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Fast and efficient chromium(VI) pertraction with Aliquat 336 in emulsion liquid membrane using sunflower oil as a high potential solvent

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ABSTRACT

In this work, pertraction of hexavalent chromium(Cr(VI)) from acidic aqueous solution by emulsion liquid membrane (ELM) using sunflower oil has been investigated. Sunflower oil was used as high potential, cost-effective and environmentally benign solvent in membrane phase. To prepare the primary emulsion, Span 80 as surfactant, Aliquat 336 as carrier and sodium hydroxide as internal stripping reagent were employed. The influences of various operational parameters such as initial pH of the feed phase solution, surfactant concentration, carrier concentration, mixing speed and treatment ratio on Cr(VI) pertraction were investigated and the optimal condition was determined. Results indicated that, at optimum condition, 99% of Cr(VI) ions could be extracted from acidic feed aqueous solution within 10 min in such a way that more than 94% of them were extracted within first 2 min. To evaluate the efficiency of sunflower oil, the effects of common petroleum diluents such as kerosene, toluene and butyl acetate are also tested and the overall mass transfer coefficient (K_{od}) in the water and oil layers at the external interface of emulsion drop was calculated. It was found that although mass transfer coefficient in sunflower oil–based ELM is lower than the others, its higher viscosity results in more stable membrane and higher extraction compared with the other solvents. Furthermore, an empirical correlation for prediction of emulsion globule size was proposed as a function of mixing speed. This paper demonstrates the feasibility of using eco-friendly, safe and cheap solvents for efficient pertraction of Cr(VI) from wastewater.

Keywords: Pertraction; Cr(VI); Emulsion liquid membrane; Sunflower oil; Green solvent; Mass transfer coefficients

1. Introduction

Great developmental growth in industrial activities in the last few decades led to the environmental pollution which is mainly related to metal ions pollutants. Chromium has been listed as one of the most toxic metals by the US Environment Protection Agency and World Health Organization [1]. The chromium (Cr) is a heavy metal that has lots of applications. It is used for manufacturing several alloys such as stainless steel, electroplating, mining, tanning leather, moulding in refractory bricks and producing cement, welding electrodes and cored wires. In addition, chromium compounds are used as wood preservers, mordant in textile dyeing, industrial catalysts and pigments [2]. The common oxidation forms for chromium are trivalent chromium(Cr(III)) and hexavalent chromium(Cr(VI)) [3]. Cr(III) is a vital trace element for glucose and fat metabolism in human body, but it can be dangerous in excess concentrations. The Cr(VI) that exists in environmental samples as anionic species is more toxic to organisms [2,4]. Hence, Cr(VI) removal from aqueous solutions is necessary. A variety of separation methodologies

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such as ion exchange [5], adsorption [6,7], precipitation [8], solvent extraction [9,10] and membrane-based approaches have been developed for the recovery and removal of Cr(VI) from the aqueous solutions.

Liquid membrane (LM) technique combines the extraction and stripping processes in a single unit operation, so this method has been utilized especially in case of low concentrations of metal solutes [11,12]. In recent years, LMs have been efficiently applied to remove heavy metal ions like cadmium [13], copper [14–17], zinc [18,19], nickel [20–23], vanadium [24], cobalt [25], mercury [26,27] and lead [28] from wastewater. Different designs for performing LM processes are bulk liquid membrane, emulsion liquid membrane (ELM), supported liquid membrane (SLM) and polymer inclusion membrane [29].

ELM was invented by Li [30] for the separation of hydrocarbons and now is a promising alternative for wastewater treatment in industrial operations. The advantages of the ELM system are high interfacial area for mass transfer because of the small size of the aqueous phase droplets, selectivity of species to be eliminated and using fewer amounts of organic solvent and greater efficiency compared with solvent extraction [4,31]. The ELM is a double W/O/W emulsion that contains a primary emulsion dispersed in a continuous phase, which is the contaminated phase to be treated. In this system, the membrane phase separates the external continuous phase from the stripping phase. The membrane phase consists of an extractant (carrier) in an organic solvent and a suitable surfactant to stabilize the emulsion. The transfer of the solute from external phase to the stripping phase is accomplished in this process [31,32].

Several studies have been carried out for Cr(VI) transport using different carriers in ELM processes [4,31,33–39]. Optimization of the parameters for the pertraction of Cr(VI) from the pharmaceutical industry wastewater using trioctylamine and Aliquat-336 as carrier and kerosene oil as the solvent has been reported by Rajasimman and Karthic [31] and Rajasimman and Sangeetha [34]. Cyanex 923 as a carrier and kerosene as the organic solvent in ELM has been applied to remove Cr(VI) from synthetic wastewater [12]. Nosrati et al. [40] studied the extraction performance of Cr(VI) with ELM by using Cyanex 923 as the carrier, Span 80 as the surfactant, kerosene as the solvent and NaOH as the stripping agent, and Kumbasar [41] used a membrane that consists of kerosene as diluent, trioctylphosphine oxide as extractant, ECA 4360J as surfactant and $(NH_4)_2CO_3$ solution as stripping phase. The extraction efficiency in these works was 99% and 99.6%, respectively.

Most of the conventional organic solvents are volatile, toxic, flammable and extremely expensive due to the limited resources. In recent times, use of alternative solvents and renewable plant sources, due to the stricter environmental regulations, leads to reduction risks to human health and protecting the environment in an economically beneficial manner in a sustainable world [42–44]. The environmentally benign solvents, such as vegetable oils, are also termed as green solvents, which can be used in ELM processes. Sunflower oil is the non-volatile oil with some advantages in comparison with other solvents such as high potential, easily available, non-toxic and low cost [45,46].

In this work, the main focus was to the feasibility of sunflower oil–based ELM in pertraction of Cr(VI) from an aqueous acidic solution. Sunflower oil was used as high potential, safe, cost-effective and green solvent and Aliquat-336 as a carrier. Also, the effects of several parameters such as initial pH of the feed solution, surfactant and carrier concentrations, mixing speed and treatment ratio on Cr(VI) transport were investigated and the optimum condition was obtained. Furthermore, at the optimum condition, results were compared with other petroleum diluents such as kerosene, butyl acetate and toluene to evaluate the efficiency of using sunflower oil for pertraction of Cr(VI).

2. Experimental details

2.1. Chemical materials

The ELM consisted of a surfactant, a mobile carrier or extractant and diluents. The sorbitan monooleate (Span 80) ($C_{64}H_{124}O_{26}$, hydrophilic–lipophilic balance = 4.5) was selected as non-ionic surfactant that was a product of Sigma-Aldrich Company (Schnelldorf, Germany). Aliquat 336 ($C_{25}H_{54}ClN$, density = 884 kg/m^3) was used as mobile carrier (product of Sigma-Aldrich Co.). Sunflower oil (density = 918.8 kg/m^3, viscosity = 0.04914 kg/m s) was used as diluent that was purchased from local NINA oil Company (Tehran, Iran). Kerosene (reagent grade) was purchased from Sigma-Aldrich. Butyl acetate, methyl acetate, *n*-hexane, toluene, hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium dichromate dihydrate ($Na_2Cr_2O_7$ $2H_2O$) were purchased from Merck, Co. (Germany).

2.2. Primary emulsion preparation

To make a primary emulsion, 30 mL of LM (consists of different portions of Span 80 and Aliquat 336 in sunflower oil) and 30 mL of 0.1 M NaOH solution as stripping phase were emulsified using ultrasonication (BANDELIN Sonopuls HD3200, 20 Hz, 200 W) for about 5 min. Aqueous stripping solution was added dropwise to the organic LM solution during the sonication process.

2.3. Feed solution preparation

Feed phase solution was made using proper amount of sodium dichromate dihydrate salt dissolved in deionized water. The feed concentration was 100 mg/L of Cr(VI). The feed phase was stirred to dissolve the salt completely. In order to make acidic feed aqueous solution and adjust the pH, 0.5 M HCl was added dropwise to the feed aqueous solution.

2.4. Experimental procedure

First of all, Primary prepared emulsion was smoothly dispersed into 400 mL beaker of feed stock to make the double emulsion. The mixture of aqueous feed solution and water in oil emulsion was stirred by propeller three-blade impeller for about 30 min. Impeller agitation speed was controlled using digital variable motor. To have complete mixing, the lowest impeller speed was selected upper than the minimum speed of dispersion forming (in our case it was 250 rpm). To study the pertraction of Cr(VI) ions, some important parameters such as initial pH of the feed phase solution, surfactant concentration, carrier concentration, mixing speed and treatment ratio (feed to emulsion ratio) were investigated. Table 1

Table 1
The range of parameters used in the pertraction of Cr(VI)

Parameter	Value
Cr(VI) concentration of feed phase (mg/L)	100
Initial pH of feed solution	1, 1.5, 2, 2.5, 3, 4
Surfactant (Span 80) concentration %(V/V)	1–4
Carrier (Aliquat 336) concentration % (V/V)	0.5, 1, 1.5, 2, 2.5, 3
Mixing speed (rpm)	300, 350, 400, 450, 500
Extraction time intervals (min)	2, 5, 10, 20, 25, 30
Feed to emulsion ratio	1:1, 2:1, 3:1, 4:1, 5:1
Sonication time and power	5 min, 200 W
Stripping reagent	30 mL, 0.1 M NaOH
Type and concentration of acid	0.5 M HCl
Diluent	30 mL, Sunflower oil
Impeller type	Propeller three-blade

displays the range of studied operating parameters. During the mixing step of ELM process, at different time intervals, small amount of samples were taken from the solution using sanitary syringes. The syringes were kept undisturbed for short time and the aqueous phase of taken samples was separated quickly. To avoid any probable mass transfer and remove remained emulsion droplets, separated aqueous phase was centrifuged. Then, the aqueous phase was analyzed by means of UV spectrophotometer (Vario 2600 Double Beam UV–Vis Scanning Spectrophotometer, England) to determine the Cr(VI) concentration. At wavelength of 350 nm, Cr(VI) UV/Visible spectrum was strong and had large molar absorption coefficient.

To observe the stability of emulsion with respect to time, the emulsion was allowed to stand. The photos of emulsion were taken at different time intervals and presented in Fig. 1. The photos were analyzed for any physical change as well as phase separation, homogeneity and uniformity. According to Fig. 1, the emulsion was stable for about 3 h and there was no phase separation. After that, the phase separation was observed. In our case, the process duration is less than 1 h. Thus, the primary emulsion is stable enough and the composition of the membrane is kept constant.

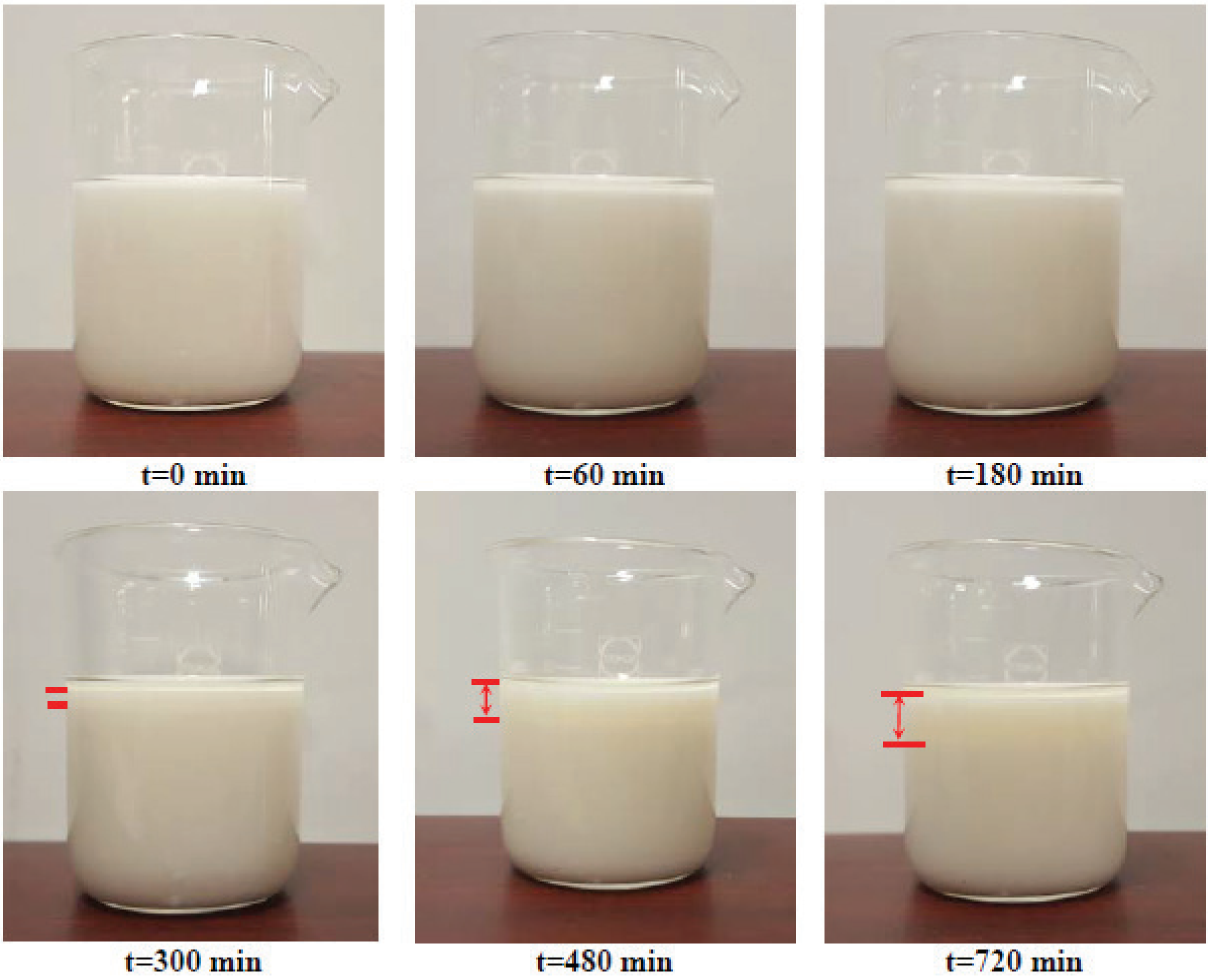

Fig. 1. Stability of primary emulsion with time (2% (V/V) Aliquat 336 in kerosene, 0.1 M NaOH as the internal phase and 3% (V/V) Span 80).

3. Results and discussion

3.1. Mechanism of Cr(VI) pertraction with Aliquat 336 in acidic aqueous solution

The chromate ions may exist in the aqueous phase in different ionic forms ($HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$). Chromate speciation is strongly dependent on the pH and Cr(VI) concentration in the external aqueous phase [41]. A Cr(VI) speciation diagram as function of pH and its concentration in the external aqueous phase is shown in Fig. 2. As can be seen, at pH below 7, $HCrO_4^-$ is the dominant species of both the shown concentrations.

Several previous reports have also reported that CrO_4^{2-} anion prevails in basic or slightly acidic solution while $Cr_2O_7^{2-}$ anions dominate in acidic aqueous solution. In addition, $Cr_2O_7^{2-}$ convert into $HCrO_4^-$ anions in acidic aqueous solution at a total Cr(VI) concentration lower than (1.26–1.74) $\times 10^{-5}$ mol/m^3 [37,41].

The following highly mobile equilibrium is considered for the aqueous solution containing Cr(VI) ions which is extremely depended on pH of solution:

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \leftrightarrow 2H^+ + 2CrO_4^{2-} \tag{1}$$

Thus, in current study, at low concentration of Cr(VI) (100 mg/L), chromium ions mainly existed in the form of $HCrO_4^-$ anions while only a little fraction of $Cr_2O_7^{2-}$ anions coexisted also in feed phase solution.

Pertraction mechanism of Cr(VI) using Aliquat 336 as a carrier is schematically illustrated in Fig. 3. According to this figure, the reaction of $HCrO_4^-$ with Aliquat 336 in order to form a complex at the outer feed phase–membrane interface is shown as follows:

$$R_3CH_3N^+Cl^-_{(mem)} + HCrO^-_{4\,(aq)} \leftrightarrow R_3CH_3N^+HCrO^-_{4\,(mem)} + Cl^-_{(aq)} \tag{2}$$

where $R_3CH_3N^+Cl^-$ represents the Aliquat 336 molecules. The complex $R_3CH_3N^+HCrO_4^-$ is diffused through the membrane phase and at the inner membrane–stripping phase interface is reacted with NaOH as a stripping reagent. The reaction resulted in Aliquat 336 and $HCrO_4^-Na^+$ salts as shown by Eq. (3):

$$R_3CH_3N^+HCrO^-_{4\,(mem)} + NaOH_{(aq)} + \leftrightarrow R_3CH_3N^+OH^-_{(mem)} + HCrO_4^-\,Na^+_{(aq)} \tag{3}$$

Aliquat 336 is transferred back to the outer interface in order to react with $HCrO_4^-$, while $HCrO_4^-Na^+$ was insoluble in membrane phase. $HCrO_4^-Na^+$ cannot diffuse back to outer interface and is surrounded by the internal stripping phase.

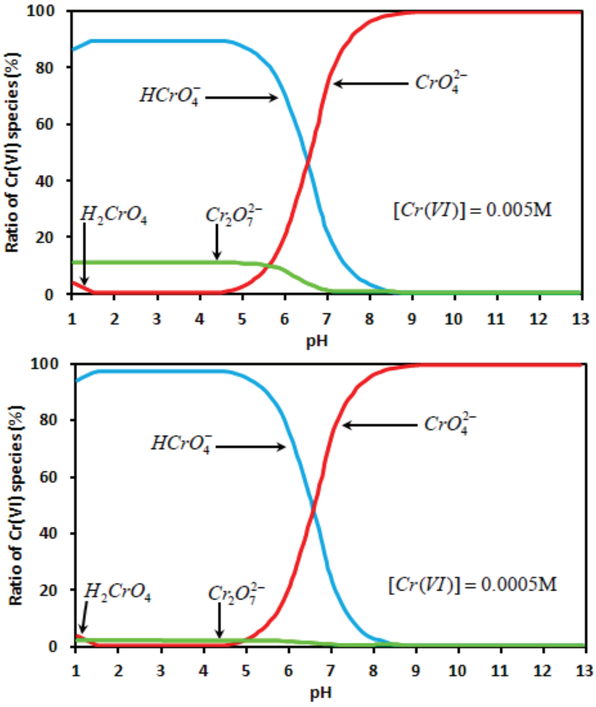

Fig. 2. The Cr(VI) speciation diagram as function of pH at two different concentrations [61].

3.2. Effect of initial feed phase pH

To investigate the influence of initial feed phase pH on the pertraction rate of Cr(VI) through ELM, the studies were conducted with pH variation in the range of 1–4 and the results are depicted in Fig. 4. Initial feed phase pH plays a vital role in pertraction of Cr(VI). In fact, differences in pH values of feed phase and stripping phase is one of the important driving force for the Cr(VI) transport through ELM.

According to Fig. 4, decreasing pH from 4 to 2 leads to about 15.5% increase in the initial pertraction amount of Cr(VI) after mixing time of 2 min. This enhancement is attributed to the simultaneous increasing of H^+ and $HCrO_4^-$ ions concentration in the feed phase by decreasing the feed phase pH. In consequence, the rate of complex formation according to Eq. (2) and the driving force for mass transfer of the complex through the oil–water interface increases which results in growth of Cr(VI) pertraction.

On the other hand, it is observed that the pertraction efficiency of Cr(VI) ion decreases with further reduction in pH values from 2 to 0.5. This behavior may be due to the great increasing of hydrogen ions concentration in feed phase

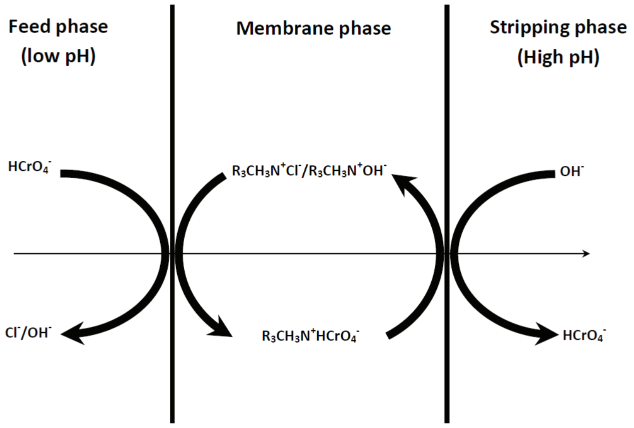

Fig. 3. Pertraction mechanism of Cr(VI) by Aliquat 336.

solution as a result of feed phase pH reduction which gives rise to forming a species like H_2CrO_4 according to the following reaction [41,47]:

$$HCrO_4^- + H^+ \rightarrow H_2CrO_4 \tag{4}$$

The quaternary ammonium salts such as Aliquat 336 exhibit reasonable extraction abilities only toward monovalent oxyanions, that is, $HCrO_4^-$ [48]. Hence, the formed H_2CrO_4 may not ionize completely to form a complex with Aliquat 336, thereby pertraction efficiency decreases with feed phase pH reduction. Moreover, the differences of hydrogen ions concentration between the feed and stripping phase dramatically increases for pH values lower than 2. In this way, osmotic pressure increases leading to membrane swelling augmentation. Consequently, this phenomenon results in membrane layer thinning, making it prone to breakage which causes Cr(VI) pertraction reduction. In fact, Cr(VI) pertraction increases with the increase in hydrogen ion concentration or the decrease in pH up to a limit value. After reaching that point, pertraction of Cr(VI) decreases by more decrease in pH value. The same results were observed by other investigators [1,2,41]. Based on the results, the pH value of 2 was chosen as optimum medium.

It should be noted that pertraction time also affects the stability of emulsion and consequently the extraction extent [49]. According to Fig. 4, pertraction of Cr(VI) increases with time during the pertraction time of 30 min for pH values greater than 2 and at this time extraction efficiency of 93%–98% has been achieved. For pH values lower than 2, pertraction of Cr(VI) decreases after a certain time. This phenomenon is owing to the progressive deterioration of emulsion stability with time. In fact, the properties of the surfactant are reduced at lower values of pH that leads to the faster destabilization of the emulsion and reduction in the pertraction percentage after a certain time [28]. In addition, membrane swelling is considered to be proportional to time and increase in the contact time (beyond a certain time) raised the swelling of the membrane which led to decrease in its performance as reported by Lende and Kulkarni [50] who investigated the effect of contact time on the recovery of tungsten and stability of the membrane in ELM process.

The same results were observed by other investigators [1,2,41]. The pH value of 2 was chosen as optimum medium.

3.3. Effect of surfactant concentration

The influence of surfactant concentration on Cr(VI) pertraction is shown in Fig. 5. According to this figure, Span 80 concentration varied from 1% to 4% (V/V). It was observed that the extraction efficiency is low at the first concentration of Span 80 and increasing Span 80 concentration from 1% to 3% (V/V) gives rise to enhancing the Cr(VI) extraction. Surfactant concentration plays an important role in the stability of the emulsion. If surfactant content in the organic membrane is not enough to stabilize the emulsion, the membrane is broken due to inadequate adsorption of surfactant on the organic–aqueous interface. Although membrane breakage at low concentration of the surfactant does not directly affect the ion transport, it can lead to decrease in extraction efficiency of the ELM procedure as reported in several papers [51–54].

In fact, the membrane breakage represents the rupture of the emulsion and the leakage of the internal reagent and extracted solute through the membrane phase to the external phase which causes a reduction in concentration gradient which is the driving force for mass transfer, thereby lowering the extraction efficiency [55]. The other reason for the decrease in extraction efficiency is that differences in pH values of feed phase and stripping phase, which is one of the important driving force of ELM process, decreases as a result of the leakage of the internal phase to the external phase.

In addition, the membrane breakage causes decrease in the volume of the internal stripping phase, number of internal droplets and stripping molecules which results in decrease in stripping rate of the Cr–carrier complex at the inner interface. Hence, the pertraction efficiency decreases. Results showed

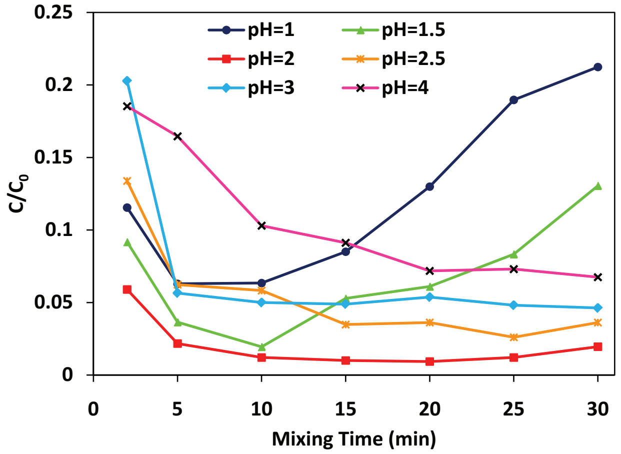

Fig. 4. Effect of initial pH of feed phase on Cr(VI) pertraction (feed concentration: 100 mg/L; Aliquat 336: 2% (V/V); Span 80: 3% (V/V); mixing speed: 450 rpm; treatment ratio: 3; phase ratio: 1:1; stripping solution: 30 mL 0.1 M NaOH).

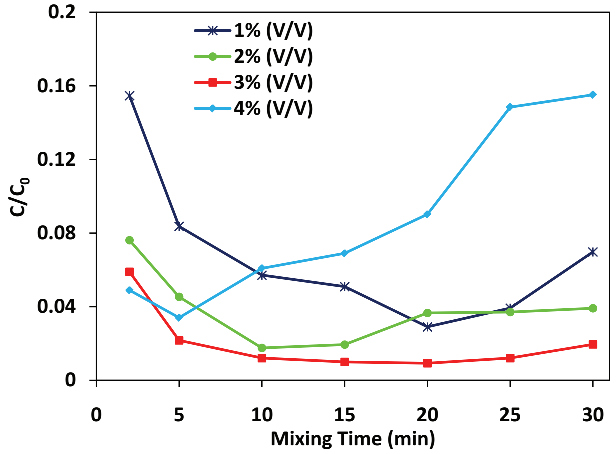

Fig. 5. Effect of surfactant concentration on Cr(VI) pertraction (feed concentration: 100 mg/L; initial pH of feed phase: 2; Aliquat 336: 2% (V/V); mixing speed: 450 rpm; treatment ratio: 3; phase ratio: 1:1; stripping solution: 30 mL 0.1 M NaOH).

that 3% (V/V) of Span 80 caused high stability of emulsion with very low breakage and membrane leakage.

Introducing more Span 80 to the system led to decrease in Cr(VI) pertraction. This is because of the enhancing in mass transfer resistance due to increasing the membrane phase viscosity. Also it led to decreasing the inner droplets movement and rate of Cr(VI) complexation. Furthermore, surfactant hydration, micelles and reverse micelles caused the transport of water molecules from feed phase to stripping phase which is called as osmotic swelling. More concentration of Span 80 resulted in enhancing the osmotic swelling. In this case, stability of emulsion reduced and led to emulsion breakage and more membrane leakage. Consequently, the rate of Cr(VI) pertraction and overall efficiency reduced. The same result has been reported by other investigators [35,56]. The 3% (V/V) of Span 80 was chosen as optimum surfactant concentration.

3.4. Effect of carrier concentration

Carrier concentration has the most important role in overall pertraction behavior among all of the chemicals or parameters in ELM processes. Also, due to expensive price of carriers, the economy of the process is extremely depended on the amount of used carrier. To study the effect of carrier concentration on Cr(VI) pertraction, Aliquat 336 concentration varied from 0.5% to 3% (V/V) and the results are indicated in Fig. 6. According to this figure, increasing Aliquat 336 concentration from 0.5% to 2% (V/V) led to increase in the Cr(VI) pertraction up to 24% after mixing time of 2 min. The reason is that the availability of carrier at the feed–membrane interface increases with an increase in the carrier concentration which results in more Cr–Aliquat 336 complex formation and Cr transport promotion. Hence, the rate and extent of Cr(VI) pertraction increased and the Cr(VI) concentration reduced in feed phase. Similar results were reported by other investigators [4,57].

However, addition of more carriers to the system from 2% to 3% (V/V) cannot improve the efficiency as depicted in Fig. 6. The reduction in Cr(VI) removal efficiency can be related to the growth in the organic membrane phase viscosity which affects the diffusion rate of Cr and its complexes through the membrane phase, according to the following formula for diffusion coefficient [58]:

$$D = \frac{7.4\times10^{-8}(M_B)^{0.5}T}{\mu V_A^{0.6}} \qquad (5)$$

where D is the diffusion-coefficient (cm^2/s), M_B is diluent molar mass (g/mol), T is the absolute temperature (K), μ is the dynamic viscosity of the LM (mPa s) and V_A is the molar volume of solute A at its boiling temperature (cm^3/mol). It can be seen that an increase in membrane phase viscosity decreases the diffusion coefficient and mass transfer coefficient. As a result, membrane mass transfer resistance is increased and the rate of Cr(VI) pertraction is reduced. Similar results were reported by Nosrati et al. [40] and Zaheri et al. [59]. The decreasing in Cr(VI) pertraction efficiency can be also attributable to the reduction in stripping reaction rate. Therefore, Cr(VI) remained unstripped in the complex form of Cr–Aliquat 336 in membrane phase without getting stripped, which could affect the final recovery by the ELM process [1]. In addition, excess amount of carrier promotes the membrane swelling, thereby diluting the stripping phase and decreases the efficiency of ELM process [60]. Therefore, in order to get a better emulsion stability and Cr(VI) pertraction efficiency, 2% (V/V) of Aliquat 336 was considered as optimum carrier concentration.

3.5. Effect of mixing speed

The mixing speed plays a vital role in mass transfer rate of ELM process. To study the influence of mixing speed on Cr(VI) pertraction and obtain the optimal speed, impeller agitation speed was varied from 300 to 500 rpm. Fig. 7 demonstrates the effect of mixing speed on Cr(VI) pertraction. As it can be seen in this figure, when the mixing speed

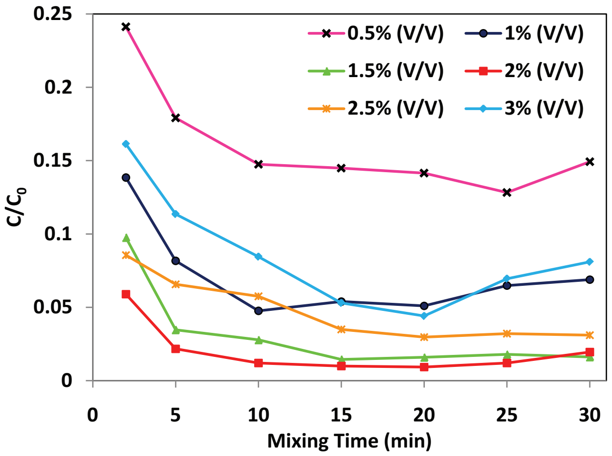

Fig. 6. Effect of carrier concentration on Cr(VI) pertraction (feed concentration: 100 mg/L; initial pH of feed phase: 2; Span 80: 3% (V/V); mixing speed: 450 rpm; treatment ratio: 3; phase ratio: 1:1; stripping solution: 30 mL 0.1 M NaOH).

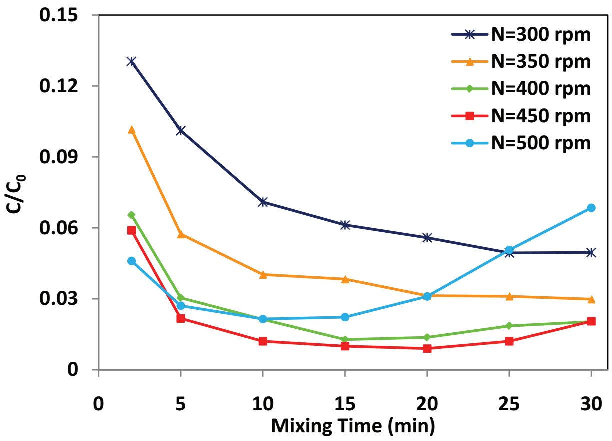

Fig. 7. Effect of mixing speed on Cr(VI) pertraction (feed concentration: 100 mg/L; initial pH of feed phase: 2; Span 80: 3% (V/V); Aliquat 336: 2% (V/V); treatment ratio: 3; phase ratio: 1:1; stripping solution: 30 mL 0.1 M NaOH).

was increased from 300 to 450 rpm, Cr(VI) pertraction was gradually increased. This could be related to enhancing the O/W emulsion globules' disintegration to form smaller globules, and interfacial area of mass transfer between feed phase and emulsion globules [61]. At lower speeds, the size of the emulsion globules was increased and the mass transfer interfacial was diminished.

Further increase in mixing speed over a critical value (in our case was 450 rpm) had a negative impact on the stability of the emulsion, which resulted in a decrease in extent of extraction. At the mixing speed of 500 rpm, the pertraction of Cr(VI) increased within the first 10 min due to formation of smaller size emulsion globules. However, after this minute, the stability of emulsion globules was unfavorably affected by the higher mixing speed simultaneously, which led to emulsion breakage and the pertraction efficiency was decreased. This can be explained as follows: at high mixing speed, the co-transport of water molecules from external to internal phase increased. The osmotic swelling of the membrane increased and made the emulsion unstable. Thus, the breakup of the emulsion droplets was more remarked and leakage of the stripping to feed phase occurred, thereby, reducing the degree of extraction [62]. In addition, increasing the mixing speed led to enhancing the shear stress on emulsion globules, which causes the emulsion breakage. The upper limit on mixing speed is imposed by the breakage of the emulsion droplets close to the tip of impeller due to high induced shear stress [1,22]. At the lower speeds, the membrane stability is higher. For the mixing speeds of 400 and 450 rpm, the emulsion breakage and membrane leakage was observed after 20 and 25 min, respectively. Although, O/W emulsions were more stable in the range of 300–400 rpm, the pertraction efficiency was found less than the speed of 450 rpm. Thus, the 450 rpm was chosen as the optimum mixing speed for the further pertraction process.

Various methods for measuring the drops size in liquid–liquid systems are available. In this study, we employed a photographic technique by means of a high-speed digital camera (Fujifilm, FINEPIX HS10) with shutter speed of 1/4,000 s. For each run, the photographs were taken, the clear images were chosen and emulsion globules diameters were analyzed using AutoCAD software. The real size of globules was determined by analogy between the globules sizes and the diameter of the mixing vessel as a guiding scale which was definite. Then, the Sauter mean diameter (d_{32}) was calculated using the following formula:

$$d_{32} = \frac{\sum_{i=0}^{k} n_i d_i^3}{\sum_{i=0}^{k} n_i d_i^2} \tag{6}$$

where n_i is the number of globules with size of d_i in each run. Fig. 8 shows the effect of mixing speed on the emulsion globules mean diameter.

The diameter of emulsion globule is important particularly in the modeling of mass transfer through ELMs. Consequently, several experimental works have been conducted to predict the mean drop size in batch mode and numbers of correlations have been proposed [63–66]. Most of these investigators correlated their experimental data based on the Hinze–Kolmogorov's theory [67]. According to this theory, the mean drop size in local isotropic turbulent flow field is related to the Weber number with an exponent of –0.6. In the majority of them, the framework of Hinze was applied. Hence, we proposed a correlation for the Sauter mean diameter based on the expression derived by Hinze as following:

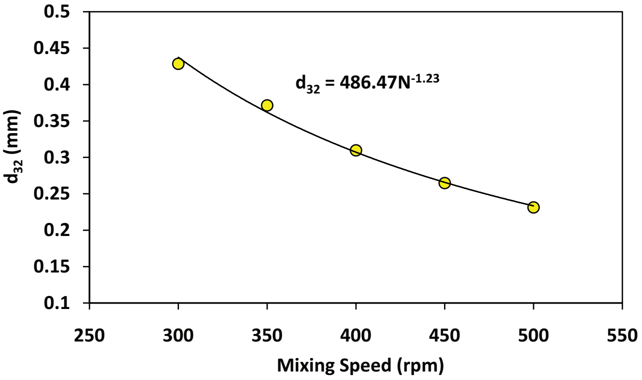

Fig. 8. The effect of mixing speed on Sauter mean diameter of emulsion globules.

$$\frac{d_{32}}{d_I} = 0.0547We^{-0.582} \tag{7}$$

The Weber exponent showed a little deviation from Hinze theory which could be related to the experimental conditions. In order to investigate the correlation accuracy, the average absolute relative deviation (AARD) was calculated using the following equation:

$$\%\text{AARD} = \frac{1}{\text{NE}} \sum_{i=1}^{m} \left| \frac{(d_{32})_{i,\text{exp}} - (d_{32})_{i,\text{cal}}}{(d_{32})_{i,\text{exp}}} \right| \times 100 \tag{8}$$

where NE is the number of experimental runs, $(d_{32})_{i,\text{exp}}$ is the experimental d_{32} and $(d_{32})_{i,\text{cal}}$ is the calculated d_{32} from correlation. The %AARD and R^2 values of Eq. (7) were calculated about 1.3% and 0.99, respectively. It showed acceptable agreement and compatibility with our experimental data and Hinze theory.

3.6. Effect of treatment ratio

Treatment ratio, defined as the volume ratio of the aqueous external solution to the emulsion, plays a major role in determining the efficiency of ELM. It also controls interfacial mass transfer and studies the volume of feed phase that can be treated for the given volume of emulsion. To make an ELM process more cost-effective over the solvent extraction, always the least volume of ELM is considered. The influence of the treatment ratio on Cr(VI) pertraction was investigated experimentally, and results are shown in Fig. 9. The treatment ratio was varied from 1 (V_{ext}:V_{em} = 1:1) to 5 (V_{ext}:V_{em} = 5:1). According to Fig. 9, increasing the treatment ratio from 1 to 3 led to enhancing the pertraction efficiency. In fact, the proper mixing of phases owing to fewer portions of the viscous emulsion phase caused reduction in the size of the emulsion globules [68,69]. Thus, the thickness of the membrane phase was decreased, which promoted the Cr(VI) diffusing process and resulted in more pertraction efficiency.

On the other hand, increasing the treatment ratio from 3 to 5 had negative influence on pertraction efficiency and caused reduction in pertraction rate of Cr(VI). This is owing to the fact that the number of available globules of emulsion and interfacial area of mass transfer per unit volume of external phase was reduced. Further increase in the treatment ratio led to more membrane swelling due to the large number of water molecules presented in feed phase. The surfactant would also provide the co-transport of water, thus diluting the internal phase. Additionally, when the feed phase content was increased, the number of transported complexes was raised. In this case, there would be the lack of stripping reagent in internal phase to react with the solute transported through the LM. Therefore, the back extraction was limited and the Cr–Aliquat 336 complexes were accumulated in membrane phase. As a result, the emulsion breakage and membrane leakage were increased and the Cr(VI) concentration of the feed phase was enhanced. Similar results were obtained by Chaouchi and Hamdaoui [70]. Consequently, the treatment ratio of 3 was chosen as the optimum value for the process.

According to aforesaid results, the optimum operating conditions for Cr(VI) pertraction was achieved and summarized in Table 2. At optimum conditions, pertraction of Cr(VI) was investigated and results demonstrated that 99% of Cr(VI) could be extracted within 10 min in such a way that more than 94% of it is attributed to the first 2 min. Also, the stability of emulsion was found to be maximum which caused least membrane leakage.

3.7. Effect of diluent type

Sunflower oil is a lipid material derived from sunflower seeds which is non-toxic, non-volatile, biodegradable and renewable. It possesses properties such as low specific gravity, high flash point, low melting point and low electric constant which makes it non-polar and allows it to be immiscible in the external phase of ELM. Sunflower oil, like the other vegetable oils, predominantly consists of non-polar lipids (>92%) and the other minor components such as polar lipids (phospholipids and sphingolipids) (<4%), free fatty acids (<2%), unsaponifiable matters contains tocopherols, sterols and waxes, among other substances. The non-polar lipids are mainly composed of triglyceride (triacylglycerol), which is glycerol molecule with three long chain fatty acids attached at the hydroxyl groups via ester linkage. It has various structures depending on the fatty acids attached at the hydroxyl groups. Table 3 presents the percentage composition of fatty acids in regular sunflower oils. According to this, oleic and linoleic acids (unsaturated fatty acids) are the major fatty acids form in typical triglycerides of sunflower oils. Hence, trilinolein (36.3%) and oleo-dilinolein (29.1%) are the most abundant triacylglycerols of regular sunflower oil [43,71].

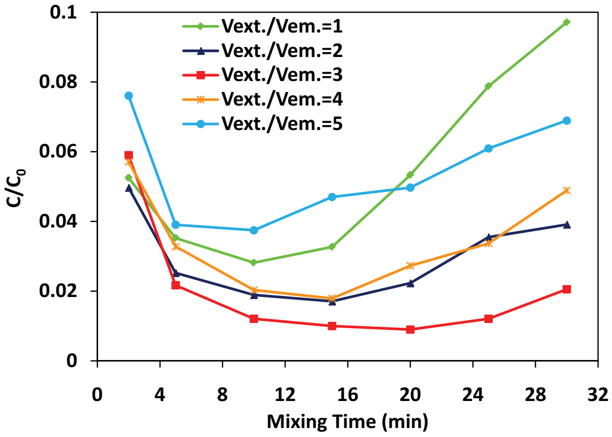

Fig. 9. Effect of treatment ratio on Cr(VI) pertraction (feed concentration: 100 mg/L; initial pH of feed phase: 2; Span 80: 3% (V/V); Aliquat 336: 2% (V/V); mixing speed: 450 rpm; phase ratio: 1:1; stripping solution: 30 mL 0.1 M NaOH).

The membrane diluent mainly affects the viscosity, ion transport and the membrane performance. The emulsion stability, extraction efficiency, enrichment factor and membrane swelling depend on the organic diluent. The polarity of the diluents is the most important parameter determining the membrane efficiency. However, the membrane stability is the major choice to be made in diluent selection step. Thus, it seems to be difficult to arrive at a firm opinion to this effect. It was reported by other researchers [72,73].

Table 2
Optimum operating conditions

Parameter	Value
Feed concentration, mg/L	100
Surfactant concentration (Span 80), % (V/V)	3
Carrier concentration (Aliquat 336), % (V/V)	2
Initial pH of feed phase	2
Mixing speed, rpm	450
Treatment ratio	3
Mixing time, min	10
Phase ratio	1:1

Table 3
Fatty acid composition (wt%) of regular sunflower oils [43]

Fatty acid	*C:D*	Composition (wt%)
Lauric	12:0	≤0.05–0.1
Myristic	14:0	≤0.05–0.2
Palmitic	16:0	5.0–7.6
Palmitoleic	16:1	≤0.05–0.3
Stearic	18:0	2.7–6.5
Oleic	18:1	14.0–39.4
Linoleic	18:2	48.3–74.0
Linolenic	18:3	≤0.05–0.3
Arachidic	20:0	0.1–0.5
Gadoleic	20:1	≤0.05–0.3
Eicosadienoic	20:2	≤0.05
Behenic	22:0	0.3–1.5
Lignoceric	24:0	≤0.05–0.5

Note: C, number of carbon atoms; *D*, number of double bonds.

Pertraction of Cr(VI) with Aliquat 336 in various diluents is shown in Fig. 10. The trend in the change of the Cr(VI) concentration is similar with increasing mixing time, however, at the same mixing time; the values of the concentrations are different. According to this figure, sunflower oil resulted in fastest and the most efficient pertraction of Cr(VI) in comparison with other petroleum-based diluents. The pertraction efficiency of Cr(VI) by the different types of diluent decreases in the order: sunflower oil, kerosene, butyl acetate, toluene, *n*-hexane. Compared with kerosene, butyl acetate, toluene and *n*-hexane, Cr(VI) pertraction using sunflower oil as diluent for Aliquat 336 is about 4%, 6%, 10% and 15% higher, respectively. Furthermore, introducing sunflower oil can reduce toxic and hazardous chemicals level in wastewater.

In order to compare the viscosity effect and mass transfer coefficients, the mass transfer resistances were considered as follows [74,75]:

$$\frac{1}{K_{\text{od}}} = \frac{1}{k_L} + \frac{1}{k_{\text{int}}} + \frac{1}{mk_m} \tag{9}$$

where K_{od} is the overall mass transfer coefficient, k_L is the external phase mass transfer coefficient, k_{int} is the mass transfer coefficient of interfacial film, k_m is the mass transfer coefficient of the organic membrane phase and m is the external phase distribution coefficient.

The K_{od} was calculated by the following equation [76]:

$$K_{\text{od}} = -\frac{d}{6t}\ln\left(1-E\right), \quad E=\frac{C_{e,0}-C_e}{C_{e,0}} \tag{10}$$

where E is the extraction ratio, d is the mean diameter of emulsion globule, t is the time of extraction, $C_{e,0}$ is the initial concentration of external phase and C_e is the external phase concentration at time t.

The mass transfer coefficient (k_L) of the external phase in agitated vessels was estimated from a correlation proposed by Skelland and Lee [77]:

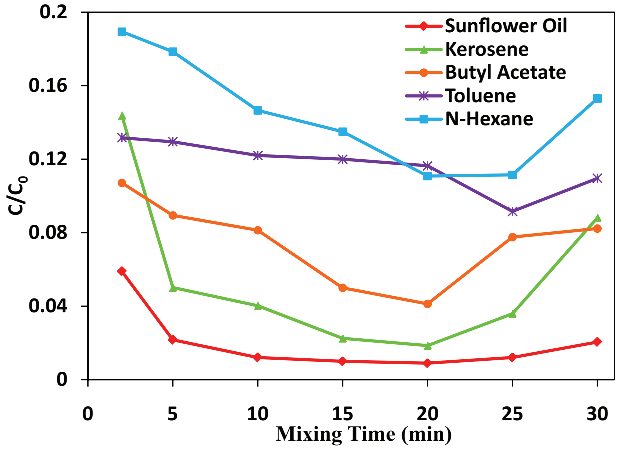

Fig. 10. Effect of diluent type on Cr(VI) pertraction (feed concentration: 100 mg/L; initial pH of feed phase: 2; Span 80: 3% (V/V); Aliquat 336: 2% (V/V); mixing speed: 450 rpm; treatment ratio: 3; phase ratio: 1:1; stripping solution: 30 mL 0.1 M NaOH).

$$\frac{k_L}{\sqrt{ND}} = 2.932\times10^{-7}\left(\frac{V_i+V_m}{V_i+V_m+V_e}\right)\left(\frac{d_I}{T}\right)^{0.548}\text{Re}^{1.371} \tag{11}$$

where N is the mixing speed (rpm), D is the diffusion coefficient (m^2/s), V_i is the volume of internal phase, V_m is the volume of organic phase, V_e is the volume of external phase, d_I is the impeller diameter, T is the mixing tank diameter and Re is the Reynolds number based on continuous phase ($\text{Re} = Nd_I^2\rho_c/\mu_c$).

The k_m was determined using the Teramoto et al.'s model [78] and Lee and Hyun's model [79]:

$$k_m = \frac{D_m}{\delta} \tag{12}$$

Effective diffusivity in emulsion globule (D_m) was calculated by the Wilke–Chang equation [58]. The δ (membrane thickness) can be defined by using d_{32} and the volume fraction of the internal aqueous phase in the emulsion phase as follows [80]:

$$\delta = 0.0765d_I(1-\phi_o^{1/3})We^{-0.6} \tag{13}$$

where ϕ_o is the volume fraction of internal phase in emulsion phase and We is the Weber number. Although determining the interfacial resistance in systems involving surfactants is important, it is difficult to measure experimentally. For this purpose, the k_{int} was estimated according to Eqs. (10)–(12).

Calculated values of mass transfer coefficients and viscosity effect of different solvents are presented in Table 4. According to it, mass transfer coefficient in sunflower oil–based ELM is lower than the others. This is due to the higher viscosity of sunflower oil compared with the other solvents. In fact, higher viscosity results in lower diffusion coefficient, thereby decreasing the mass transfer coefficient. On the other hand, higher viscosity produces more stable membrane and higher extraction compared with the other solvents. This finding is in agreement with the other authors who confirmed that the lower viscosity has a negative effect on the emulsion stability and thus it may cause lower transport rates and poor performance of ELM process [81].

The extraction efficiency obtained at the optimum condition in this work was compared with that in the other papers on Cr(VI) pertraction through LM by using Aliquat 336 and the results are presented in Table 5. As observed, the extraction efficiency in this work is higher than that in the SLM systems and also the other ELM systems reported. In fact, using sunflower oil in ELM process not only is beneficial from environmental and economic point of view but also has resulted in more extraction efficiency compared with them.

3.8. Membrane stability

In order to investigate the membrane stability, the measurement of swelling and breakage of the membrane were

Table 4
Mass transfer coefficient for different solvents

Solvent	μ (mN s/m^2)	*D* (m^2/s)	k_L	k_m	K_{od}	k_{int}
Kerosene	1.64	3.62E-10	6.12E-05	6.58E-04	5.51E-04	5.38E-04
n-hexane	0.297	1.42E-09	6.12E-05	2.59E-03	2.21E-03	2.18E-03
Toluene	0.55	7.93E-10	6.12E-05	1.44E-03	1.22E-03	1.20E-03
Butyl acetate	0.685	7.15E-10	6.12E-05	1.30E-03	1.12E-03	1.10E-03
Sunflower oil	39.14	3.44E-11	6.12E-05	6.58E-04	5.97E-04	5.83E-04

Table 5
Extraction efficiency of different systems for Cr(VI) pertraction

Method	Diluent	Carrier	Stripping phase	Surfactant	%Extraction	Reference
ELM	Sunflower oil	Aliquat 336	NaOH	Span 80	99	This work
ELM	Hexane	Aliquat 336	NaOH	Span 80	90	[48]
ELM	Kerosene	Aliquat 336 + Tri-*n*-octyl amine	NaOH	Span 80	98	[82]
SLM	Kerosene	Aliquat 336	NaOH	–	94.63	[83]
SLM	Sunflower oil	Aliquat 336 + TBP	NaOH	–	95.2	[84]

considered. A tracer method was used to determine the breakage and swelling simultaneously. KCl was used as tracer in internal phase. The concentration of K$^+$ in both external and internal phases was measured and analyzed by ICP-AES (Thermo Jarrell Ash, Model Trace Scan, Canada). The membrane swelling and breakage are determined by the following equation [85]:

$$\eta = \left[\left(1 - \frac{C_{e,I}}{C^0_{i,I}}\right)\left(\frac{C^0_{i,I} - C_{i,I}}{C_{i,I} - C_{\mathrm{e},I}} - \frac{C_{e,I}(1 + R^0_{\mathrm{oi}})}{R^0_{\mathrm{ew}}(C_{i,I} - C_{\mathrm{e},I})}\right) + \frac{C_{e,I}(1 + R^0_{\mathrm{oi}})}{R^0_{\mathrm{ew}} C^0_{i,I}}\right] \times 100\% \quad (14)$$

$$\varepsilon = \frac{C_{\mathrm{e},I}}{C^0_{\mathrm{i},I}(C_{i,I} - C_{e,I})}\left[\frac{1 + R^0_{\mathrm{oi}} + R^0_{\mathrm{ew}}}{R^0_{\mathrm{ew}}} C_{\mathrm{i},I} - C^0_{\mathrm{i},I}\right] \times 100\% \quad (15)$$

where η is the swelling ratio and ε is the breakage ratio of the membrane; $C^0_{i,I}$, $C_{i,I}$, $C_{e,I}$ are the initial concentration of tracer in the internal phase, the concentration of tracer in the internal and external phase at time *t*, respectively. R^0_{oi} and R^0_{ew} are the initial volume ratio of the oil phase to the internal phase and the initial volume ratio of the external phase to the emulsion, respectively.

Fig. 11 demonstrates the swelling and breakage ratios of membrane along mixing time. Membrane swelling and breakage increased with increase in mixing time. This can be attributed to the fact that longer mixing time caused higher water transport inside internal phase which led to membrane swelling [86,87]. As a result, swelling caused dilution of the internal phase, reduction in the driving force, changing the rheological properties of the emulsion and increasing in membrane breakage. According to figure, at the mixing time of the 10 min, the swelling and breakage of the membrane was measured about 17.5% and 8.4%, respectively.

At the end of the experiments, the remained emulsion was collected and heated to certain temperature which resulted in separation of membrane organic phase and internal aqueous phase. Fig. 12 demonstrates the demulsification efficiency of Span 80 at different temperatures. As can be seen in Fig. 12, demulsification efficiency is about 70% at 80°C. It showed that the heat-induced demulsification of Span 80 is practical. Similar result has been reported by other investigators [87,88].

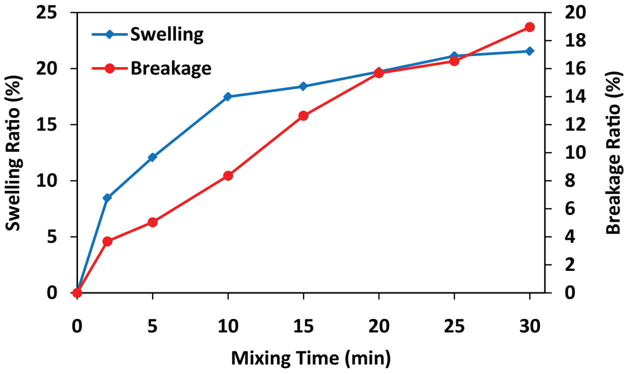

Fig. 11. Swelling and breakage ratios of membrane along mixing time.

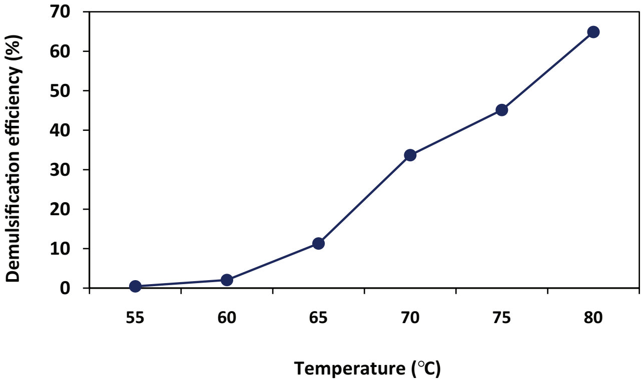

Fig. 12. The demulsification efficiency at different heating temperatures.

4. Conclusion

In this work, the pertraction of Cr(VI) by ELM using sunflower oil as cheap, safe and green solvent and Aliquat 336 as an extractant was investigated. First of all, the influence of various parameters on the extraction of chromium(VI) has been investigated. Then, the pertraction experiments under experimentally determined conditions were conducted and optimum condition was obtained. Finally, results were compared with other common petroleum-based diluents. The obtained results can be summarized as following:

- The chromium(VI) pertraction was affected by various parameters like the initial pH of feed solution, surfactant and carrier concentrations, mixing speed and treatment ratio.
- Sunflower oil revealed high potential for pertraction of toxic chromium metal and also made the ELM process economic and more environmentally friendly.
- Although the calculated mass transfer coefficient (K_{od}) in the water and oil layers at the external interface of emulsion drop for sunflower oil–based ELM was lower than the other solvents, its higher viscosity results in more stable membrane and higher extraction compared with the other solvents.
- By applying optimum experimentally determined conditions, 99% of Cr(VI) found to be extracted within 10 min in such a way that more than 94% of them were extracted within first 2 min and emulsion showed maximum stability.
- In order to predict the emulsion globule size, an empirical correlation was provided as function of mixing speed.
- The results demonstrated the validity of ELM processes using eco-friendly and cost-effective green solvents for efficient pertraction of Cr(VI) from wastewater.

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