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Removal of chromium(III) from aqueous solutions using an advanced extraction technique (AET)

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ABSTRACT

The removal of chromium(III) from aqueous solution using an advanced extraction technique (AET) such as emulsion liquid membrane (ELM) was investigated. Tri-butyl phosphate (TBP) and tri-n-octylphosphine oxide (TOPO) as carriers, commercial kerosene as an organic solvent, sorbitan monooleate (Span 80) as hydrophobic surfactant agent, sodium hydroxide, and sulfuric acid or ammonium persulfate as a stripping phase were used. The influence of the carrier concentration (5–30% w/w), surfactant (2–8% w/w), and external phase (5–50 mg/L), contact time, internal phase type (H_2SO_4, $(NH_4)S_2O_8$ or NaOH), stirring speed (100–1200 rpm), W/O emulsion/external aqueous phase volume ratio (0.05–1) and the diluent type (hexane, heptane, and kerosene) on the extraction process was investigated. The obtained results showed that, at the optimum condition, practically all the chromium (III) ions were removed from the feed solution during the first 25 min of operational time. The best TBP/TOPO ratio in the organic phase that conducted to very good removal efficiency (≥99%) and excellent emulsion stability was 90/10% (w/w). The use of ultrasound irradiations in the emulsification step enhanced the emulsion stability. The US-ELM process appears to be a suitable alternative to develop a method for heavy metal ions removal from aqueous solution, and has been identified to give highest heavy metals recovery.

Keywords: Advanced extraction technique (AET); Emulsion liquid membrane (ELM); Chromium; Tri-butyl phosphate (TBP); Ultrasound

1. Introduction

Chromium is a toxic heavy metal that is usually produced during leather tanning, metallurgy, electroplating, and steel making. The chromium oxidation states range from −2 to + 6 and the trivalent and hexavalent states are the most prevalent states in the environment [1]. These two oxidation states have different chemical, biological, and environmental properties [2]. Though Cr(III) compounds are not toxic as Cr(VI) compounds, the possibility of their oxidation to Cr(VI) is a potential hazard. Therefore, it is of great importance to adopt novel technologies to eliminate them from wastewater in order to reach acceptable limits as set by governmental regulations, and at the same time allowing for the reuse of the recovered solute.

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Many methods have been developed for the removal and recovery of chromium from wastewaters. Only a little attention has been paid to the removal of trivalent forms of chromium [3–11] by advanced extraction techniques (AETs) such as emulsion liquid membrane (ELM) or surfactant liquid membrane (SLM). ELM is one of the promising techniques for the separation of such effluents, invented by Li and Norman [12]. The ELM process combines extraction and stripping steps in one unit, which leads to simultaneous purification and concentration of the solute. ELMs are not only an important method for separation, concentration, and recovery, but also of fundamental importance from an environmental engineering point of view in understanding the transport mechanism of different species.

ELM is created by forming a stable emulsion, such as water-in-oil emulsion, between two immiscible phases, followed by dispersion of the emulsion into a third continuous phase by agitation. The membrane phase is the oil phase that separates the encapsulated, internal aqueous droplets in the emulsion from the external continuous phase. The organic membrane phase contains an extractant (extracting agent), a diluent (solvent) and a surfactant (emulsifier). The internal aqueous phase contains a stripping agent. The external, continuous phase is the aqueous feed solution containing the target species. Target species in the aqueous feed phase is transferred via the membrane phase (barrier film) into the internal phase during an extraction step. Membrane (ELM) has the advantage of having fast extraction rates, high specific surface area, high removal efficiency, and low energy input. In the ELM process, both extraction and stripping steps are combined in a single stage thereby achieving concentration and separation of the solute from the aqueous solutions to a very low level. Furthermore, it has been considered as a promising technology for heavy metal ions separation and concentration, when the component to be removed is present in very low concentration.

Relatively few works have addressed the combined effect of ultrasound in all the ELM process steps (emulsification, extraction, and demulsification) [13,14]. The utilization of ultrasound for the production of water-in-oil (W/O) emulsions in water/oil/water system results in the formation of an *in situ* emulsion, when the cavitational events are initiated. Various methods have been developed for the removal of heavy metal ions from wastewater. These methods include a conventional ELM [15–20], which have also been applied for dyes separation [21–24], and pharmaceutical separations from aqueous solution [25]. Ultrasonic-assisted ELM offers a promising technology for the removal of heavy metal ions from aqueous solution. ELM enhances the extraction efficiency and shortens the equilibrium time substantially. In this study, the effectiveness of ultrasonic-assisted ELM technology to eliminate Cr(III) from aqueous solution was investigated. The Cr(III) removal was investigated at different conditions, such as carrier concentration, surfactant concentration, external phase concentration, contact time, internal phase type, stirring speed, W/O emulsion/external aqueous phase volume ratio, agitation energy, diluents type, and TBP, and/or TOPO as extracting agent. The influence of TOPO–TBP composition ratio on extraction efficiency is also studied. The chromium ion transport mechanism derived from the experimental results was proposed.

2. Experimental

2.1. Materials

The non-ionic surfactant Span 80 (sorbitan monooleate) purchased from Aldrich was used as an emulsifier. Carriers TBP (Tri-butyl phosphate) and TOPO (tri-n-octylphosphine oxide) were used without further purification. Commercial hexane, heptane, and kerosene produced by Fluka were used as diluents. A stock solution of chromium(III) purchased from Fluka was prepared by dissolving chromic nitrate ($Cr(NO_3)_3$) in deionized water. Other chemical reactants such as sulfuric acid, hydrochloric acid, sodium hydroxide, and ammonium persulfate purchased from Sigma were of analytical grade.

2.2. Membrane preparation and stability tests

The ELM used in this work is prepared by mixing a requisite volume of the organic phase which contained the extractant with Span 80 as a surfactant in the diluent (hexane, heptane, or kerosene). Internal aqueous phase were prepared by dissolving the required amount of the appropriate solution (H_2SO_4, $(NH_4)S_2O_8$ and NaOH) in deionized water. Water-in-oil (W/O) emulsion was formed by adding together the internal phase and the organic membrane phase in a 150 mL glass under an intense emulsification for 3 min by means of ultrasonic processor with an operating frequency of 22.5 kHz. A 3 mm diameter titanium probe head was used throughout. The experimental set-up is shown in Fig. 1(a). A 20 mL of the prepared W/O emulsion was then added to 100 mL of external aqueous in a 250 mL cylindrical jacketed glass vessel. The ELM system was stirred by means of ultrasonic system operated at low frequency or with a mechanical agitator of the type Junke &

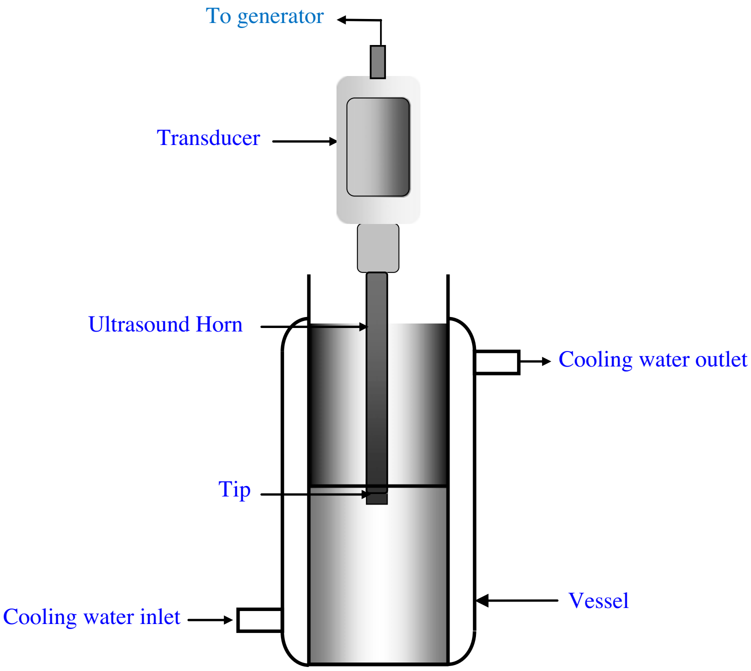

Fig. 1(a). Experimental set-up for ultrasound-assisted preparation of the W/O emulsion.

Kunkel RW20 (120 W). The agitator used was equipped with a four-paddle impeller (20 mm diameter). The pH of the aqueous solution was measured continuously using WTW pH-meter. The leakage of the internal phase ions to the external aqueous phase results in a membrane break-up due to the change in

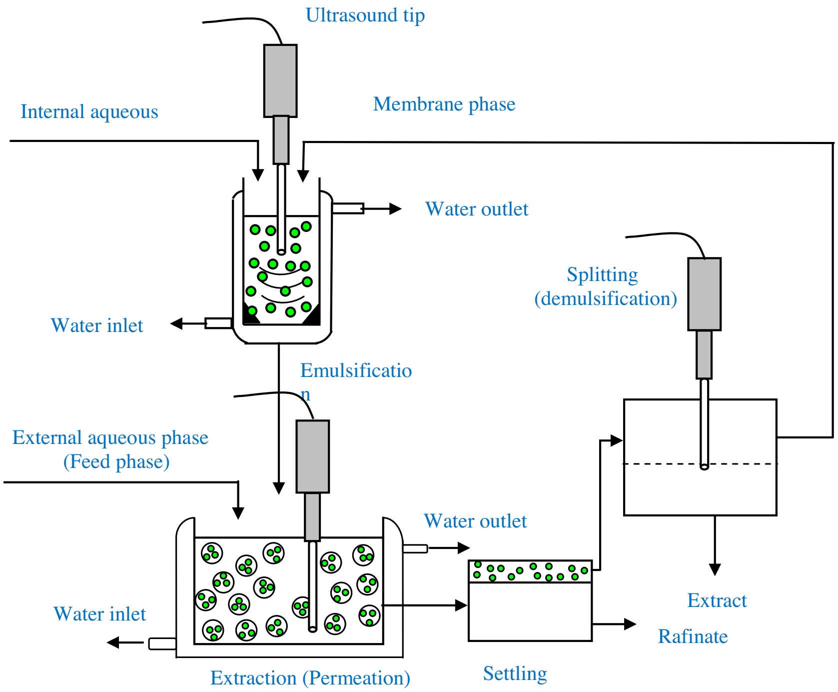

Fig. 1(b). The advanced extraction technique (US-ELM).

the initial pH of the external aqueous solution. All experiments were carried out at regulated temperature of 25 ± 1˚C.

2.3. Analytical method

Known sample portions were withdrawn from the external phase, and the chromium(III) concentrations was analyzed by atomic absorption spectrophotometry (AAS, Shimadzu A. A-6601 F, Atomic Absorption Flame Emission Spectrophotometer). All the experiments were duplicated and the reproducibility was 3% on average for selected samples. The pH of the aqueous solution was determined by WTW pH-meter (pH-730 equipped with SenTix 41 electrode). Acoustic power dissipated in the reactor was determined using standard calorimetric method [26,27].

2.4. Chromium permeation through the membrane

Permeation experiments were carried out by mixing the W/O emulsion and the aqueous phase in a volume ratio of 1/5 (double emulsion). The agitation was performed with a magnetic stirrer or by sonication for different contact times (Fig. 1(b)). The content was stirred in order to disperse the W/O emulsions in the external phase at variable speeds (100–1,200 rpm) for different contact times to make the W/O/W double emulsions. The aqueous phase consisted of 50 mg/L of Cr(III) aqueous solution unless otherwise stated. Extraction experiments were carried out in a batch reactor designed specifically to prevent vortexing phenomenon. Once started, the permeation experience testing samples of the external aqueous phase were regularly taken at various time intervals for analysis. Extraction efficiency was calculated using the following equation:

$$\text{Extraction efficiency } (\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

where, C_0 is the initial concentration of pollutant in the external phase (mg/L) and C is the concentration of pollutant in the external phase at any time (mg/L).

3. Results and discussion

3.1. Optimization of the operation parameters for the chromium(III) extraction by ELM

To study chromium(III) removal efficiency, it is necessary to optimize various parameters that can affect the process. The optimized parameters were the carrier concentration, the carrier composition, the contact time, the stirring speed or the ultrasonic power, the internal phase concentration, the type of internal phase, the surfactant concentration, emulsion phase/external aqueous phase volume ratio (treatment ratio), the diluent type and the solute concentration.

3.1.1. Effect of carrier concentration on the removal efficiency of chromium

The use of TBP as a carrier facilitates the heavy metal ions transport through the membrane phase. As shown in Fig. 2, the effect of TBP concentration on the removal efficiency of chromium was studied using different concentrations of TBP from 2 to 30% (w/w). The other experimental conditions (unless otherwise mentioned) were: chromium(III) concentration in the external aqueous phase, 50 mg/L; emulsion volume, 20 mL; internal phase/organic phase volume ratio, 1; emulsification time, 3 min; ultrasound power, 40 W; stirring speed, 200 rpm; Span 80 concentration, 5% w/w; W/O emulsion/external aqueous phase volume ratio, 0.4; internal phase concentration, pH 4; kerosene and contact time of 18 min. The Cr(III) removal efficiency increases as the TBP concentration increases up to 20% (w/w). This effect is due to the increase of the

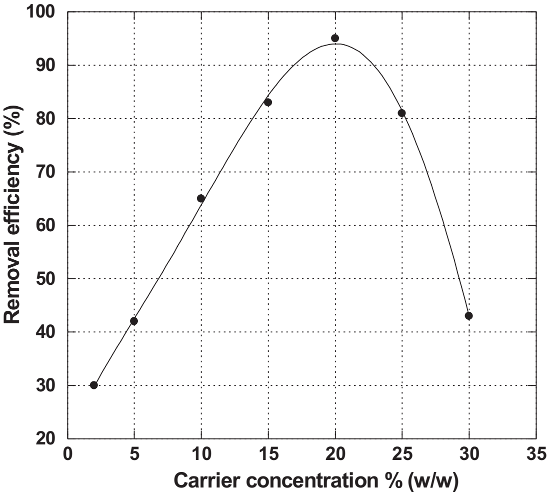

Fig. 2. Effect of carrier concentration on the removal efficiency of chromium(III) (50 mg/L) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration: 2–30% w/w; volume ratio of W/O emulsions to external phase: 0.4; internal phase concentration H_2SO_4 pH 4; diluent, kerosene; contact time, 18 min; Distance of the tip horn from the bottom of vessel: 20 mm).

formation of TBP/chromium complexes with increasing TBP concentration in the prepared ELM. As a result, the diffusion rate of chromium through ELM increases. Further increase in the TBP concentration (20–30% (w/w)) showed a decrease in extraction efficiency of Cr(III). This may be attributed to the increase of osmotic swelling and mass transfer resistance induced by increasing the extractant concentration. Similar results were obtained by Kumbasar et al. [28] and Luo et al. [29]. It is well known that the carrier is the most expensive agent among the other components involved in the liquid membrane system. These results and the above comments indicate that 20% (w/w) of TBP in the organic phase is the most adequate quantity to obtain the highest removal, so it was decided to carry out the rest of the work using this concentration.

3.1.2. *Effect of using a second carrier in the membrane composition on the removal efficiency of chromium Cr (III)*

The use of TOPO-TBP binary system in the membrane composition allows improving the solute transport efficiency through the membrane film. This parameter was subsequently studied by several researchers [30,31]. The removal efficiency of chromium (III) was carried out by two carriers. The removal efficiency of the chromium(III) with different TOPO-TBP concentration in various compositions (weight ratio) is described in Fig. 3. It is evident that at TOPO-TBP concentration values between 2 and 20, the extraction efficiency increases sharply and reached a maximum value at a carrier concentration of 20%. A sharp decrease in the removal efficiency was then observed. Under the range investigated, it can be observed that good extraction efficiency was obtained in the range of TOPO-TBP composition ratio analyzed; however, the carrier composition of 10% TOPO and 90% TBP showed the higher removal of chromium. The results confirm that the diffusion of heavy metal ions through the membrane was governed by the formation of complex solute extractant. The transport mechanism of the chromium through the membrane was found to be positively influenced by the presence of the second carrier. Thus, an organic phase (membrane) composed of 10% TOPO and 90% TBP was chosen for the rest of the experiments.

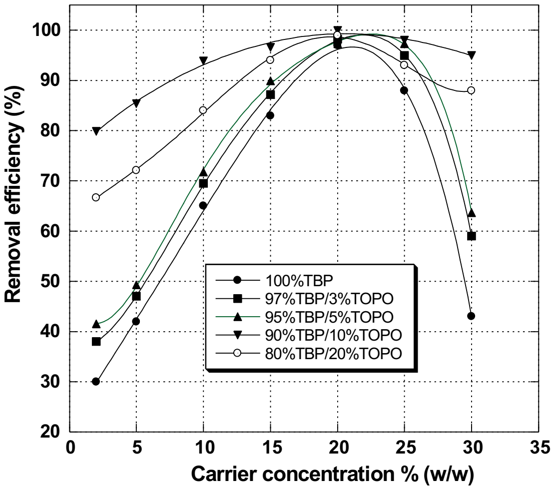

Fig. 3. Effect of carrier composition on the extraction efficiency of chromium(III) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 20 W, concentration of Span 80, 4% w/w; carrier concentration, 2–30% w/w; volume ratio of W/O emulsions to external phase, 0.4; internal phase concentration (H_2SO_4), pH 4; diluent, hexane; contact time, 18 min; Distance of the tip horn from the bottom of vessel, 20 mm).

3.1.3. *Effect of contact time on the removal efficiency of chromium(III) at different ultrasonic powers*

The effect of ultrasound power on the removal efficiency of chromium(III) is presented in Fig. 4. From Fig. 4, at different contact time, it is observed that with increase in the ultrasound power, the removal efficiency increased up to a certain limit. As the ultrasound power increases, the removal efficiency increases due to the micro-streaming phenomenon. Initially, an efficient emulsification occurs with increase in ultrasound power and time. When the ultrasound power and contact time increases, the shear force, which acts on the large emulsion globule, makes the globules smaller for which the surface area available for permeation of Cr(III) ion increases. Also, the emulsion stability increases. Increasing the stirring speed above a critical value (40 W) not only decreases the extraction efficiency slightly, but also affects the stability of the emulsion and makes the emulsion unstable. Beyond this value, the coalescence phenomenon is more significant. The latter is in a good agreement with the results of Freitas et al. [32], they found that oil droplets of 5–10 μm diameters could be observed in an emulsion processed at an ultrasonic power of 25 W and practically no droplets were microscopically visible at 32 W. The equilibrium time for the extraction process of chromium(III) observed to be 18–20 min.

3.1.4. *Effect of stirring speed on the removal efficiency of chromium(III) and comparison with ultrasonic powers*

The effect of the agitation speed on the extraction efficiency of chromium(III) is described in Fig. 5. The

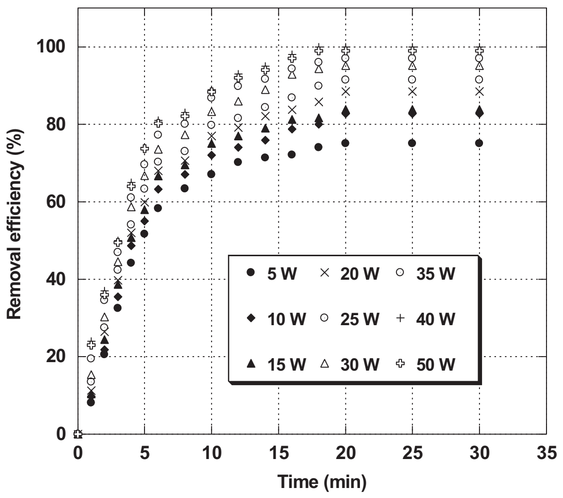

Fig. 4. The removal efficiency of chromium(III) by AET as a function of the contact time and at different ultrasonic power (W): (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration, 20% w/w; volume ratio of W/O emulsions to external phase, 0.4; internal phase concentration (H_2SO_4), pH 4; diluent, hexane; contact time, 18 min; distance of the tip horn from the bottom of vessel, 20 mm).

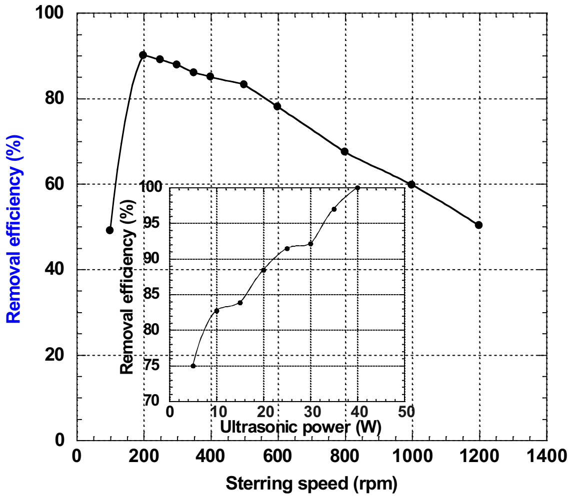

Fig. 5. Effect of stirring speed compared to ultrasonic power on the removal efficiency of chromium(III) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration, 20% w/w; volume ratio of W/O emulsions to external phase, 0.4; internal phase concentration (H_2SO_4), pH 4; diluent, hexane; contact time, 18 min; distance of the tip horn from the bottom of vessel, 20 mm).

experimental conditions are summarized as: surfactant concentration; 4% (w/w), carrier concentration; (90% TBP + 10%TOPO) 20% (w/w), commercial kerosene; 76% (w/w), internal aqueous phase, emulsification power; 40 W and emulsification time of 3 min. Fig. 5 shows that an increase in the stirring speed from 100 to 200 rpm results in an increase in the removal efficiency from 49 to 90%. By increasing the stirring speed from 100 to 200 rpm, the shear force, which acts on the emulsion globules, increases and this makes the globules smaller. Consequently, increasing the agitation speed not only increases the area for mass transfer, but also the removal efficiency increase. However, when the stirring speed increases from 200 to 500 rpm, the removal efficiency of chromium(III) decreased to 83.20%. This might be due to the reduction of both the droplets size and the membrane thickness which would affect the emulsion stability. A significant decrease in the removal efficiency is observed when the stirring speed increases above 500 rpm. The results indicated that 50.2% of chromium(III) was removed from their solutions when the stirring speed was 1,200 rpm. Increasing the stirring speed above a critical value (500 rpm), the stability of the emulsion decreased considerably with a corresponding decrease of removal efficiency. An excessive stirring speed produced coalescence and ultimately collapse of globules, making the primary emulsion unstable. Therefore, the optimum value for stirring speed is found to be 200 rpm.

The energy consumption for specific degree of removal is considered to be one of the factors to compare among the mixing techniques used in this study. The amounts of chromium(III) extracted when the ELM system was stirred with a magnetic stirrer is always less than that removed when ultrasonic irradiation was applied at low frequency (22.5 kHz) (Fig. 5). When the ELM system was subjected to ultrasonication (40 W), it was observed that 99% removal was achieved, while only 90% removal could be obtained using mechanical agitation (120 W). It is evident that ultrasound irradiation plays a primary role in the removal process, due to the micro-streaming effect observed in the rich cavitations region. In addition, ultrasound irradiations at low frequency not only increase the number of droplets and surface area of ELM, but also the solute diffusion coefficient through the interfacial film increases.

3.1.5. Effect of the stripping reagent concentration on the removal efficiency of chromium(III)

The choice of suitable stripping phase is considered to be one of the important factors to design an effective ELM. The stripping tests were performed using an organic phase loaded with 50 mg/L of Cr(III) and three different stripping phases, sulfuric aqueous solution, sodium hydroxide aqueous solution and ammonium persulfate aqueous solution. The sulfuric acid and sodium hydroxide concentration varied from 0–1% (w/w). The ammonium persulfate concentration varied from 0.025 to 0.5 M. All the other parameters had the following values; contact time, 20 min; emulsification power, 40 W; constant carrier concentration, 20% (w/w); surfactant concentration, 4% (w/w); diluent (commercial kerosene) and W/O emulsions/feed phase volume ratio of 0.4. Fig. 6(a) showed the effect of sulfuric acid concentration on the removal percentage of Cr(III). It was found that, the removal of Cr(III) increases with increasing the sulfuric acid concentration. For a pH value of 5, the removal efficiency decreased. It seems that the optimum pH value in the internal phase is 4 due to the very good removal efficiency (99%). The chromate ion may present in aqueous phase in various ionic forms such as Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2{}^{+}$, $Cr(OH)_3{}^{0}$, $Cr(OH)_4{}^{-}$, and $Cr_3(OH)_4{}^{5+}$. It is well known that in aqueous solution the predominance of Cr(III) species depends directly on the hydrogen ion concentration. At pH 4, the Cr^{3+} started to disappear and was converted to $Cr(OH)^{2+}$ complex. Accordingly, the complexes formed during the extraction process at pH > 4 are primarily concerned to the reactions between the carrier with predominant ion species $Cr(OH)^{+2}$ and in lesser extension with Cr^{3+} and $Cr(OH)_2^+$ species.

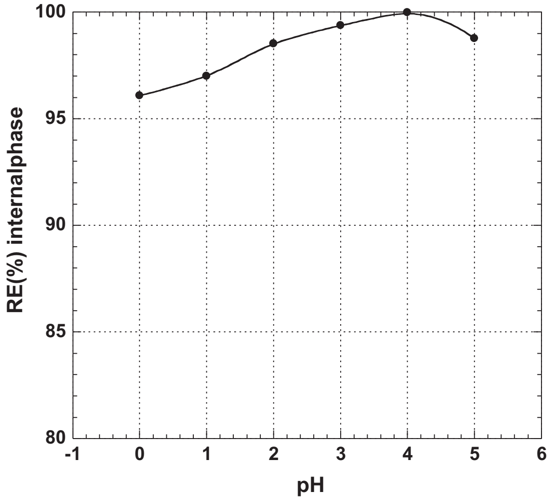

Fig. 6(a). Effect of sulfuric acid concentration in internal phase on the removal efficiency of chromium(III) (50 mg/L) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration, 20% w/w; volume ratio of W/O emulsions to external phase, 0.4; diluent, kerosene; contact time, 18 min; Distance of the tip horn from the bottom of vessel, 20 mm).

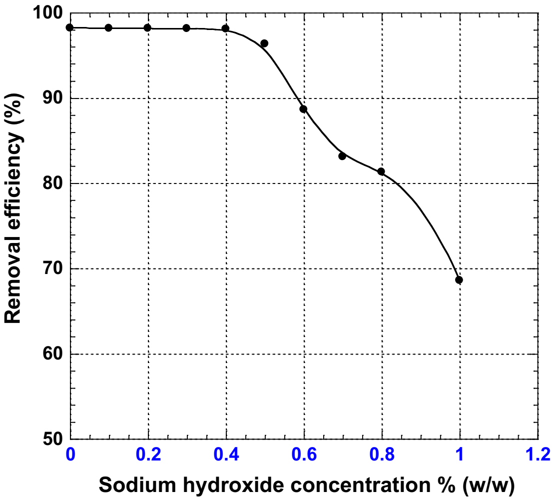

Fig. 6(b). Effect of sodium hydroxide concentration in internal phase on the removal efficiency of chromium(III) (50 mg/L) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration, 20% w/w; volume ratio of W/O emulsions to external phase, 0.4; diluent, kerosene; contact time, 18 min; Distance of the tip horn from the bottom of vessel: 20 mm).

The results showed that the influence of sodium hydroxide concentration on the removal of Cr(III) is practically constant regardless of its content in the internal phase (Fig. 6(b)). However, the extraction efficiency of chromium(III) is inhibited with the increase of the sodium hydroxide concentration from 0.5 to 1%. As can be expected, the removal of Cr(III) increases as the ammonium persulfate concentration increases in the internal phase (Fig. 6(c)). It suggests that, Cr(III) was already almost totally removed (>99%). This fact indicates a strippant concentration of 0.5 M provides an adequate amount of persulfate to oxidize Cr(III) to Cr(VI). Kumbasar [28], concluded that selective extraction of chromium(VI) can be efficiently carried out by using TBP as extractant. Thus, H_2SO_4 (pH 4) solution was selected as the suitable stripping agent.

3.1.6. Effect of surfactant concentration on the removal efficiency of chromium(III)

The effect of surfactant concentration on the process efficiency was investigated for chromium(III) solutions containing: constant carrier concentration,

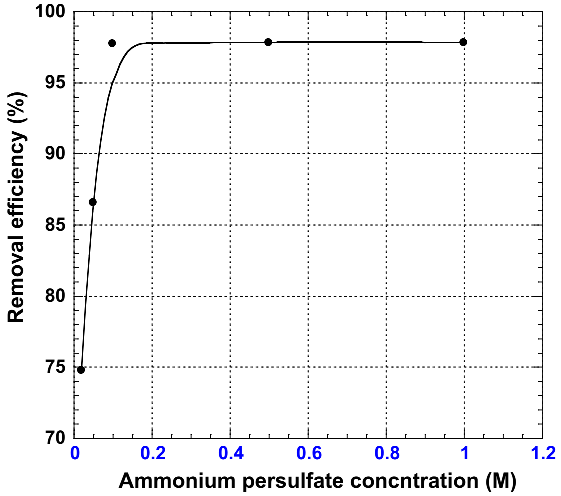

Fig. 6(c). Effect of ammonium persulfate concentration in internal phase on the removal efficiency of chromium(III) (50 mg/L) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration, 20% w/w; volume ratio of W/O emulsions to external phase, 0.4; diluent, kerosene; contact time, 18 min; Distance of the tip horn from the bottom of vessel, 20 mm).

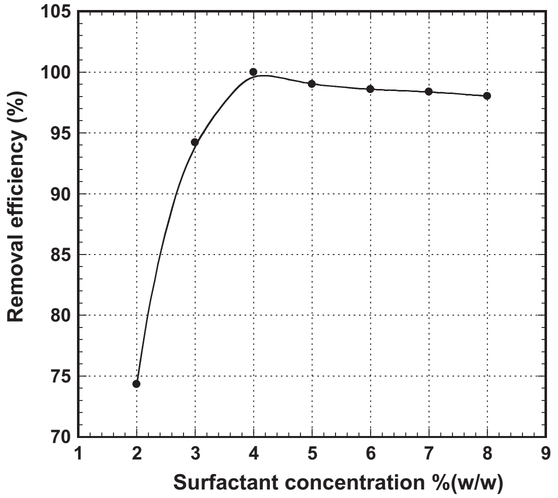

Fig. 7. Effect of surfactant concentration on the removal efficiency of chromium(III) (50 mg/L) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase,1:1; emulsification time, 3 min; ultrasound power, 40 W, carrier concentration: 20% w/w; volume ratio of W/O emulsions to external phase: 0.4; internal phase concentration H_2SO_4 pH 4; diluent, kerosene; contact time, 18 min; Distance of the tip horn from the bottom of vessel: 20 mm).

20% (w/w), internal phase concentration (H_2SO_4 pH 4), diluent (commercial kerosene), W/O emulsions/feed phase volume ratio of 0.4, with emulsification power of 40 W and contact time of 18 min. Fig. 7 illustrates the removal of chromium(III) as a function of surfactant concentration (2–8% (w/w)). Fig. 7 shows that chromium(III) removal increase with the increase of surfactant concentration up to 4%. Nevertheless, after a critical value of concentration of the surfactant, the removal rate of chromium(III) became constant. High amounts of surfactant (8%) lead to a slight decrease in the removal efficiency. This effect may be attributed to the improvement of mass transfer resistance and osmotic swelling induced by a large amount of surfactant present in the system. These results and the above comments show that 4% w/w of surfactant concentration is the most sufficient quantity to stabilize the emulsion. Analogous results were found by Kargari et al. [33] who showed that the optimum surfactant concentration ranging from 2 to 5 wt%.

3.1.7. Effect of the emulsion phase/external aqueous phase volume ratio on the removal efficiency of chromium(III)

The effect of the volume ratio of emulsion phase to external aqueous phase on the extraction efficiency was studied in the ratio range of 0.05–1 and the results are shown in Fig. 8. From this figure, it was observed that the extraction efficiency increased from 74.3 to 99.9% with increasing volume ratio of internal phase to membrane phase. The lower treatment ratio means less emulsion quantities are required to transport the pollutant, which is desirable from a processing point of view to ensure maximum enrichment with respect to the external feed phase. The results clearly showed that the emulsion/external phase volume ratio of 0.4 gives the maximum removal of chromium(III). This ratio ensures a good dispersion of emulsion globules in the continuous external phase solution and concentrates the solute in the stripping phase. This trend may be due to a higher efficient interfacial surface in the case of an emulsion phase/external aqueous phase volume ratio < 1 and, in addition, to the higher viscosity emulsion resulting from a larger volume of external aqueous phase. Comparable results were obtained by Chiha and others [13].

3.1.8. Effect of diluent type on the removal efficiency of chromium(III)

The fact that the selection of the organic diluent is key factor for a solvent extraction process goes

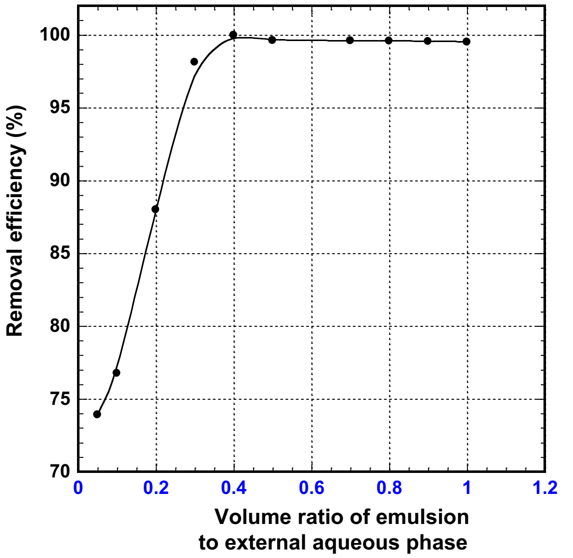

Fig. 8. Effect of volume ratio of emulsion to external aqueous phase on the removal efficiency of chromium(III) (50 mg/L) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration, 20% w/w; internal phase concentration H_2SO_4 pH 4; diluent, kerosene; contact time, 18 min; Distance of the tip horn from the bottom of vessel, 20 mm).

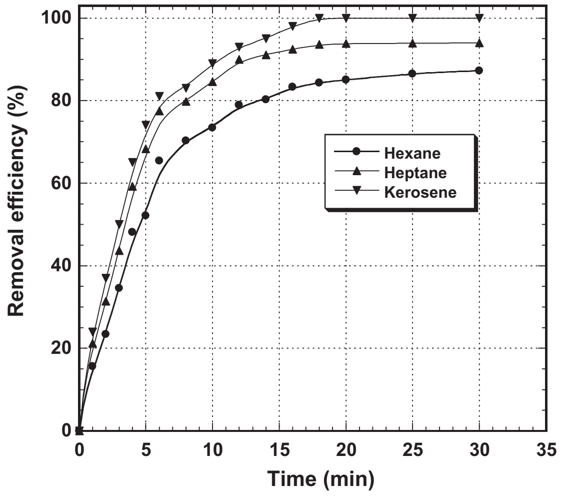

Fig. 9. Effect of diluent types on the removal efficiency of chromium(III) (50 mg/L) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration, 20% w/w; volume ratio of W/O emulsions to external phase, 0.4; internal phase concentration H_2SO_4 pH 4; contact time, 18 min; Distance of the tip horn from the bottom of vessel, 20 mm).

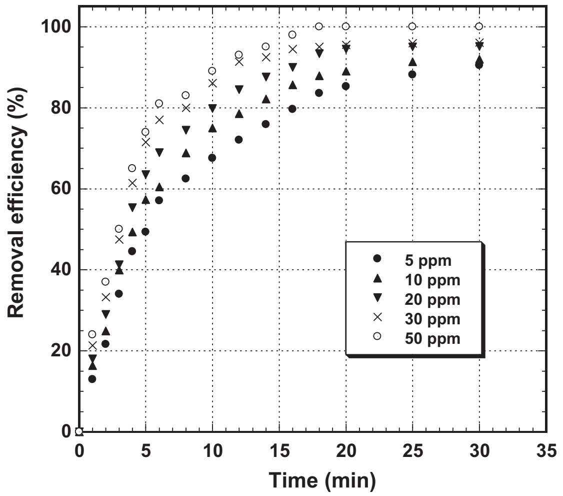

Fig. 10. Effect of solute initial concentrations on the removal efficiency of chromium(III) by AET (experimental conditions: emulsion volume, 20 mL; external phase volume, 100 mL; volume ratio of internal phase to organic phase, 1:1; emulsification time, 3 min; ultrasound power, 40 W, concentration of Span 80, 4% w/w; carrier concentration: 20% w/w; volume ratio of W/O emulsions to external phase, 0.4; internal phase concentration H_2SO_4 pH 4; diluent, kerosene; contact time, 18 min; Distance of the tip horn from the bottom of vessel, 20 mm).

without saying. Several factors, such as e.g. solubility, compatibility with the extractant and surfactant, inability to form new phase, viscosity, density, toxicity, quality of energy etc. each have their place in the planning of a solvent extraction system. The permeation behavior of chromium(III) using hexane, heptane, or kerosene as diluent is presented in Fig. 9. As reported in Fig. 9, the kerosene provided the best performance. Additionally, the extraction process is relatively rapid and equilibrium is almost attained after a maximum of 25 min contact time. The sequence of chromium(III) removal by the different organic diluent is in the order: kerosene > heptane > hexane, kerosene was used as the organic diluent. Following this results, the effect of diluent types does not depend as viscosity and density of diluent, but also related to the composition of organic phase and the species to be extracted. Similar observations were made by Chakravarti et al. [34].

3.1.9. Effect of solute concentration in external aqueous phase on the removal efficiency of chromium(III)

Effect of variation of Cr(III) concentration in the range of 5–50 mg/L was studied. A solvent extraction

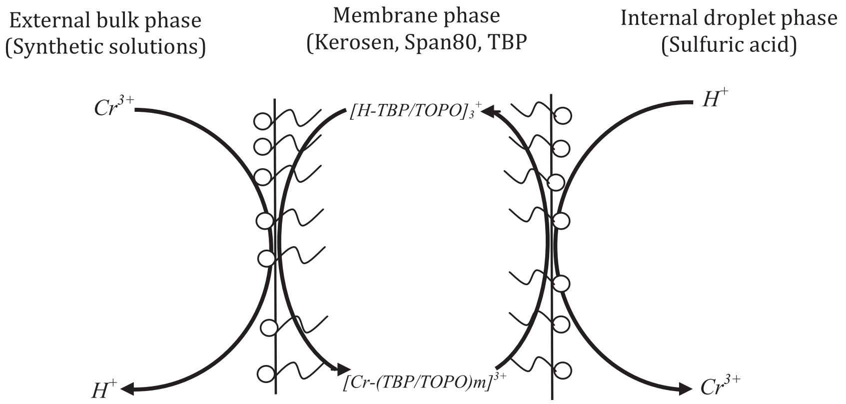

Fig. 11. Extraction mechanism of chromium ion by AET using TBP/TOPO as carrier from the synthetic solution.

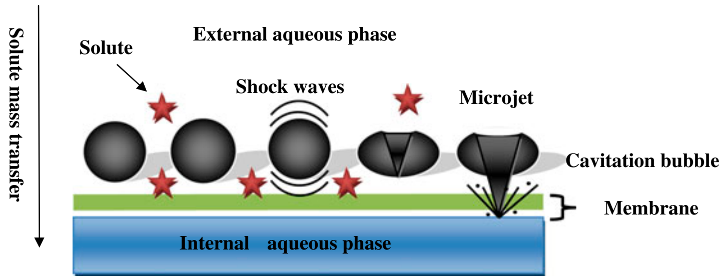

Fig. 12. Advanced Extraction Technique (AET, ELM-US).

denotes the transfer of a solute, for example a heavy metal ion, from one liquid phase (the feed phase) into another liquid phase (internal aqueous phase) through the membrane film. It is well known that the heavy metal ions transport mechanism in ELM consists in a chemical reaction combined a diffusion process with, and several elementary steps are considered, such as: (i) solute diffusion to the stagnant layers of feed phase; (ii) complexation reaction at the feed/membrane phases interface; and (iii) diffusion of the metal-carrier complex in the membrane/stripping phases interface. "In most cases, complexation reactions do not show chemical limitations, because reaction rates in the membrane are very large relative to the diffusion rate. In this case, the heavy metal ions transport through the liquid membrane is primarily governed by the (i) and (iii) steps, where the heavy metal ions transport through the stagnant layer and organic membrane phase is generally represented by the Fick's law" [11].

The results presented in Fig. 10 showed that the removal efficiency of chromium(III) increases with the augment of Cr(III) concentration. These results are in agreement with the above assumptions. Based on Fick's law, an increase in the Cr(III) concentration will result in an increase of the chromium driving force in both the aqueous layer and the organic phase, which consequently improves the overall chromium flux rate through the ELM. The proposed mechanism for the extraction of chromium(III) is exhibited in Fig. 11. And the principal steps of extraction by ELM assisted by ultrasonic radiation is mentioned in Fig. 12.

4. Conclusion

Chromium(III) removal by means of an ELM has been studied. The liquid membrane was prepared by dissolving TBP/TOPO as carriers, kerosene as diluent, Span 80 as surfactant. The removal efficiency is influenced by number of variables like carrier concentration, surfactant concentration, ultrasound power, internal phase concentration, stirring speed, treatment ratio, nature of diluent, and solute concentration in feed phase. The extraction process was fast and equilibrium reached in a relatively short period of time. Under the optimum operational conditions, a total removal of 99% of Cr(III) during the first 25 min can be achieved. An increase in the stirring speed resulted in an increase of the removal efficiency. However, a maximum limit to increase this variable should be considered. An excessively high stirring speed produced coalescence, and ultimately collapse of globules, turning the primary emulsion unstable. The removal percentage of chromium(III) was found to be higher than 99% in the presence of second carrier in the membrane composition.

Optimum operating conditions for higher extraction efficiency and meta-stable W/O emulsion are summarized below: carrier concentration: 20% (w/w); carriers ratio (TBP/TOPO):90/10; ultrasound power: 40 W; stirring speed:200 rpm; internal phase concentration: H_2SO_4 at pH 4; concentration of Span80: 4% (w/w); volume ratio of W/O emulsion to external phase: 0.4; diluent: kerosene. Finally, it can be concluded that AET is a promising technology for the removal of chromium(III) from aqueous effluents, allowing their recovery and reuse.

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