the flow around a microporous hollow-fibre, where boron molecules from the flowing aqueous side are extracted in the pores filled with the organic phase and transported to the bulk organic phase. Aqueous samples (of 3 ml) were taken periodically from the reservoir and the concentration was measured by atomic absorption spectrophotometer. At the end of run the samples were checked for any leakage, very small drops of oil was observed floating in the aqueous phase (aprrox. 0.1%). The mass transfer experiment was not conducted for a long time as the initial boron concentration in the sample considered was low around 1 ppm and only the initial stage data are required for the determination of mass transfer. Duplicate experiments show similar performance of the liquid membrane system.

3.5 Analytical procedure for boron 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×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 Eq. (2).

3.6 The percentage of removal or extraction

The percentage removal or extraction is related to the distribution constant that can be determined at various experimental conditions. A large value of DE suggests good extraction. The removal (or extraction) percentage is calculated, *E* (%), from the following expression [34, 36]

$$\mathrm{E\ (\%)} = \frac{\mathrm{DE\ x\,100}}{(1+\mathrm{DE})} \tag{7}$$

4. Results and discussion

The results for removal (or extraction) experiments are presented as the distribution coefficient (D_E) and percentage extracted or removed *E* (%), as a function of

- The organic phase composition at various boron concentrations
- The aqueous feed (containing boron) solution pH
- Concentration of other components (i.e., metal ions) in the groundwater sample.

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

4.1 Sunflower oil as solvent for extractions

Sunflower oil performed well at the natural pH of 6.8 for all boron concentrations (deionised water with no additional chemicals were added). The experimental results are shown in Table 2. Without the addition of the carrier (BEPD) the distribution coefficient was in the range 1.9-2.2 for

Table 2 Values of distribution coefficient using only sunflower oil*

Diol % (v/v)	Boron conc (ppm)		%E	DE
	Initial	Final		
0.0	1.0	0.3403	67.3	2.06
2.5	1.0	0.1503	85.5	5.92
5	1.0	0.041	96.1	24.4
0.0	10.0	3.742	66.7	1.92
2.5	10.0	1.646	83.5	2.99
5.0	10.0	1.51	84.9	5.63
10.0	10.0	0.833	91.7	8.36
0.0	20.0	6.238	68.8	2.21
2.5	20.0	2.582	87.1	6.75
5.0	20.0	1.998	90.0	9.07
10.0	20.0	1.120	89.3	16.86

*the contact time for all equilibrium experiments were 2 hr

all the feed concentrations considered. This gives a good extraction percentage of 66-69%. With the addition of the carrier in sunflower oil the values of the distribution coefficient increased greatly with the concentration of carrier for all boron concentrations. The extraction percentage was higher (ca. 96%) at lower boron concentration with 5% diol in sunflower oil. The extraction percentage decreased with the boron concentration and attained 89% at boron concentration of 20 ppm with 10% diol in sunflower oil. These results can be used to propose a possible mechanism for extraction of boron. The components of sunflower oil may undergo a reaction with boron forming a compound that is more soluble in the oil phase and thus being able to extract boron to a moderate value. With the addition of BEPD in the oil phase those reactions must have been enhanced providing higher extraction of boron. Further studies are required, especially with a neutral solvent like butyl acetate to determine the details of the mechanism (Matsumoto, Kondo *et al*. 1997) and then compare the applicability in the case of vegetable oil. With the given sunflower composition it cannot be considered inert and the mechanism proposed for inert solvent need to be examined step by step. The purpose in this report is to show the effectiveness of a commercially available sustainable solvent, compared to those toxic ones that have been studied in the literature.

This results reported here are comparable to those obtained by previous researchers using toxic solvents like chloroform, toluene, chlorobenzene (Karakaplan, Tural *et al*. 2004) and kerosene (Hossain and Dean 2008). These results were obtained with sunflower oil (a renewable source and environmentally benign solvent) at normal room temperature and pressure and without change in feed pH (i.e., no addition of chemicals to adjust pH). Hence it can be suggested that this solvent system has the potential to replace other solvents like kerosene and toluene for removal of boron. In addition the cost of this new solvent system is expected to be much lower compared to the solvents mentioned above that are considered toxic and corrosive with added environmental issues. The other factors to be considered are: sunflower oil is a non-volatile substance, does not contribute to the emission of volatile organic compounds. This particular brand of sunflower oil does not have any trans-fatty acid, low in saturated fatty acid and therefore is resistant to oxidation. Hydrolysis of sunflower oil is not expected because of the fact that there is no use of

Table 3 Effect of feed solution pH (removal with pure sunflower oil)*

pH	Boron conc (ppm)		%E	DE
	Initial	Final		
6.8	4.707	1.622	65.5	1.9
9	4.707	1.762	62.5	1.67
11	4.707	1.854	60.6	1.54

*the contact time for all equilibrium experiments were 2 hr

Table 4 Effect of feed solution pH (5% diol in sunflower oil)**

pH	Boron conc (ppm)		%E	DE
	Initial	Final		
6.8	4.707	0.695	85.2	5.77
9	4.707	0.668	85.8	6.05
11	4.707	0.746	84.2	5.31
9*	4.707	0.904	80.8	4.21
11*	4.707	1.032	78.1	3.56

*5% diol + 5% decanol + 90% sunflower oil
**the contact time for all equilibrium experiments were 2 hr

acid or alkali (which can act as catalyst) or enzyme catalyst, no high pressure and high temperature.

The stability of this new organic phase with sunflower oil is also required to be examined in long-term experiments by varying pH. This phase is expected to undergo minimum alcoholysis, as the organic system does not require any addition of other chemical and higher temperatures. Therefore it is expected that the sunflower-based extraction phase could retain its stable performance in the long-term processing of aqueous boron containing wastewaters.

4.2 Effect of aqueous phase pH

The values of the distribution coefficient and percentage extraction at three pHs (from neutral to the alkaline range) is listed in Table 3 (with sunflower only) and Table 4 (BEPD and decanol in sunflower oil), for removals at feed concentration of approx. 5 ppm. There seems to be some decrease in percentage removal as the pH is increased for both the systems without or with BEPD. It is worthwhile to discuss that boron exists in the molecular form for pH less than 8, a mixture of ionic and neutral forms in the pH range 8-10 and at pH higher than 10 the ionic form dominates (Mnif *et al*. 2009). These various forms might have influenced the reaction involved with the components of sunflower oil and BPED. The dissociated form of boron might have not been available for the reactions with the components of sunflower oil and with BPED (being non-ionic), resulting decreased removal at higher pH. This trend was observed in both the cases at higher pH of 11 with the organic phase containing diol performing better at all pHs. That means that the process can be applied with aqueous feed in this range of pH (6.8-11) which is the natural pH of many wastewater and surface water systems. Addition of other pure solvent such as decanol (as used by many investigators as phase modifier) was tried but it did not enhance the extraction percentage (last two rows in Table 4).

Table 5 Composition of the sample from a local groundwater source in Al Ain, UAE

Components of the industrial sample	Initial concentration (ppm) of various components	Final concentration (ppm) of various components
Calcium (Ca)	50.9	55.2
Potassium (K)	39.8	36.0
Magnesium (Mg)	45.1	50.8
Sodium (Na)	223.7	220.0
Strontium (Sr)	13.9	12.7
Chromium (Cr)	0.81	0.61
Boron (B)	1.57	0.87

Table 6 Removal (%) of boron from the groundwater sample (boron concentration approx. 1 ppm) with and without BEDP in sunflower oil

Organic phase	B concentration (ppm)		%E
	Initial	Final	
5% (v/v) diol, 5% (v/v) decanol and 90% (v/v) sunflower oil	1.57	0.87	44.6
100% sunflower oil	0.91	0.84	7.7

4.3 Removal of boron from groundwater using a hollow-fiber membrane contactor

In the real examples, it is common to find other metal ions such as Na^+, K^+, Ca^{2+}, Mg^{2+} and Sr^{2+} being present in groundwater sources, domestic and industrial effluents. The experiments in this section were purely designed to investigate the organic carrier's affinity for boron in presence of other metal ions (i.e., metal salts) during the extraction or removal process. The composition of a groundwater sample (at a pH 7.2) obtained from a local distribution company is presented in Table 5. The initial concentration of boron varied from sample to sample and they were used as supplied. The feed concentration of boron was low (900.9 ppb and 1570 ppb at pH 7.2). Two experiments with sample sizes of 1 litre were conducted: (i) without BEPD in sunflower oil (for feed with 900.9 ppb boron) and with BEPD in sunflower oil (for feed with 1570 ppb). The removal of boron with sunflower only (without diol) was small (ca. about 8%). It is observed that all other ions were removed in minute proportions with the organic system of BEPD-sunflower oil (Table 6). The extraction percentage of boron was about 45% boron removal (within 10 minutes of treatment in a single pass) with a final boron concentration of 855 ppb (0.85 ppm). The concentration seem to decrease after this time and this percentage could have increased. Within this time the feed solution has been circulated 7 residence times (the tube side volume is 145 ml) and further data was not taken. With multi-staging of the contact more removal of boron is expected. At this stage this result is encouraging as the sample conditions (pH, temperature and ionic composition) were not adjusted and the other ions of the groundwater sample were not removed significantly (Table 5).

This process is also expected to reduce the cost of overall treatment process as the reactive separation step is selective and retains the nutrient ions instead of removing them (as in RO process). More work is required to optimise the conditions (the effect of flow rate and the

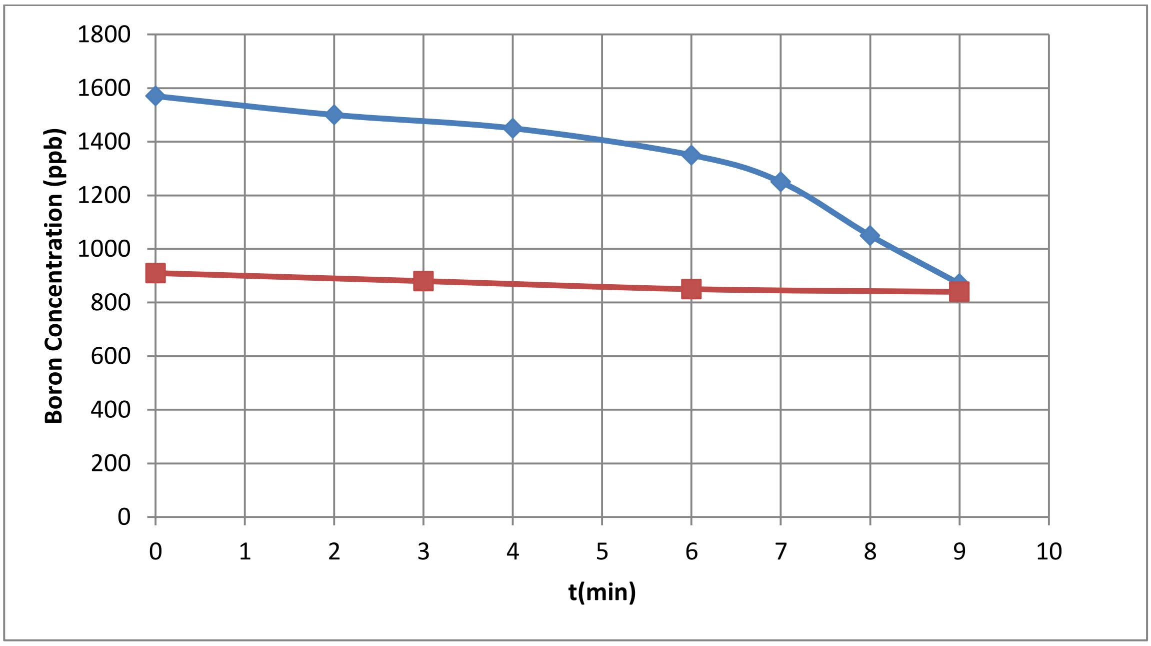

Fig. 3 Boron concentration (in ppb) versus time (mins). The data points in red were for sunflower oil only and data points in blue were obtained using 5 % BEDP (v/v), 5% (v/v) decanol and 90% (v/v) in sunflower oil

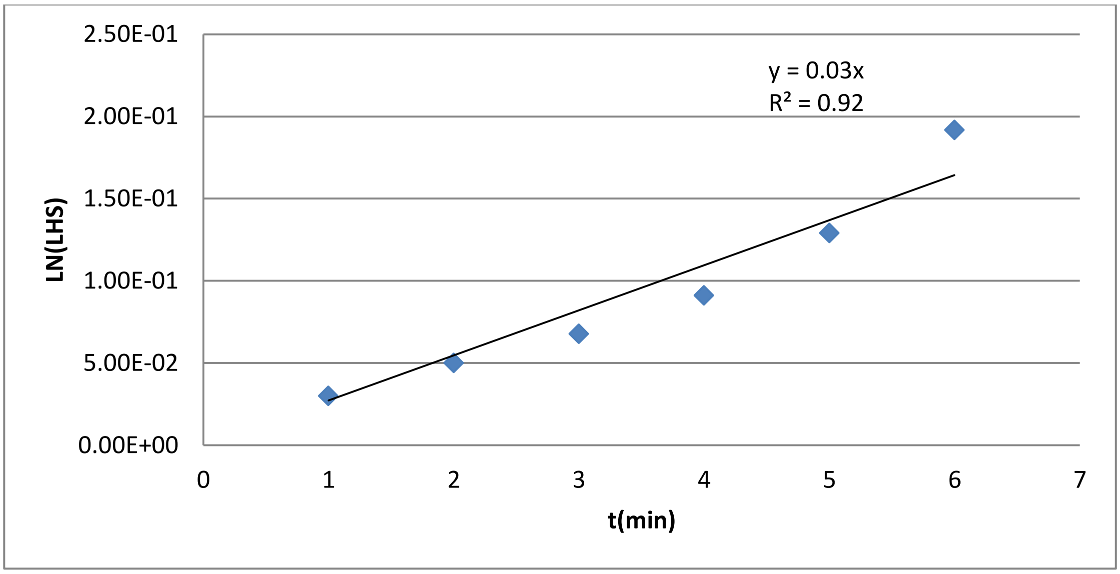

Fig. 4 LHS of Eqn (5) using boron concentration in Fig. 3 versus time. Only the concentration data using 5 % (v/v) BEDP, 5 % (v/v) decanol and 90% (v/v) in sunflower oil were used

composition of the organic phase) of extraction and possible scale-up of the process. This new removal process when optimized will allow the treated water to be recycled and reused in the processes where they are generated or sourced. In addition boron recovered from the organic will generate addition sources for industrial use.

4.4 Overall mass transfer coefficient

The overall transfer coefficient (K_{of}) was calculated from the slope of the plot of the left-hand side (LHS) of Eq. (5) versus time using the experimental data of boron with BPED in the liquid membrane (shown in Fig. 3). A plot of the LHS of Eq. (5) using the concentration of boron at various time and the apparent distribution coefficient is shown in Fig. 4. The concentration data of the experiment conducted with the hollow-fibre contactor over the period of 6-7 minutes were analysed and these data give a good correlation. This is in consistent with the model solution which is more accurate during the initial stage and not for the time when equilibrium or near equilibrium is reached. From the slope of the plot and using the value of B in Eq. (6), the overall mass transfer coefficient for the extraction has been calculated. The overall mass transfer coefficient is ca. 1.66×10^{-5} cm/s for processing a volume of 1000 ml at a flow rate of 100 ml/min and this is comparable to values in the literature.

5. Conclusions

Experimental results are reported for the removal of boron using 2-butyl-2-ethyl-1, 3 propanediol (BEPD, a neutral carrier) in sunflower oil (a non-traditional and non-toxic solvent). The main concluding remarks are:

(i) The values of the partition coefficient (DE) for diol-sunflower oil are very good. The conditions for the highest value of DE and removal percentage were: 5%-10% (v/v) diol in sunflower oil, for 0.5-20 ppm of boron at the natural pH 6.8.

(ii) The values of DE are significantly affected by the feed solution pH and the composition of the organic phase (diol concentration in sunflower oil).

(iii) The performance was very good for removal at the natural pH of boron solution, approx. 45% removal was achieved in a single-stage operation within 10 minutes when the process is upgraded to a pilot-scale hollow-fibre membrane module,.

(iv) An overall mass transfer coefficient of 1.66×10^{-5} cm/s was determined from experimental data of concentration at various time.

(v) The performance of the BEPD - sunflower oil system is better than sunflower oil alone. The new solvent-carrier system (sunflower-based) have several merits including less toxicity, less corrosiveness, low environmental, health and safety issues and it is compatible with the large-scale membrane contactors

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Notations

A	surface area (m^2)
B	defined in Equation (6)
BEPD	2-Butyl-2-Ethyl-1,3-Propanediol
B(OH)3	boric acid
B(OH)4-	borate ion
C	concentration of boron (mg/L)
Ca+2	calcium cation
Cl-	chloride ion
di, do	inner diameter, outer diameter of a hollow fiber (cm)
D_E	distribution coefficient of boron defined in Eq. (2)
E (%)	percentage extraction of boron, defined in Eq. (7)

K_{of}	mass transfer coefficient in Equation (1), (cm/sec)
L	length of the fiber (cm)
Mg+2	magnesium cation
N	steady state flux, defined in Eqn. (1)
Na+	sodium cation
n_f	number of fibers
t	time (s)
ppb	parts per billion
ppm	parts per million
q	flow rate, L/s
RO	reverse osmosis
u	linear velocity in the hollow fibers (cm/s)
V	volume (L)
WHO	World Health Organization
Z	axial distance in the module (cm)

Subscripts

aq	aqueous phase
Brc	aqueous phase in the hollow-fibre contactor
Bri	liquid phase in the hollow-fibre contactor at the initial time
BrO	Organic phase in the hollow-fibre contactor
Brt	liquid phase in the tank (reservoir)
f	feed phase
i	initial condition
o, org	bulk organic phase