Treatment of ground waters in a hollow-fibre liquid membrane contactor for removal of ions

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Abstract.   Metal ions exist in seawater, groundwater and industrial wastewaters. These source waters can be recycled if their concentrations are reduced. A number of processes can be applied for this purpose. Liquid-liquid extraction is one of the promising methods. In this paper, experimental results are presented on the removal of Cr(VI) using Aliquat-336, a reactive carrier, in sunflower oil (a non-toxic solvent). The performance of this new system is compared with those of kerosene (a toxic solvent). The extent of removal of Cr(VI) from samples with high and low concentrations are presented. The process was upgraded to a bench-scale module that can selectively remove about 50-90% Cr(VI) from samples of groundwater. Thus this process can produce water within the acceptable range for recycling and for use in secondary purposes such as irrigation.

Keywords: ground waters; liquid membrane contactor; removal; chromium; sunflower oil; solvent

1. Introduction

A significant proportion of metal ions such as chromium is released to the environment through the effluents from tannery, electroplating and chemical treatment processes (Papp 1994, Bartlett 1998). As a result, the ground water sources may also contain chromium and other heavy metals. In order to reuse and recycle these waters complete or partial removal of these ions is necessary. This may also lead to the sustainable development and create additional sources of the depleting resources (Papp 1994, Bartlett 1998).

The methods such as precipitation (Kongsricharoern 1995), ion exchange (Cavaco 2007), adsorption (Huang 1977) and reverse osmosis (Frenzel 2006) to treat such effluents are available. 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 application at industrial-scale (Melita 2008, Cerna 1995, Rao 1980, Alonso 1997, Ho 2001).

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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 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 (Samaniego 2006, Bringas 2006, Gameiro 2008, Samaniego 2007, Carrera 2009). The efficiency of the systems is determined by the distribution coefficient of the "target" molecules in the solvent and its effective diffusivity (Bringas 2006, Oritz 2004, Yang 2003, Klassen 2001). A number of research groups have been engaged in various stages of development including the determination of equilibrium partition constant and extraction/stripping efficiency (Alonso 1996, Logsdail 1993, Molinari 1989, Huang 1998, Malkoc 2006). The processes based on liquid-liquid extraction, especially reactive extraction using ionic molecules, such as Aliquat-336 (a quaternary methyl ammonium salt) as selective carrier in the organic phase, have been being actively considered as the potential candidate. In most studies the solvent or diluent used were of hydrocarbon-based (e.g., hexane, kerosene), 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. More details of the organic system, their structure, performances are available in a recent literature (Bachmann 2010).

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, occupational health and safety and renewable sources. Recently, a renewable energy powered systems has been reported to remove inorganic contaminant from groundwaters (Richards 2011). Another feasibility study is reported (Bachmann 2010) on the recovery of hexavalent chromium from a simulated effluent using Alamine 336 in refined palm oil. The results are encouraging and applicable to wastewaters at acidic pH. Most of the wastewaters from various industries and ground waters, especially from the Middle East region (Murad 2010) exist at near neutral and alkaline pH (6–8 pH range). Therefore the above methods are to be examined at higher pH for the removal of chromium from these sources, preferably without adjusting their natural pH.

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 investigate the removal of *Cr*(VI) from aqueous solutions using the reactive system of Aliquat 336 in the diluents: sunflower oil (non-toxic) and kerosene (toxic). The plan includes the following stages:

(a) Determine the partition/distribution coefficient of *Cr*(VI) in these solvents and identify the favorable conditions for chromium removal.

(b) Evaluate the performance in a bench-scale membrane contactor using "real" feed samples such as groundwater samples.

The solvent kerosene is included mainly because most of the previous studies in the literature used this as the organic phase although it has shown some incompatibility with the industrial-scale membrane modules. Our main aim is to show effectiveness of sunflower oil which is less toxic and corrosive, more user-friendly and can remove *Cr*(VI) to the similar degree as the kerosene. The systems are applied for the treatment of polluted samples of groundwaters.
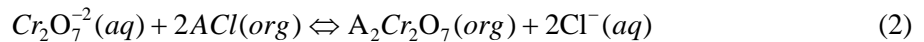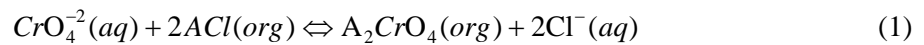
2. Materials and methods

Aliquat 336 (tricaprylylmethylammonium chloride, CH_3N $((CH_2)_7CH_3)_3Cl$) and hexan-1-ol ($CH_3(CH_2)_4CHOH$) were obtained from Aldrich, New Jersey, USA. Solvents: kerosene and lubricating oil (Emarate engine oil, brand: Motor oil 400) were purchased from ADNOC, Abu Dhabi and sunflower oil (Noor brand) from Emirates Refining Co., UAE. The industrial sample was supplied by a local company in Abu Dhabi, UAE. 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 pH was measured using a pH meter (Thermo Orion pH meter, USA) calibrated at pH 4 and 10. The metal concentrations were determined by ICP spectrophotometer (Varian 710-ES 03, Australia). The effect of temperature was examined using a water bath (Grant Industry, Cambridge Ltd, England) and a magnetic stirrer hotplate (Stuart Co., England).

2.1 Procedure for equilibrium measurements of solutes

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 experiments were conducted at room temperature of 25°C except for those specifically conducted to study the effect of the operating temperature. A feed solution containing Cr(VI) was 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 solution in the tubes was mixed for a period of 2 hours using magnetic stirrer. After mixing the solutions were allowed to settle for 1 hour to separate the two phases and obtain a clear bottom aqueous phase. The bottom aqueous layer was removed using a Pasteur pipette and analyzed for its chromium (VI) content.

2.2 Reactive solvent extraction

T The chemical equilibrium between the chromate ion and the carrier can be described by the following equations (Cerna 1995, Melita 2008).

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

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

where ACl represents the carrier Aliquat 336, $A_2Cr_2O_7$ and A_2CrO_4 represent the complexes with dichromate and chromate ions , respectively. It is noted that at higher pH (more than pH 6) the dominating ion is the chromate ion, not the dichromate ion (Brito 1997).

The apparent distribution coefficient for extraction, *DE*, is defined as the ratio of the concentration of Cr(VI) in the organic phase over that in the aqueous phase at equilibrium

$$DE = \frac{C_{ECr*(org)}}{C_{ECr*(aq)}} \tag{3}$$

where $C_{ECr\,(org)}$ and $C_{ECr\,(aq)}$ represent the concentrations of Cr(VI) in the organic and aqueous

phases, respectively, and * denotes the values at equilibrium.

All the concentrations in the above equations can be measured and the distribution coefficient can be determined. A large value of *DE* suggests good extraction or removal. The equilibrium constant, *KE*, is calculated from the following expression

$$KE = \frac{C^2_{Cl\,(aq)}\, C_{ECr^*(org)}}{C^2_{ACl\,(org)}\, C_{Ecr^*(aq)}} \qquad (4)$$

where C_{Cl} and C_{ACl} represents the concentrations of chloride ion and Aliquat 336 in the aqueous and organic phases, respectively.

2.3 Mass transfer experiments in the membrane contactor

These experiments were carried out by circulating the feed and the organic phase solutions through the fibre side and shell side, respectively. A schematic diagram of the experimental set-up is presented in Fig. 1. Before loading the organic phase both the fibre side and shell side were washed with distilled water for about 60 min to remove any solvent (e.g., ethanol) which is normally used during the storage of the module. Then the organic solution was circulated at a slow flow rate of 10 ml/min through the shell side for about 120 min to impregnate the micropores with this phase. The feed solution was then pumped through the fibre side. A small pressure of 0.1–0.2 bar was applied from the aqueous side to stabilize the organic phase in to the pores. When a stable flow was reached on both the sides, the initial time of the experiment was set and then samples of the feed solutions were taken periodically. The percentage of *Cr*(VI) removed or extracted was determined from the measured values of the *Cr*(VI) feed concentrations.

2.4 Procedure for Cr(VI) concentration 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 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 removal percentage, *E*(%), was calculated from the following equation

$$\%E = \left(1 - \frac{C_{fo(aq)}}{C_{fi(aq)}}\right) x100 \qquad (5)$$

where C_{fo} (*aq*) and C_{fi} (*aq*) are the concentrations of *Cr*(VI) at the exit of the module and at initial feed solutions, respectively.

3. Results and discussion

The results for extraction are presented as percentage extracted or removed *E*(%), and as the distribution coefficient (*DE*) under varying conditions of
- Feed solution pH
- Type and composition of the organic phase

- Concentration and temperature of the feed solution and
- Feed composition with 'real" groundwater sample.

All the extraction experiments were repeated and the results are within 7% of error.

3.1 Effect of feed pH on extraction in various solvents

The effect of pH on the extraction of chromium (VI) using 5% Aliquat-336 and 10% 1-hexanol in sunflower oil and kerosene are presented in Figs. 2 and 3, respectively. It can be seen from these figures that the trends are similar both for the distribution coefficient and extraction percentage. With the increase in feed pH from 6 to 12 the values of DE decreased, the largest drop was observed when the pH increased from 6 to 7 and after that the decrease of DE was gradual. This could be due to the change in the ionic form of Cr(VI) (converting from $Cr_2O_7^{-2}$ to CrO_4^{-2}) with decreasing proportion of the former ion (Brito 1997) and the reactive extraction being dominated by the former ionic form. This sharp reduction of available dichromate ion concentration might have produced smaller concentration of chromate-carrier complexes at pH greater than 6 and
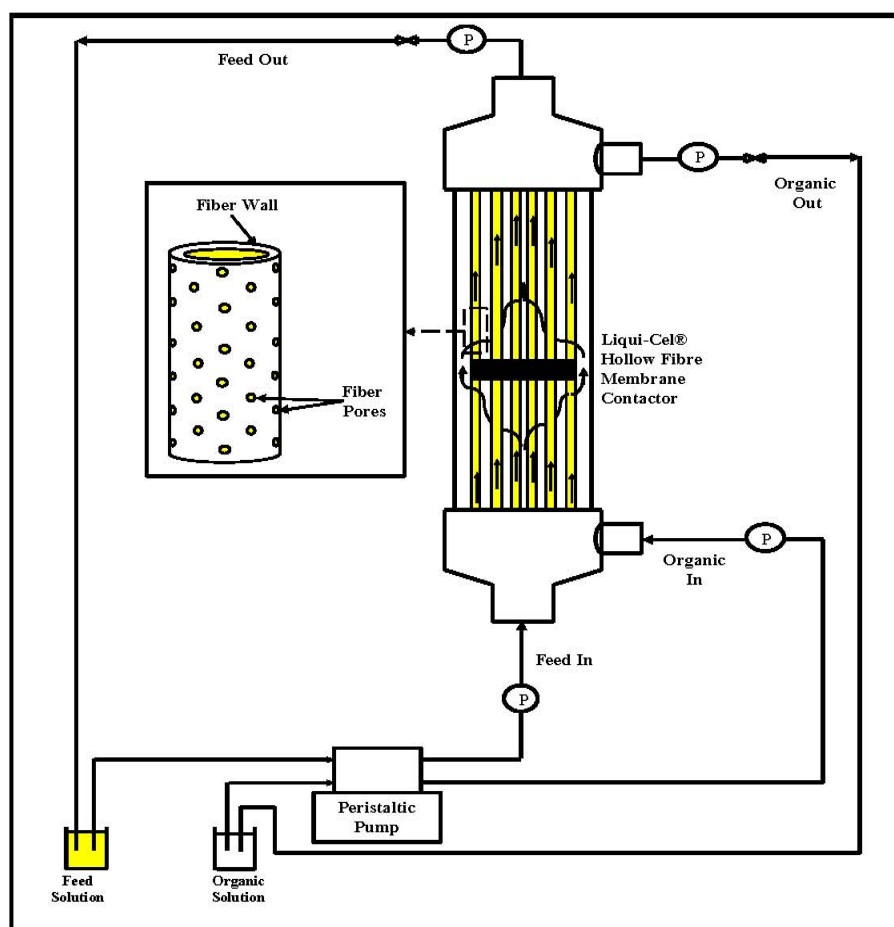

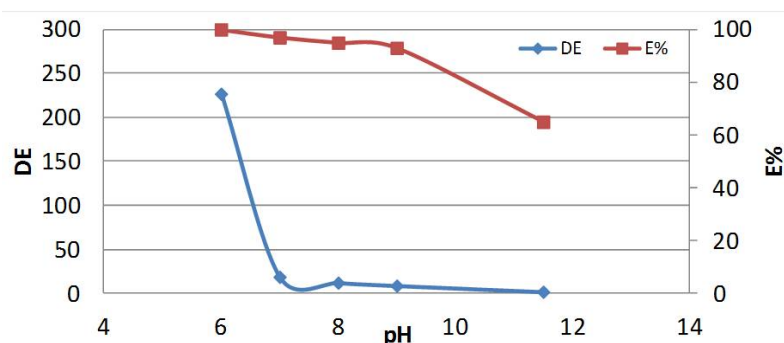Fig. 1 A schematic diagram of the hollow-fibre module experimental set-up

Fig. 2 Effect of pH on *DE*(-) and *E*(%) of *Cr*(VI) at 400 mg/L using fresh sunflower oil, organic phase: 5% Aliquat 336, 10% n-hexanol and 85% diluent (sunflower oil)
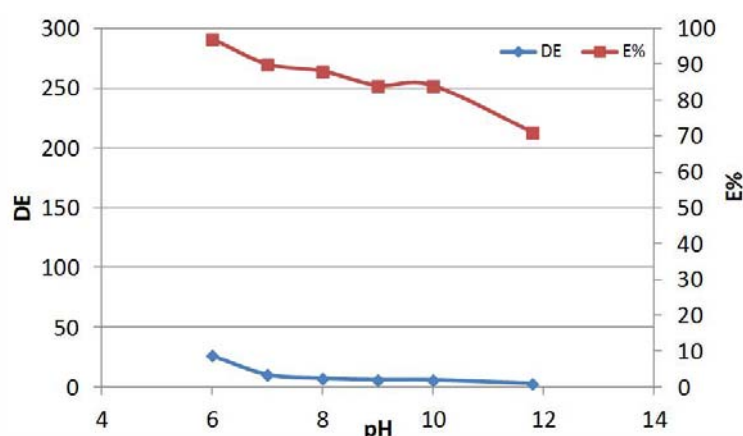

Fig. 3 Effect of pH on *DE*(-) and *E*(%) of *Cr*(VI) at 400 mg/L using the organic phase: 5% Aliquat 336, 10% n-hexanol and 85% diluent (kerosene)

resulted in lower values of *DE*. However, a good removal (75–90%) was still possible in the pH range 7–9 which is the natural pH of many industrial effluents and groundwaters.

It is evident that sunflower oil, with all the benefits of health and safety and being environmentally benign, has the potential to replace kerosene as a renewable and sustainable solvent. It is noted that kerosene has been used commercially in the treatment of wastewaters from environmental polluting sources (Alonso 1997, Ho 2001, Alonso 2007). It has been effective as an extracting solvent but it is toxic, environmentally harmful, and unpleasant to the operators. It has also been found to be incompatible with many industrial membrane separation modules, caused swelling of the polymeric membranes and created difficulties during long-term operation.

3.2 Effect of the diluent type (sunflower oil and kerosene)

The comparative results for removal of *Cr*(VI) with three diluent systems are presented in Fig. 4. The difference in removal percentages is small in the pH range 6–7; this becomes greater with the increase of feed solution pH. Beyond feed pH 8, the performance of sunflower oil decreases
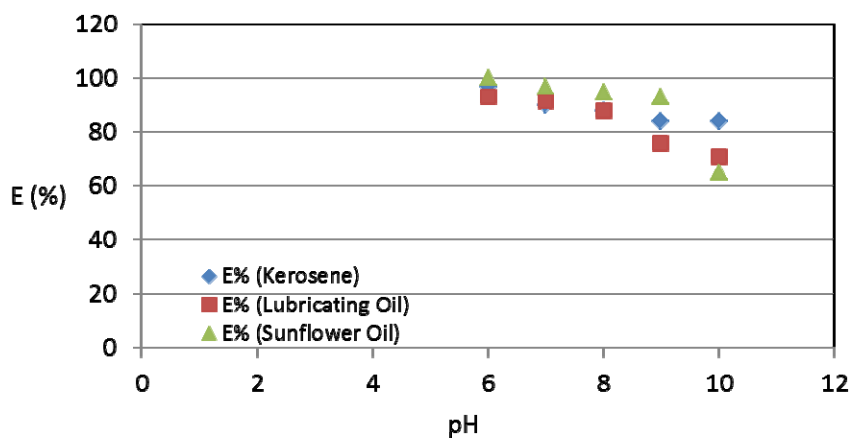
Fig. 4 Effect of solvent type on extraction of *Cr*(VI) at pH 7, organic phase: 5% Aliquat 336, 10% *n*-hexanol and 85% diluent (sunflower oil)

Table 1 Effect of Aliquat 336 in sunflower oil for removal at feed pH 7

| 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

Table 2 Values of the equilibrium extraction constant

Aliquat 336% (v/v)	Initial concentration of Cr(VI) in (mg/L)	$KE \times 10^3$	Solution pH
10	150	0.8[a]	Not mentioned
10	100	0.7[a]	Not mentioned
10	50	0.15[a]	Not mentioned
10	400	0.6[b]	7
5	400	0.4[b]	7
2.5	400	0.4[b]	7
2.5	325	0.3[b]	7
2.5	215	0.15[b]	7
2.5	110	0.13[b]	7
2.5	75	0.11[b]	7

[a]Alonso and Ortiz (1996)
[b]This research for extraction with sunflower oil

slightly but it has the added advantage of being the least expensive, less toxic, operator friendly and compatible with membrane contactors.

The effect of Aliquat 336 concentration in sunflower oil for extraction from 400 mg/L *Cr*(VI) feed is shown in Table 1. Both *DE* (the range 1–27) and %E (50%–96%) are significantly affected by the concentration of Aliquat 336. the higher concentration gave the better performance.

The values of the extraction reaction coefficient, *KE*, were calculated and these are compared in Table 2 with those available in the literature using kerosene-based organic phase. Comparable values were obtained with this new system of sunflower over a wide range of the concentrations of *Cr*(VI) and Aliquat 336. This system can be recommended as a potential candidate for further development. The other factors in favour are: sunflower oil is a food grade substance can be obtained from renewable sources, 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 minor leakage to the feed side can be acceptable.

3.3 Effect of initial Cr(VI) concentration

3.3.1 High concentration of Cr(VI)

Based on the above findings, i.e., smaller *Cr*(VI) concentration would require less amounts of Aliquat-336, an organic phase containing 5% Aliquat-336, 10% 1-hexanol and 85% fresh sunflower oil was used to study the effect of *Cr*(VI) concentration from a low (10 mg/L) to high value of 500 mg/L. The experimental results are presented in Fig. 5. It is clearly observed that both *DE* and *E*% decrease with the increase in the initial feed concentration. At lower feed concentration of 25 mg/L, the value of the distribution coefficient still attained more than 100 and %*E* is approx. 99%. Within the feed *Cr*(VI) concentration 10–100 mg/L, the values of *DE* decreased and was in the range 100–40. The extraction percentage, *E*(%), decreased slightly to 92%. Beyond this feed concentration, both the distribution coefficient and the E% decreased considerably. At very high concentrations (approx. about 500 mg/L), the distribution coefficient is less than 10 with *E*% being approx. 85%. These observations suggest that the removal process at
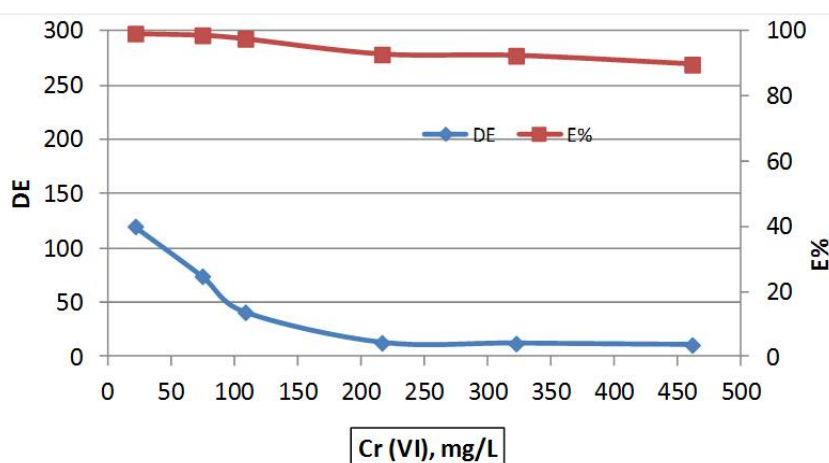

Fig. 5 Effect of initial *Cr*(VI) concentration on *DE*(-) and *E*(%) using sunflower oil as diluent, organic phase: 5% Aliquat 336, 10% n-hexanol and 85% diluent (sunflower oil)

higher initial *Cr*(VI) concentrations may require longer contact time, multiple stages of contact and may demand higher Aliquat 336 concentration.

3.3.2 Low concentration of Cr(VI)

The effect of dilute feed concentrations (range 0.1–1 mg/L) at pH 7 are presented in Table 3 using an organic phase containing 1% Aliquat-336, 10% 1-hexanol and 89% fresh sunflower oil. Because the initial concentration of *Cr*(VI) was very low (compared to those presented in previous sections), a small amount of Aliquat 336 was used. It is clearly observed that the system is able to remove *Cr*(VI) at low feed concentrations. The performance was best at *Cr*(VI) concentration around 0.5 mg/L, the values of *DE* and *E*% were 4.5 and 82%, respectively. These values were low at concentrations higher than o.5 mg/L and decreased slightly with the decrease in the initial feed concentration.

3.4 Effect of temperature

The effect of temperature in the range 25–46°C on extraction at feed pH 7 was examined using 5% v/v Aliquat 336 in fresh sunflower oil. This was investigated because many industrial samples exist or are produced at temperatures higher than the normal temperatures. The results for feed concentration of approximately 100 mg/L show that the effect is minimal. Even at 39°C high values of *DE* (more than 100) and %*E* (approx. 99%) were obtained (results not shown).

3.5 Removal of Cr(VI) from groundwater sample in the hollow-fibre contactor

The removal of *Cr*(VI) from a local ground water source was examined in the hollow-fibre membrane contactor. The existing concentration of *Cr*(VI) was low at 0.18 mg/L and at a feed pH of 6.3 (Table 4). The sample contained a lot of other ions and 2 % (higher than that for equilibrium study) of Aliquat 336 was added to the organic phase. The results, i.e. the ions removed after 90 mins of treatment in the liquid membrane contactor are shown in the last row of Table 4. It is observed that other ions are also removed when *Cr*(VI) is present at this low concentration.

Table 3 Removal from low concentration feed at pH 7 with 1% Aliquat 336

Cr(VI) concn in (mg/L)		Removal percentage	Distribution Constant
Initial	Final	%E	DE(-)
1.0946	0.4734	56.8	2.77
0.5005	0.091	81.9	4.53
0.2712	0.0695	74.4	2.95
0.0964	0.0279	75.3	2.46

Table 4 Composition of groundwater sample from Jabel Hafeet, Al Ain

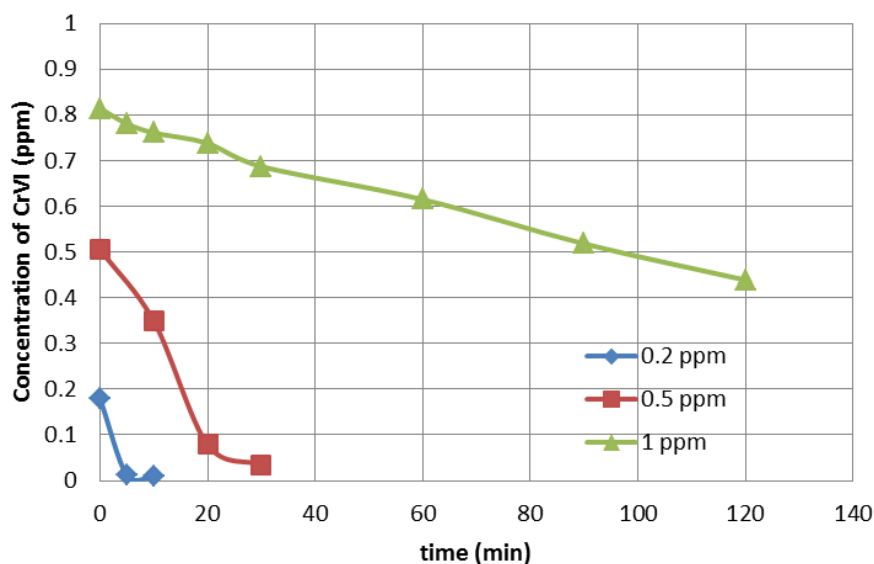| Na (mg/L)	K (mg/L)	Sr (mg/L)	Mg (mg/L)	Ca (mg/L)	*Cr*(VI) (mg/L)	B (mg/L)
360.4	21.8	4.0	5.5	81.9	0.18	1.4
118.5	3.8	0.07	0.7	1.5	0.01	0.4
67%	82%	98%	87%	98%	94%	70%

Fig. 6 Outlet *Cr*(VI) concentration versus time (min) in hollow-fibre contactor at low feed
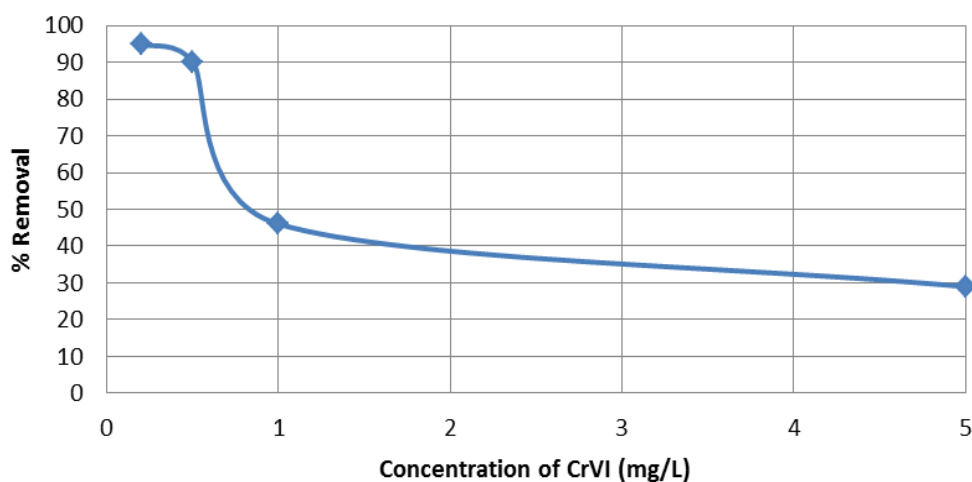concentrations using 2%Aliquat 336, 10% hexanol and 88% sunflower oil

Fig. 7 Effect of initial *Cr*(VI) concentration on the removal percentage, *E*(%)

Additional amounts of *Cr*(VI) was added to examine the effect of reactive liquid membrane
treatment at higher concentrations (more than 0.18 mg/L). The results are plotted as the effluent
Cr(VI) concentrations as a function of treatment time in Fig. 6. It is noted that at smaller
concentrations (0.5 mg/L or less) the treatment time was short (about 30 mins). Within this time
approx. 90-95% percentage removal was achieved. For *Cr*(VI) concentrations higher than 0.5
mg/L the treatment time was extended to 90-120 mins to achieve more removal. The percentage of
Cr (VI) removed is plotted as a function of the initial *Cr*(VI) concentration in Fig. 7. It shows that
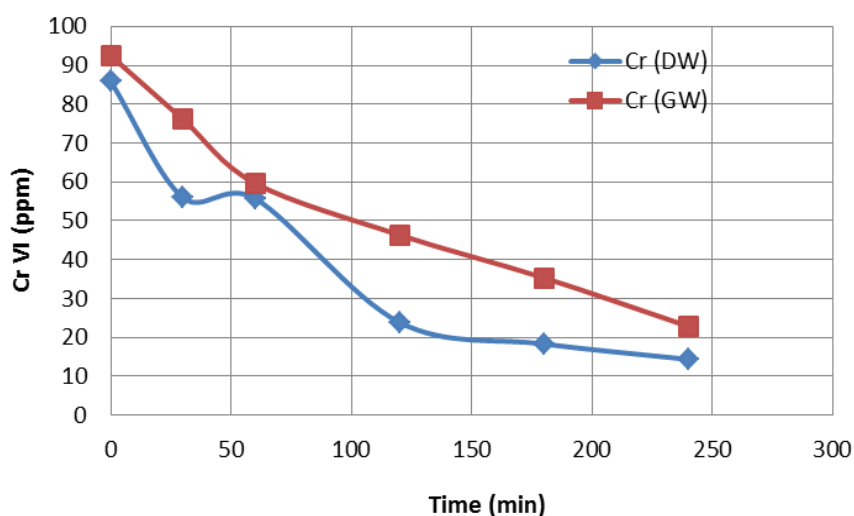with this organic phase composition the removal percentage decreased at higher feed

Fig. 8 *Cr*(VI) concentration versus time (min): comparison of distilled water and groundwater samples

concentrations (at 1 mg/L and above). By using a higher Aliquat 336 and operating at longer time, this removal percentage can be improved as shown in Fig. 8 and will be discussed in the next section.

It is emphasized that the real groundwater sample was at low concentrations (less than 0.2 mg/L) for which the removal is excellent and treated water concentration (ca. 0.01 mg/L) was within the recommended limit (0.05 mg/L) of the regularity authority.
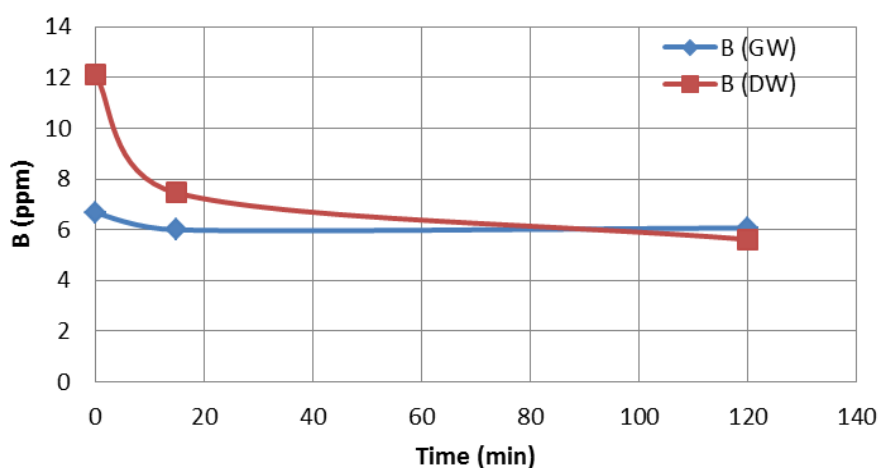

Fig. 9 Outlet B concentration versus time (min) in the hollow-fibre membrane contactor: comparison of distilled water and ground water feed samples

3.6 Removal of Cr(VI) and B in the hollow-fibre membrane contactor

The percentage removal of *Cr*(VI) and B from high concentration feed using 5% Aliquat 336, 10% hexanol and 85% fresh sunflower oil is shown in Fig. 8. Additional amounts of *Cr*(VI) and B were added to make up these concentrations in ground water. Similar feed solutions were prepared in distilled water as well. It is observed that longer time is are required to achieve a removal of approx. 80% of *Cr*(VI) and single stage operation does not seem to be sufficient. The removal percentage is slightly lower if *Cr*(VI) is prepared in groundwater rather than in distilled water. This could be due to the variation of the compositions of the feed in terms of ions that offer different degrees of competition especially in ground water.

It is shown in Fig. 9 that this new system has the ability to simultaneously remove other ions such as B that exist in many groundwater samples. The removal (approx. 53%) from distilled water sample was more than that prepared in groundwater (only 14%). More investigations are required to completely examine the effect by varying the feed concentrations and the ratio of the concentrations of various ions.

4. Conclusions

Experimental results are reported for the removal of chromium using sunflower oil (a non-toxic solvent). The main concluding remarks are

(i) The values of the distribution coefficient (*DE*) for Aliquat 336-sunflower oil-hexanol are as good as those reported for systems using kerosene and has the potential to replace kerosene which is being commercially used.

(ii) The new solvent system based on sunflower has several merits including less toxicity, less corrosiveness, low environmental impact, good health and safety record and compatibility with the large-scale membrane contactors.

(iii) The conditions that gave good performance was 5% Aliquat 336-sunflower oil-10% 1-hexanol, for extraction from 10–500 mg/L feed at natural pH 6–7.

(iv) The values of *DE* are significantly affected by the feed solution pH and its initial concentration and the composition of the organic phase (Aliquat 336 concentration), and not much by the operating temperature.

(v) This process was applied to the samples of groundwater at its natural pH (no addition of chemicals) and the removal process gave excellent results, approx. 94% removal was possible in a bench-scale hollow-fibre membrane contactor; the treated water attained concentration which is much less than 0.05 mg/L, the acceptable to the local regularity authority.

(vi) The treated water thus produced can provide additional sources to be recycled in the processes where they were initially generated and/or can be used for irrigation purposes.

Acknowledgments

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