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Effect of solvent type on removal and recovery of hexavalent chromium from industrial wastewaters

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ABSTRACT

Metals, especially chromium exists in a wide range of concentrations in natural water and wastewaters from various industrial operations. Reactive liquid extraction can be used for removing chromium. In this report, equilibrium experiments are presented on the removal of hexavalent chromium (Cr(VI)) using Aliquat 336 in various non-traditional solvents. The solvents are sunflower oil (fresh and recycled) and lubricating oil (fresh and recycled). The results are presented for the removal of Cr(VI) from aqueous solutions in the concentration range 0.5–500 ppm using Aliquat 336 (in the range 1.0–20% (v/v)). It is shown that sunflower oil and lubricating oil, both in the fresh and recycled forms, are able to remove Cr(VI) from ground waters and industrial wastewaters at their natural pH (range 6–8). These solvents gave satisfactory percentage extractions, producing water that can be recycled and they also offer advantages from health and safety, and environmental points of view. The results of the re-extraction process using KCl, K_2CO_3 and seawater are also presented. Seawater at its natural pH of 8 has shown potential for re-extraction. The findings have been applied to remove Cr(VI) from complex industrial wastewaters. The results provide good guidelines to the development of Cr(VI) removal and recovery processes using renewable, biodegradable, safe and cheap solvent systems demonstrated in this paper.

Keywords: Chromium; Removal; Sunflower oil; Recovery; Seawater

1. Introduction

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 the 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 [1–5]. The efficiency of the systems is determined by the ability of the "target" molecules to form complex with the carrier and the effective diffusivity of the solute-carrier complex in the organic solvent [6–9]. A number of research groups have been engaged in various stages of development, some have focused on the thermodynamic and kinetic properties of the systems, especially determination of equilibrium partition coefficient and extraction/stripping rate constant [10–14]. Despite the increase in number of research in this field, there is a 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 [15] 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 [16] exist at near neutral and alkaline pH (6–8 pH range). Therefore, the methods are required for the removal of chromium from these sources, preferably without adjusting their natural pH (i.e. without adding any extra chemicals).

Effluents from tannery, electroplating and timber treatment processes form the major sources of chromium (Cr) contamination into aquatic and industrial environments. Chromium is also being used in chemical and refractory industries and the use has increased considerably [17]. A significant proportion of this chromium is released to the environment [18]. As a result, the ground water sources may also contain chromium and other heavy metals. 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 recycling them. This may add to the sustainable development by applying these pollution control measures and creating additional sources of the depleting primary resources [17,18].

The methods such as precipitation [19], ion exchange [20], adsorption [21] and reverse osmosis [22] 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 easy scale-up as an industrial separation technology [23–27].

The processes based on liquid–liquid extraction, especially reactive extraction using ionic molecules, such as Aliquat 366 (a quaternary methyl ammonium salt) as selective carrier in the organic phase, have been being actively considered as the potential candidates. There have been studies using various ionic molecules, such as Aliquat 100 (tetrabutyl ammonium bromide), Aliquat 336 (trioctyl methyl ammonium chloride), Alamine 336 (trioctylamine), TIOA (tri-iso-octylamine), etc. [28–36]. In most cases, the solvent or diluent used was of hydrocarbon-based (e.g. hexane and kerosene), halogenated organics (chloroform and dichloromethane). 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. More details of the organic system, their structure and performances are available in a recent literature [15].

Chemical equilibrium in the reactive extraction process can be described by any of following equations (depending on the solution pH) [23,24]

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

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

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 except at lower pH (less than pH 6.5) the dominating ion is the chromate ion [39], as shown in Fig. 1.

It is difficult in practice to measure accurately the concentration of chromium-carrier complex ($A_2Cr_2O_7$ or A_2CrO_4) in the organic phase at equilibrium. This can be calculated by knowing the initial and equilibrium concentrations of Cr(VI) in the aqueous phase as the total concentration of Cr(VI) is experimentally measured (assuming negligible adsorption at the interface). Similarly, the concentration of carrier in the organic phase is also difficult to measure accurately, but given the stoichiometry that every mole of $K_2Cr_2O_7$ reacts with 2 mol of carrier, the concentration of carrier in the organic phase is therefore given by the difference between the initial carrier concentration and twice the concentration of the chromium-carrier complex. The chromium ions (the chromate and dichromate anions) react with carrier in a similar way

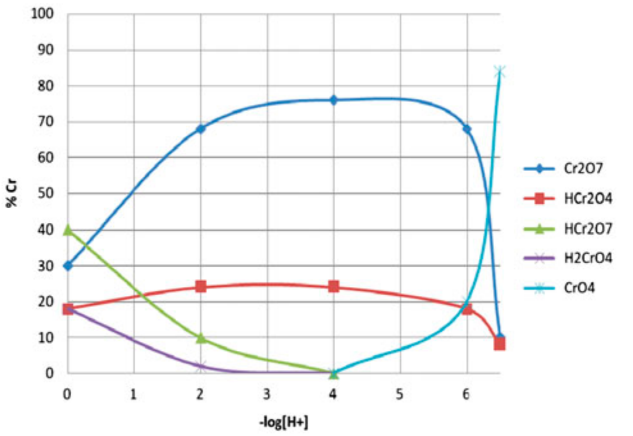

Fig. 1. Distribution diagram of chromium species for at 50 mM at 25°C as a function of pH (Brito et al., 1997).

and the equations to calculate their concentrations would be similar. This relationship can be expressed as follows:

$$C_{\mathrm{ACl^*(org)}} = (C_{\mathrm{ACl^*(org)}})_{\mathrm{i}} - 2(C_{\mathrm{fCri}} - C_{\mathrm{ECr^*(aq)}}) \tag{3}$$

where $C_{\mathrm{ACl\,(org)}})_i$ and C_{fCri} are the initial carrier and total Cr(VI) concentration, respectively. $C_{\mathrm{ECr^*(aq)}}$ and $C_{\mathrm{ACl^*(org)}})$ are the equilibrium concentrations of total Cr(VI) in aqueous phase and the carrier, respectively, measured experimentally, after removal or extraction.

The concentration of ACl at equilibrium is determined similarly by stoichiometry (shown in Eqs. (1) and (2)), as expressed below,

$$C_{\mathrm{Cl^*(aq)}} = 2(C_{\mathrm{fCri}} - C_{\mathrm{ECr^*(aq)}}) \tag{4}$$

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 and can be described by the following expression

$$\mathrm{DE} = \frac{C_{\mathrm{ECr^*(org)}}}{C_{\mathrm{Ecr^*(aq)}}} \tag{5}$$

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

$$\mathrm{KE} = \frac{C^2_{\mathrm{Cl(aq)}} C_{\mathrm{ACr^*(org)}}}{C^2_{\mathrm{ACl(org)}} C_{\mathrm{Ecr^*(aq)}}} \tag{6}$$

These equations have been used by previous investigators [26,33] and therefore comparison can be made with our calculated results.

During stripping with an aqueous chloride solution (KCl or K_2CO_3), the decomplexation of the chromium-carrier complex takes place and the chromium is released according to the reaction

$$(\mathrm{A_2Cr_2O_7})_{\mathrm{org}} + (2\mathrm{KCl})_{\mathrm{aq}} \Leftrightarrow (\mathrm{K_2Cr_2O_7})_{\mathrm{aq}} + (2\mathrm{ACl})_{\mathrm{org}} \tag{7}$$

It is noted that by using an aqueous chloride solution, the carrier can be replenished and then reused in the extraction process. This suggests that seawater containing chloride is expected to re-extract following a similar reaction.

A distribution coefficient in the strip-organic solution is defined by the following equation.

$$\mathrm{DS} = \frac{C_{\mathrm{SCr^*(org)}}}{C_{\mathrm{SCr^*(aq)}}} \tag{8}$$

where $C_{\mathrm{SCr^*(org)}}$ and $C_{\mathrm{SCr^*(aq)}}$ are the concentrations of Cr(VI) in the organic phase and in the stripping phase, respectively, after equilibrium has reached in the re-extraction process.

A lower value of DS determines a better re-extraction or recovery from the organic solution. The performance Cr(VI) extraction and recovery using the liquid membrane can be indicated by the percentage extraction and recovery as expressed in the following equations:

$$\%\,E = (1 - \frac{C_{\mathrm{ECr^*(aq)}}}{C_{\mathrm{fCri(aq)}}}) \times 100 \tag{9}$$

$$\%\,R = \mathrm{DS} \times 100 \tag{10}$$

It is noted that the mass balance equations, Eqs. (3), (4) and (9) are presented for a phase ratio (the ratio of the volume of the organic to that of the aqueous phase) of 1:1. The volumes of the separate phases (the aqueous and the organic) should be taken into consideration when the phase ratio is different from 1:1.

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 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 solvents: sunflower oil (both fresh and recycled forms), lubricating oil (both fresh and used forms) and compared with those obtained using kerosene. The experimental plan includes the following stages:

(a) Screening of a number solvents such as vegetable oil (sunflower oil – fresh and used), and lubricating oil (fresh and used) as a potential organic phase.
(b) Determining of partition/distribution coefficient of Cr(VI) in these solvents with or without any ionic carrier and the favourable conditions for chromium removal.

(c) Identifying recovery solutions and evaluating their effectiveness in the re-extraction from the organic phase loaded with Cr(VI).
(d) Examining the performance of the process with "industrial" and groundwater samples in a bench-scale hollow-fibre membrane contactor.

The solvent kerosene is also included in the study 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 that the other solvents, e.g. sunflower oil and lubricating oil with less toxicity and more environmental-friendliness, can perform the removal to the similar degree as the kerosene. The systems were applied for the treatment of polluted samples of ground water and refinery wastewater.

2. Materials and methods

2.1. Chemicals and reagents

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 (Emarat 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 chloride and potassium carbonate AnalaR 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 pH was measured using a pH metre (Thermo Orion pH metre, 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).

Kerosene is mainly a mixture of paraffins, aromatics cycloalkanes with a boiling range 165–265˚C [37]. Sunflower oil is very high in mono-unsaturated fatty acids (a healthier form of fat). 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. The lubricating oil contained mainly heavier components of aromatics (long chains attached to cyclic structures) and no volatile components with a flash point of 250˚C (manufacturer"s information).

2.2. Preparation of solutions and the analytical procedure for Cr(VI) concentration

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

Re-extraction or recovery was conducted with aqueous solutions of KCl/K_2CO_3. Solutions of KCl and K_2CO_3 were prepared by dissolving known amounts of these salts separately in distilled water. Seawater was used and whenever required was pH adjusted using 1 M HCl (for acidic pH) and 1 M NaOH solutions (for alkaline pH).

2.3. Procedure for equilibrium measurements of solutes at ambient temperature

All the removal and recovery 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) 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. A schematic diagram of the experimental set-up is shown in Fig. 2. The addition of hexanol as modifier was required to keep Aliquat 336 in solution and to maintain a clear interface after the equilibrium, about 10% (v/v) hexanol were required.

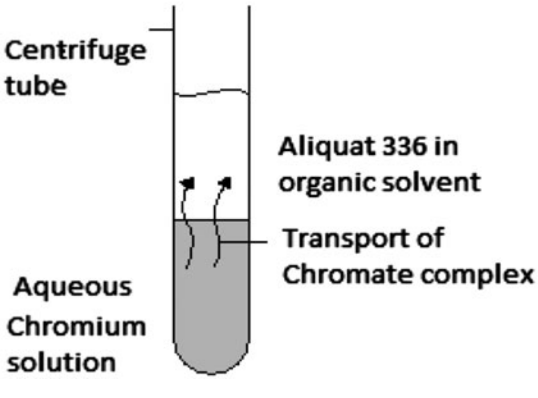

Fig. 2. A schematic of the experimental set-up for equilibrium experiments.

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 h using a magnetic stirrer. After mixing the solutions were allowed to settle for 60 min 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.

For the recovery of Cr(VI) from the organic phase, it was contacted with aqueous solutions of either KCl (1 M) or K_2CO_3 (1 M) or seawater. The volume of the organic and that of the aqueous recovery phase was identical. The same set-up (Fig. 2) was used for the recovery from the oil phase that was loaded with Cr (VI) during the extraction experiments.

The time allowed for this process was about 2 h. The samples were taken from the aqueous solution, allowed to stand for about 30 min and if required centrifuged to get a clear solution. The concentration of Cr(VI) was then measured by the spectrophotometric method.

2.4. *Analytical procedure 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× 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. 5.

3. Results and discussion

The results for extraction are presented as percentage extracted or removed E (%), and distribution coefficient (DE) as a function of

- Feed solution pH,
- Type and composition of the organic phase,
- Concentration of Cr(VI) in the feed solution and
- Concentration of other components (such as strontium) in an industrial effluent sample.

The results for recovery of Cr(VI) into the stripping solution are presented as percentage recovered R (%), and stripping distribution coefficient (DS).

All the extraction and re-extraction experiments were repeated and the results are within 5% 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 various solvents including vegetable oil (fresh), lubricating oil (fresh) and kerosene are presented in Fig. 3. It can be seen from the figure that the trends are similar both for the distribution coefficient and extraction percentage. With the increase in feed pH within 6–12 the values of DE decreased, the largest drop was observed when the pH decreased from 6 to 7 and after that the decrease was gradual. This could be due to many reasons: (i) Cr(VI) changes its ionic form in this pH range, going from $Cr_2O_7^{-2}$ to CrO_4^{-2} with decreasing proportion of the former ion [39] (ii) the reactive extraction could be dominated by the former ionic form which decreased in concentration with the increase in pH and/or (iii) the reverse reaction could have more influence as the pH is increased. To further explain the point in (i) it is mentioned that at pH 6.5 the concentration of CrO_4^{-2} increased from 20% at pH 6 to 85% at pH 6.5 and those for $Cr_2O_7^{-2}$ decreased from 70% at pH 6 to 10% at pH 6.5. This reduction of available chromate ion concentration might have produced smaller concentration of chromate-carrier complexes at pH 6.5 and resulted in lower values of DE. The percentage distribution of chromate ions are shown in Fig. 1 from literature [39]. The other factors

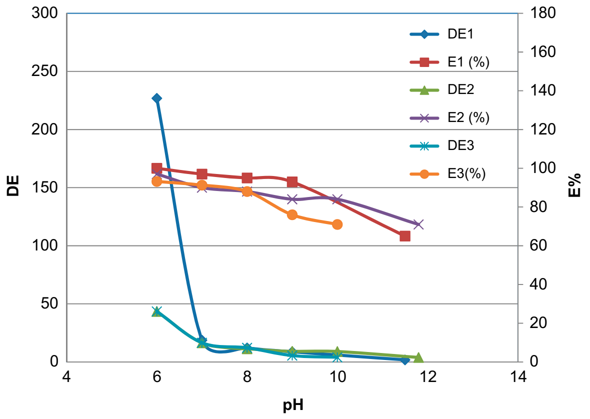

Fig. 3. Effect of pH on DE (–) and *E* (%) at 400 ppm Cr(VI) using 5% Aliquat 336, 10% n-hexanol and 85% diluent; DE1 and E1—fresh sunflower oil; DE2 and E2 (%)—fresh kerosene and DE3 and E3(%)—fresh lubricating oil.

mentioned above might have contributed to the decrease in the removal of chromium as pH was increased, but still a good removal (90–75%) was achieved in the pH range 7–9 which is the natural pH of many industrial effluents. It is observed that sunflower oil, with all the benefits of occupational health and safety, performs well and has the potential to replace kerosene as a renewable and biodegradable solvent for removal of metals such as Cr(VI). Lubricating oil-based organic phase also gave good extraction but the cost could be much higher compared to sunflower oil and definitely it does not come from a renewable source. It is noted that kerosene has been trialled in many industrial extractions and treatment of environmental polluting sources [26,27,32,33]. It has been effective as an 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.

The stability of the organic phase with sunflower oil is discussed in this paragraph. This phase can undergo alcoholysis, especially with the addition of 1-hexanol as a modifier. In the literature [40–42], pyrolysis and distillation have been mentioned to produce biodiesel from sunflower oil but these procedures require temperatures around 200°C, alcohol (ethanol or methanol in excess of stoichiometric proportion) as a reactant and presence of a catalyst like NaOH or KOH. So alcoholysis is not a possibility in the sunflower-based organic phase as 1-hexanol (not a reactive component) was used only 10% v/v and NaOH/KOH was not added in the phase. Therefore it is expected that the sunflower-based extraction phase could retain its stable performance in the long-term processing of aqueous Cr(VI) containing wastewaters.

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

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 this pH (i.e. pH greater than 7) sunflower oil did not perform as good as the others but it has the advantage of being the least expensive, less toxic, operator friendly and it can be obtained from renewable sources. The other factors to be considered are: sunflower oil is a food grade substance and 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 addition of acid or alkali (which can act as catalyst) or enzyme catalyst, no high pressure and high temperature.

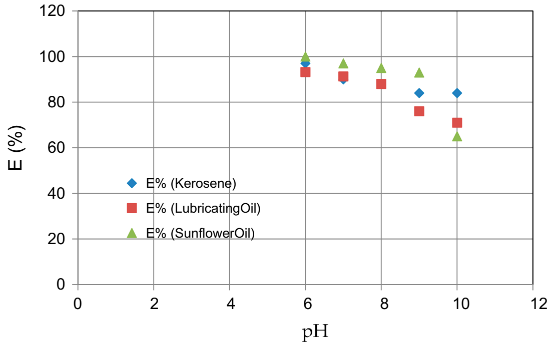

Fig. 4. Effect of solvent type on extraction of Cr(VI) at pH 7, organic phase: 5% Aliquat 336, 10% n-hexanol and 85% diluent (sunflower oil/kerosene/lubricating oil).

3.3. Effect of the use of recycled diluents (sunflower oil and lubricating oil)

The effect of pH on the extraction of Cr(VI) using 5% Aliquat 336 and n-hexanol in recycled solvents: sunflower oil (used a few times in domestic cooking) and lubricating oil (used in a car for a few weeks) are presented in Tables 1 and 2, respectively. It can be seen that the trends are similar both over the entire range of pH, i.e. the values decreased with the increase in pH. Recycled sunflower oil-based system performed best at pH 6 with maximum Cr(VI) removal of 95%. Surprisingly, the recycled lubricating oil gave better values for the distribution coefficient and extraction percentage at higher pH (more than pH 7). These results cannot be explained at this stage and more work need to be done especially change in oil composition with the usage. Nevertheless, the results suggest that both the recycled diluents can remove Cr(VI) in moderate percentages and can be considered as potential candidates to replace kerosene/toluene and any similar solvent that have been tried to treat effluents with alkaline characteristics.

3.4. Effect of carrier concentration

Experimental results on the effect of carrier concentration for extraction of Cr(VI) at pH 7 with sunflower oil are listed in Table 3. The choice of this pH was based on the observation that the values of

Table 1
Effect of pH on extraction with 5% Aliquat 336 and 10% n-hexanol in recycled vegetable oil (RSO)

pH	Cr(VI) conc (ppm)		%*E*	DE
	Initial	Final		
6	474.78	5.478	98.91	88.5
7	470.61	96.83	79.42	3.86
8	475.11	198.10	58.3	1.4
9	471.12	221.66	52.95	1.13
10	485.48	203.04	58.2	1.4

Table 2
Effect of pH on extraction with 5% Aliquat 336 and 10% n-hexanol in recycled lubricating oil (RLO)

pH	Cr(VI) conc (ppm)		%*E*	DE
	Initial	Final		
6	497.40	76.48	84.6	5.5
7	467.67	96.49	79.4	3.8
8	461.67	104.32	77.40	3.4
9	469.63	100.34	78.63	3.68
10	480.88	172.69	64.09	1.78

the DE and E (%) were low at 500 ppm feed and the effect of Aliquat concentration could be observed in a pronounced manner. 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 molar ratio. This increase in removal percentage can also be explained by the change in transport property such as viscosity at an increased concentration of Aliquat 336 that may allow faster diffusion of concentrated chromate ions (as the processing time was maintained the same for low and high concentrations of Aliquat 336) in the oil phase.

The results obtained with sunflower phase are compared with those reported in the literature in Table 4. The values of the extraction equilibrium constants are of similar value for the sunflower-based organic system, suggesting good effectiveness of this new system.

3.5. *Effect of temperature*

The effect of temperature 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 200 ppm are shown in Table 5. At this high feed concentration the effect is minimal. Even at 39˚C high values of DE and %E were obtained, i.e. more than 100 (for DE) and more than 99% for the removal of Cr(VI).

Table 3
Effect of Aliquat-336 concentration in fresh sunflower oil (FSO) for extraction of Cr(VI) at pH 7

Aliquat 336% (v/v)	Cr(VI) conc (ppm)		%*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 4
Comparison extraction equilibrium constant with the literature values for systems with Aliquat 336 in kerosene and sunflower oil

Aliquat 336% (v/v)	Initial Cr(VI) concentration in ppm	KE × 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.

Table 5
Effect of temperature on Cr(VI) extraction with 10% Aliquat 336 and 10% n-hexanol in fresh sunflower oil (FSO)

Temperature (°C)	Cr(VI) conc (ppm)		%*E*	DE
	Initial	Final		
25	194.505	0.915	99.6	226.9
32	194.505	1.906	99.02	101.05
39	194.505	1.375	99.3	140.51
46	194.505	0.924	99.5	209.41

3.6. Removal of Cr(VI) from an industrial effluent sample

3.6.1. Aliquat 336 in fresh sunflower oil

In the real-life situation, it is common to find other metal ions such as Na+, K+, Ca2+, Mg2 + and Sr2 + being present in industrial effluents and ground water sources. This experiment was purely designed to investigate the organic carrier's affinity for Cr(VI) (more specifically chromate ions) in presence of other metal ions (i.e. metal salts) during the extraction or removal process. The composition of an industrial sample (at a pH 5.9) obtained from a local refinery is presented in Table 6. Because the initial concentration of Cr(VI) was low, 400 ppm Cr(VI) was added to the sample to observe the effect of the presence of other components. It is clearly observed that other ions such as Na+, K+ and Sr2 + are also removed to some extent with the organic system of Aliquat 336–fresh sunfloweroil–1-hexanol (Table 7). The ions Ca2+ and Mg2+ were not removed but Sr2+ ions even at low concentrations approx. 0.20 ppm were removed at high percentages (more than ca. 93%). The competition for Aliquat 336 by other ions might have caused a small drop in the removal of Cr(VI), especially at pH equal to or greater than 7. The extraction percentage was still very good showing the affinity of Aliquat 336 greater than other ions [43]. The extraction percentage was similar to that obtained for single component Cr(VI) solution at pH 6 (close to the natural pH 5.9 of the industrial sample). The extraction percentages of Cr(VI) dropped with the increase in pH. At pH of 7 the percentage extraction dropped to 64% and further decrease in removal was observed with the increase in pH. The removal percentage of Sr2+ was very high over the entire range of pH. The final Sr2+ concentration was lower (less than 0.05 ppm) than the recommended value for effluent discharge. It is noted that the removal of Sr2+ is also required in many industrial effluent samples (with a low initial concentration) which can be simultaneously removed to a great extent by using this Aliquat 336–sunflower oil system. It is interesting to observe that the essential metal ions (Na+, K+, etc.) were only slightly extracted with this organic system keeping the water characteristics to an acceptable level for many secondary as well as primary purposes. This removal process when

Table 6
Composition of the industrial wastewater sample at pH 5.6

Components of the industrial sample	Initial pH 5.9 and component concentration (ppm)
Calcium (Ca)	2.05
Potassium (K)	365.70
Magnesium (Mg)	0.04
Sodium (Na)	1193.37
Strontium (Sr)	0.21
Chromium (Cr)	0.07
Chromium (Cr) added to the sample	400.00

Table 7
Effect of pH on extraction (400 ppm Cr(VI) added) from an industrial sample using 5% Aliquat 336, 10% n-hexanol and 85% fresh sunflower oil (FSO)

Feed pH	Cr(VI) conc (ppm)		%*E* (Cr(VI))	%E^* (Cr(VI))	Final Sr + 2 (ppm)	%*E* (Sr2+)	%*E* (Na+)	%*E* (K+)
	Initial	Final						
6	422.78	19.57	95.37	99.56	0.011	94.80	13.4	11.8
7	412.99	150.85	63.47	94.94	0.07	64.3	13.7	13.9
8	406.41	222.16	45.34	92.34	0.095	50.8	18.1	17.4
9	413.12	267.167	35.33	89.78	0.121	42.1	–	2.54

optimised will allow the treated water to be recycled and reused in the processes where they are generated. More work need to be done to determine the extractability of other components in presence of Cr(VI) and possible scale-up of the process.

3.6.2. Aliquat 336 in recycled sunflower oil

The removal of Cr(VI) from the industrial sample was also examined using the organic system of Aliquat 336 in recycled sunflower oil. The initial Cr(VI) concentration was low (0.07 ppm, pH 5.9) and so additional amounts were added to examine the ability of recycled sunflower oil system to remove it in presence of other components. It is observed that the percentage removal was from moderate to high (Table 8), approximately in the range 65–98%. The recycled sunflower oil system performed better than the fresh one especially in the removal of Cr(VI) and Sr + 2 at pH greater than 7. This effect could not be explained without analysing the recycled sunflower oil and the effect of chemicals used for pH adjustment of the feed sample. However, at the natural pH both gave similar results with removal of Cr(VI) in the range 95–98%. More work is underway to determine the extractability of other components of various "polluted" water samples and the effect of other process parameters.

3.7. Recovery of Cr(VI) from the organic phase

The effect of the type of stripping solution and its concentration on the recovery of Cr(VI) in equilibrium experiments are illustrated in Table 9. With aqueous potassium salts, the recovery was low in the range 23–37%. Both KCl and K_2CO_3 performed slightly better in recovering from lubricating oil-loaded Cr(VI) samples, followed by the recovery from sunflower oil-loaded sample. Using seawater (especially at alkaline pH) the recovery from fresh sunflower oil-loaded sample improved to a great extent being in the range 58–60% at the natural pH of 8 (Table 10). This is an important result as the seawater is available in abundance at a nominal cost and being able to recover Cr(VI) without any pH adjustment and thus shows a good potential for industrial application. However, to increase the recovery from sunflower oil-loaded phase, seawater requires pH adjustment from its natural value of 8–11. Seawater did not perform well at acidic pH and only 22–20% of Cr(VI) could be recovered from all the organic phases. This is consistent with the result obtained previously using an acidic strippant, HCl, and approx. 27.85% recovery was obtained at 1.5 M [30]. For optimal rate of recovery, it is recommended to operate the stripping process with seawater at its natural pH and use sunflower oil in the removal process.

Table 8
Effect of pH on extraction (400 ppm Cr(VI) added) from an industrial sample using 5% Aliquat 336, 10% n-hexanol and 85% recycled sunflower oil (RSO)

Feed pH	Cr(VI) conc (ppm)		%*E* (Cr(VI))	%*E** (Cr(VI))	Final Sr + 2 (ppm)	%*E* (Sr + 2)	%*E* (Na+)	%*E* (K+)
	Initial	Final						
6	484.48	10.95	97.7	99.56	0.013	93.8	13.7	11.6
7	481.84	96.45	80.0	94.94	0.015	93.0	13.9	13.7
8	483.28	164.62	65.9	92.34	0.01	95.2	18.9	18.1
9	486.00	170.05	65.0	89.78	0.006	97.1	–	3.1

*Results obtained from aqueous solutions of pure Cr(VI).

Table 9
Effect of KCl and K_2CO_3 as stripping agent

Solutions		Cr(VI) conc (ppm), pH 7		%*R*	DS
Stripping agent	Organic phase	Initial (in initial feed solution)	Final (in stripping solution)		
KCl (1 M)	FSO	453.5	131.6	29.01	3.44
KCl (1 M)	USO	453.5	103.9	22.9	4.36
KCl (1 M)	FLO	453.5	168.7	37.2	2.69
K_2CO_3 (1 M)	FSO	429	143.8	33.5	2.98
K_2CO_3 (1 M)	USO	429	128.6	30.0	3.34
K_2CO_3 (1 M)	FLO	429	154.9	36.1	2.77

Table 10
Effect of sea water at various pH on stripping of Cr(VI)

Solutions		Cr(VI) conc (ppm), pH 7		%*R*	DS
Stripping agent	Organic phase	Initial (in initial feed solution)	Final (in stripping solution)		
Seawater (pH 11)	FSO	431.7	248.7	57.6	1.74
Seawater (pH 11)	USO	431.7	228.9	53.0	1.89
Seawater (pH 11)	FLO	431.7	154.8	35.9	2.79
Seawater (pH 8)	FSO	448.5	264.7	59.0	1.69
Seawater (pH 8)	USO	448.5	150.1	33.5	2.99
Seawater (pH 8)	FLO	448.5	101.1	22.5	4.44
Seawater (pH 4)	FSO	444.8	95.0	21.3	4.72
Seawater (pH 4)	USO	444.8	88.5	19.9	5.03
Seawater (pH 4)	FLO	444.8	129.5	29.1	3.43

It was reported earlier in our previous work that 0.4 M NaCl at pH 4 performed much better when it was used for recovery from kerosene-loaded Cr(VI). Approx. recovery of 98% Cr(VI) was achieved at acidic (pH 4) and alkaline (pH 10) conditions. However, our aim in this paper was to determine a sustainable solvent with less environmental issues, better health and safety benefits, and therefore recovery from kerosene-loaded samples were not examined.

4. Conclusions

Experimental results are reported for the removal of chromium using various solvents, e. g. sunflower oil (fresh and recycled), lubricating oil (fresh and recycled) and kerosene. The values of the partition coefficient (DE) for Aliquat 336–sunflower oil—1-hexanol and Aliquat 336–lubricating oil–1-hexanol are as good as those reported for kerosene. The performance of the sunflower oil and lubricating oil are very good. This suggests that the new solvents such as vegetable oil and lubricating oil either in the fresh or used form have the potential to replace kerosene which is presently being commercially used. The new solvent system especially sunflower based have several merits including less toxicity, less corrosiveness, low-environmental impact and good health and safety benefits and compatibility with the large-scale membrane contactors.

The conditions that gave good values of DE and percentage removal were 5% Aliquat 336 in sunflower oil with 10% 1-hexanol, from feed with Cr(VI) in 25–500 ppm at pH 6–7. 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.

When applied to an industrial sample at its natural pH the removal process was found to be affected by the presence of other components. As a result, removal of chromium decreased (compared to that obtained from single component Cr(VI) solution), still reasonable percentage removal was obtained within 2 h of treatment. In addition, the system of Aliquat 336–1-hexanol–sunflower oil was able to remove other toxic components such as strontium from the industrial sample.

At a very low concentration (equal to or less than 0.5 ppm) of Cr(VI) added to ground water, the removal percentage was also good at the natural pH of the sample and the treated water Cr(VI) composition was within the approved limit for reuse.

The recovery of Cr(VI) from the oil-loaded phase was low to moderate (in the range 20–59%) using KCl (1 M), K_2CO_3 (1 M) and seawater. Seawater at its natural pH 8 performed the best. Although the percentage recovery is smaller than previous investigations the use of seawater (a much cheaper recovery solution) is considered a good alternative.

The new system has an additional benefit that it removes (only in small amounts) some of the essential components such as sodium and potassium, calcium and magnesium when Cr(VI) is present in higher ppm. Therefore this treated water can be reused in the processes where they were generated and the chromium recovered can be an additional source of supply.

Symbols

C_{Acl}	—	Aliquat 336 concentration in organic phase, mole/l
C_{AP}	—	concentration of the chromium complex, mole/l
C_{Cl}	—	chloride ion concentration, mole/l
C_{fri}, C_{Ecr}, C_{SCr}	—	solute concentration at stages of initial, after extraction and after striping
DE, DS	—	distribution coefficient of solute for extraction and stripping, respectively

Subscripts

Aq	—	aqueous phase
Org	—	organic phase
E	—	extraction process
S	—	stripping process

Superscripts

*	—	at equilibrium

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