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Arunava Choudhury[a]; Siddhartha Sengupta[a]; Chiranjib Bhattacharjee[a]; Siddhartha Datta[a]
[a] Department of Chemical Engineering, Jadavpur University, Kolkata, India

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Extraction of Hexavalent Chromium from Aqueous Stream by Emulsion Liquid Membrane (ELM)

Arunava Choudhury, Siddhartha Sengupta, Chiranjib Bhattacharjee, and Siddhartha Datta

Department of Chemical Engineering, Jadavpur University, Kolkata, India

Emulsion Liquid Membrane (ELM) separation technique is an effective procedure for the removal of Chromium (VI) ions from the wastewater stream. In the present study, the effect of changes of different parameters such as the pH of feed solution, the stirring speed, and the emulsification time, carrier concentration, surfactant concentration, the effect on the presence of other metal ions, are systematically investigated. The membrane phase consists of kerosene with hexane as diluant, Aliquat 336 as extractant, sorbitan mono-oleate (span 80) as surfactant. 1 (N) Sodium hydroxide is the stripping solution. Results show that by the ELM process, 90% Cr(VI) can remove successfully in optimum condition from feed.

Keywords Chromium (VI) ion extraction; emulsion liquid membrane; facilitated transport; mass transfer; tannery waste water

INTRODUCTION

Wastewater treatment is one of the major problems which are globally accepted from the viewpoint of pollution. According to the World Health Organization (WHO) the most toxic metals are chromium, aluminium, iron copper, zinc, nickel, cobalt, cadmium, mercury, and lead (1,2). The major industries contributing to water pollution by chromium are leather tanning, textile, dyeing, and electroplating plants. In aqueous solution chromium frequently exists as Cr(VI) or Cr(III). These two oxidation states of chromium have different chemicals, biological and environmental properties, among which the hexavalent form is more toxic and also carcinogenic. The Cr(VI) generally exists as anionic species such as $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-}. The oxidizing potential of these Cr(VI) species make them highly toxic for the biological system. However Cr(III) readily precipitates as $Cr(OH)_3$ under alkaline or a slightly acidic condition. The tolerance limit of Cr(VI) is 0.05 mg/lit (3).

Various techniques have been developed for the separation of Cr(VI) from wastewater along with the recovery of the same. Convention treatment techniques like coagulation and precipitation, filtration, electrochemical process, ion exchange process, reverse osmosis, electro dialysis, ultrafiltration etc. are mostly the cost-intensive separation process with addtional solid waste. Liquid – Liquid Membrane Extraction for metal recovery from the effluent is another option. Emulsion liquid membrane (ELM) also called surfactant liquid membrane, is basically double emulsions formed by emulsifying two immiscible phases (e.g., water droplets in an oil phase and vice versa) and dispersing the resulting emulsion in another external feed (or donor) phase containing solutes to be removed.

The water/oil/water (W/O/W) ELM configuration is the target of the present study in which solutes are present in aqueous phase. The ELM process is very unique and promising in the separation of mixtures (e.g., industrial wastewater containing toxic organic or inorganic substances). The ELM separation process has several attractive characteristics. It requires low energy input compared to other separation process. High selectivity with rapid extraction efficiency is observed due to large surface area available for mass transfer. Moreover the spent emulsion can regenerate by the demulsification process.

The ELM technology was first introduced by Li in 1968 (4) Salzer et al. (5) investigated the influence of the membrane composition and of the surfactant, on the recovery of Cr(VI) coming from sulphuric acid baths used in electroplating processes and from washing operations of final metallic products. Bhowal and Datta (6) studied the extraction of Cr(VI) from aqueous acidic solution by ELM using Aliquat 336 as extractant and NaOH as stripping agent, and developed a mathematical model which accounted for the existence of different forms of Cr(VI) ions in the aqueous phase depending on pH conditions. Madhi Chiha et al. (7) studied the extraction of Cr(VI) by W/O/W system using Tributyl Phosphate as carrier, Span 80 as surfactant, and NaOH as internal phase. Berta Galan et al. (8)

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Address correspondence to Chiranjib Bhattacharjee, Department of Chemical Engineering, Jadavpur University, Kolkata 700032, India. Tel.: +91 98364 02118; Fax: +91 33 2414 6203. E-mail: cbhattacharyya@chemical.jdvu.ac.in

had done their experiment to separate Cr(VI) with a newer process called Emulsion protraction (PERT). This is a combination of membrane permeation and solvent extraction. Chakraborty et al. (9) investigated the effect of different parameters during the separation of Cr(VI) with ELM and also studied the stability of emulsion during the time of experiment. Rania Sabry, et al. (10) introduced a new methodology to separate transition of heavy metals from waste water by ELM. Sarvanan et al. (11) had done their experiment with bis (2 ethyl hexyl)–phosphate as a carrier to separate Cr(VI) by ELM. Lee (12) developed an ELM system for the extraction of a neutral species with PARANOX 147 (non-ionic polyamine surfactant) as a liquid membrane. The applicability of liquid membrane in environmental protection was developed by Kaminski and Kwapinski (13). Matsumiya et al. (14) developed redox driven transport of metals ion in an ELM system. Recovery of Cr(VI) from effluent using span 80, monosuccimide and bisuccimide as surfactant was investigated by Hongxia Li et al. (15). Salazer et al. (16) have investigated the influence of the membrane and surfactant compositions on the recovery of the Cr(VI). Fuller and Li (17) analysed the extraction of Cr(VI) and Zn (II) from cooling tower effluents by ELMs containing a polyamine as surfactant, Aliquat 336 as extractant, and nonyl–decyl alcohols for the solubilization of the complex in the solvent phase. Mori et al. (18) used an ELM containing tri-n-octyl amine as extractant, Span 80 or ECA-4360 as surfactants, and LiOH as the stripping reagent in the recovery and concentration of Cr(VI) from aqueous sulphuric acid solutions. Salazer et al. (19) used the model equations of the advancing front approach proposed by Ho et al. (20), which assumed reactions to be instantaneous and irreversible to correlate the kinetic data for the separation concentration of Cr(VI) with ELM. A liquid membrane [W/O/W] method of separation of Cr(VI) from simulated wastewater has been described by Chakraborty et al. (21). The effects of the variation of the oil-membrane constituents and different types of chemical reactions at the interface using aqueous solutions of various strippants (internal phase) have been studied for a critical appraisal of the efficiency of the process (22).

The present work has been undertaken with an objective to elucidate the effectiveness of W/O/W ELM technology to remove Cr(VI) from a simulated solution, representative of typical tannery wastewater. Attempts have been made to investigate the effects on separation of Cr(VI) due to the changes of different parameters such as pH of the feed, mixing time, speed of mixing, carrier concentration, and most importantly, the presence of other metal ions. Attention was also given to the stability of the emulsion. An optimum condition is evaluated to separate Cr(VI) from the feed solution. In view of that, all the experiments have been carried out using NaOH as internal stripping phase, Aliquat 336 as a carrier, Span 80 as a surfactant, and commercial grade Kerosene as an organic phase.

EXPERIMENTAL

Instrument, Apparatus and Measurement

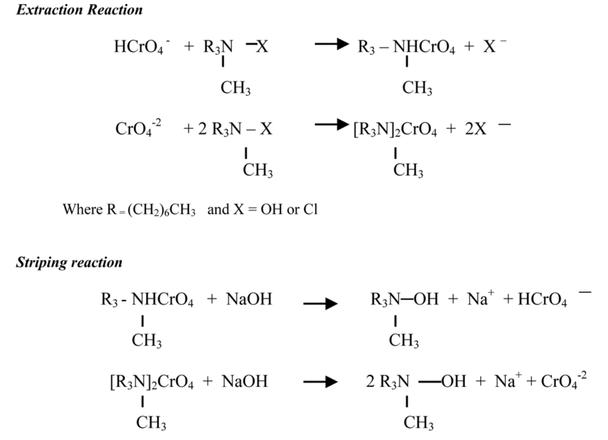
All the experiments were carried out in batch process. The spectrophotometer used for measuring the Cr(VI) concentration was a VARIAN (CARY 50) model, Australia. The pH was measure with an AELICO make LI 127 pH meter. The determination of Cr(VI) was carried out using the diphenylcarbazide method as per the standard method (23). The mixing and stirring was done by LABSONIC^{TM} (Sartorius, Germany) sonicator. It generated a longitudinal mechanical vibration with a frequency of 30,000 Hz (in 100% amplitude).

Reagent

A solution of potassium dichromate (99.99% pure, MERK made, CAS No. 7778-50-9) was used as a feed solution throughout the experiment. Commercial grade kerosene (sp gr 0.798 & boiling range 150C to 230C) was used as organic membrane phase. Aliquat 336 – Tricaprylmethyl ammonium chloride, (ALDRICH, CAS No. 63393-96-4) and Span 80 (LOBA Chemicals, CAS No. 1338-43-8) were used as carrier and surfactant respectively. n-Heptane (MERCK, CAS No. 142-82-5) was used as diluents. $CuSO_4$ was used as the source of Cu(II) ion. Sulphuric acid (N/10) was used to maintain the pH of simulated feed. The internal phase was 1 (N) NaOH. For preparation of aqueous solutions double distilled water has been used. The ultra-pure deionized (DI) water, used in this study was obtained from Arium 611DI ultrapure water system (make: Sartorius A.G., Göttingen, Germany). The feed for the DI water system was distilled water prepared by reverse osmosis (RO) system (Model: Arium 61315, make: Sartorius AG, Göttingen, Germeny).

Reaction of Chromium (VI) Extraction Process in ELM

The emulsion used in this study is of the water-oil-water type. The ELM process largely consists of two steps, emulsion preparation and solute extraction/emulsion separation. The configuration and key components of ELMs can vary depending on their application and the types of target solutes and the external feed phase treated. The reaction mechanism for chromium (VI) transport from the external phase across the liquid membrane to the internal phase is shown in Fig. (1) for monovalent $HCrO_4^-$ and divalent CrO_4^{-2} with quaternary amine Aliquat 336^{TM} (methyl tricaprylyl ammonium chloride) (24).



$$HCrO_4^- + R_3\underset{\displaystyle CH_3}{N}{-}X \longrightarrow R_3{-}\underset{\displaystyle CH_3}{N}HCrO_4 + X^-$$

$$CrO_4^{-2} + 2\,R_3\underset{\displaystyle CH_3}{N}{-}X \longrightarrow [R_3\underset{\displaystyle CH_3}{N}]_2CrO_4 + 2X^-$$

$$R_3{-}\underset{\displaystyle CH_3}{N}HCrO_4 + NaOH \longrightarrow R_3\underset{\displaystyle CH_3}{N}{-}OH + Na^+ + HCrO_4^-$$

$$[R_3\underset{\displaystyle CH_3}{N}]_2CrO_4 + NaOH \longrightarrow 2\,R_3\underset{\displaystyle CH_3}{N}{-}OH + Na^+ + CrO_4^{-2}$$

FIG. 1. Reaction of Chromium (VI) extraction process in ELM.

Emulsion Liquid Membrane Preparation

Emulsion was prepared by mixing Kerosene, Span 80, Aliquat 336, and n-heptane with aqueous solution of dichromate in volume-by-volume ratio. Subsequently the emulsion was achieved by stirring the whole mixture under a sonicator with different frequency ranges for 10 minutes. Then NaOH was added and the mixture was stirred again. In this way a good, stable emulsion was formed. For the purpose of analysis, samples of about 5 ml were withdrawn from the emulsion at different time intervals. The sample was filtered through normal filter paper and filtrate was allowed to separate in a separating funnel. The clear bottom aqueous phase in the separating funnel was then collected for measurement of chromium concentration under a spectrophotometer. All experiments were performed at a temperature of 32C. A summary of the experimental condition for recovery of Cr(VI) are tabulated in Table 1.

TABLE 1
Summary of experimental conditions for ELMs batch tests

Membrane Phase (O):	
Volume	50 ml
Carrier (Aliquat 336 and tri-n-octylamine)	10% V/V
Diluent (n-heptane)	5%, V/V
Surfactant Span 80	5%, V/V
Kerosene	80%, V/V
Exterior phase (W):	
Volume	200 mL
Cr (VI)	100 ppm
pH	2–10
Interior phase (W):	
Volume	25 mL
Base conc.	1 N (NaOH)

For preparation of aqueous solutions double distilled water has been used.

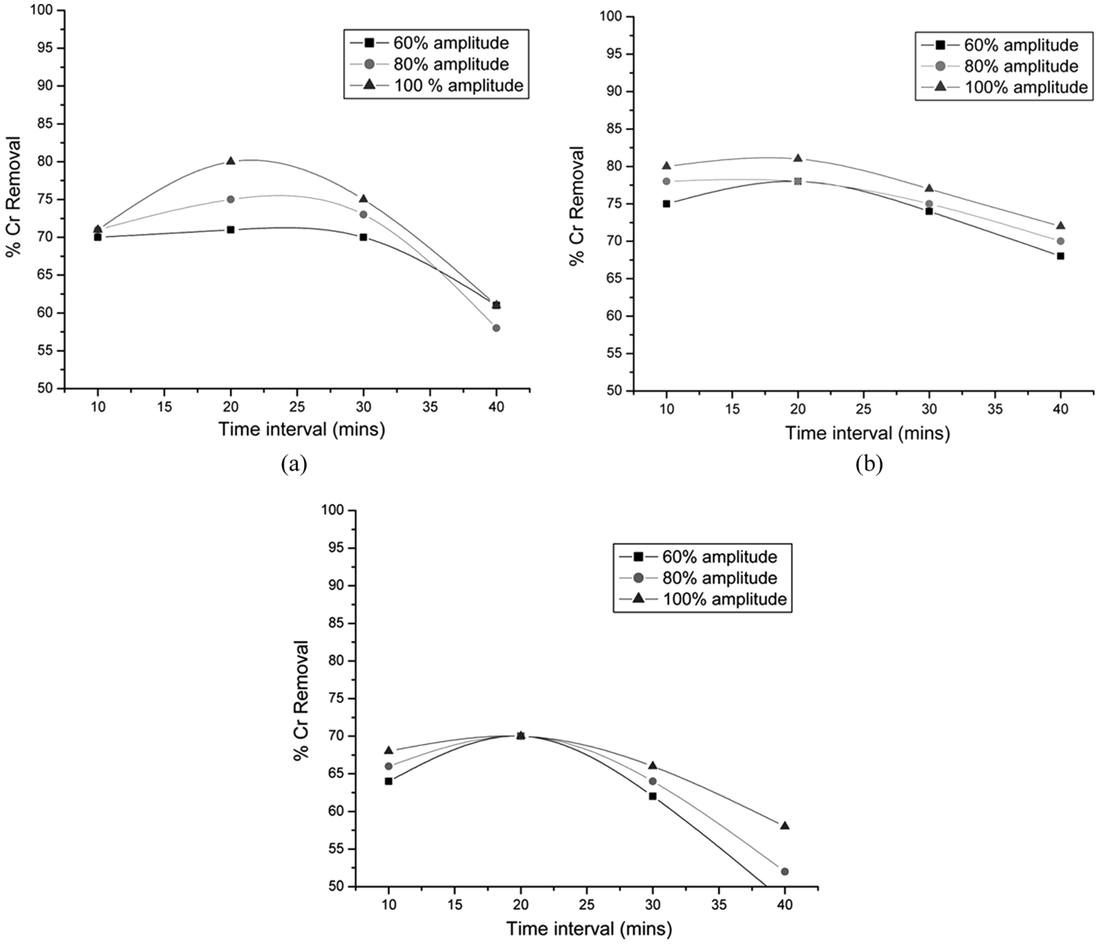
RESULTS AND DISCUSSION

Effect of Speed of Sonicator (Effect of Agitation Time)

The speed of the sonicator or agitation speed means sonication energy (vibration energy in terms of frequency, Hz) that is introduced in the system. The effect of the agitation speed at different pH of the external feed solution is described in Figs. 2a, 2b, 2c. The experiments were conducted for an emulsification time of 40 minutes with a ratio of organic membrane phase to aqueous phase (external phase) of 0.25 (v/v) and a ratio of stripping phase to organic phase of 0.5 (v/v). The pH of the feed solution was maintained by using (N/10) sulphuric acid and (N/10) caustic soda, as required. From Figs. 2a, 2b, 2c, at different pH it is observed that with increase in the speed of agitation, the separation efficiency increased up to a certain time limit. As the agitation time increases the separation efficiency decreases irrespective of the speed of agitation. Initially, an efficient emulsification occurs with increasing in agitation speed and time. When the sonicator speed and time of stirring increases the shear force, which acts on the large emulsion globule, makes the globules smaller for which the effective surface area for permeation of Cr(VI) ion increases. Also the stability of emulsion increases. Increasing the speed of the sonicator and time of agitation above a critical value, the stability of emulsion reduced significantly with a corresponding reduction of recovery efficiency. This may be due to the initiation of demulsification, which is induced by leakage from the internal stripping phase from the system. Since the size of the drops become smaller and smaller, the continuous ultrasonic agitation of the sonicator shears the surface of the drops. Hence the optimum sonicator speed was taken as 100% amplitude (30,000 Hz).

Effect of Emulsification Time

From Figs. (2a, 2b, 2c) it is clear that with increase in time of emulsification the percentage of recovery increase up to a certain time but after 20 minutes, the stability of emulsion gradually decreases resulting in decline in percent recovery. Initially more and more small droplets are formed in the system, which gives a large surface area for mass transfer and increase the recovery efficiency of metal ion. But at the same time, due to the smaller size of the emulsion globules leakage of the internal phase might occur, which could be further enhanced by osmotic swelling of the membrane. Though the area of mass transfer increases with time, but spilling of the internal stripping phase into the outer continuous phase resulted in the rupture of membrane phase. Results show, 20 minutes was the optimum time for mixing.



(a)

(b)

(c)

FIG. 2. (a) Effect of sonicator speed with percentage removal at pH 2.4. (b) Effect of sonicator speed with percentage removal at pH 6.5. (c) Effect of sonicator speed with percentage removal at pH 10.45.

Effect of pH of Feed Solution

The chromate ion may exist in aqueous phase in different ionic forms such as $HCrO_4^-$, CrO_4^{-2}, $Cr_2O_7^{-2}$, $HCr_2O_7^-$. There is no significant change in percent recovery of Cr(VI) with changes of pH from 6.5 to 2.4. But in higher pH it is observed that the recovery efficiency of metal ion substantially decreases with time. The distribution coefficient decreases sharply when the equilibrium pH exceeds 6 to 7 for the extraction of Cr(VI) oxyanions with Aliquat 336. This is because the quaternary ammonium salts exhibit reasonable extraction abilities only toward monovalent oxyanions, i.e., $HCrO_4^-$, while CrO_4^{-2} is the dominant species at that pH. Stable emulsion does not form in pH more than 7. But in the range at pH $6-6.5$ the interfacial reaction rate becomes high and the driving force for mass transfer of the complex through the oil–water interface increases. The rate of the complex formation depends directly on the hydrogen ion concentration. So at pH 2.4 more and more complex structure forms with Cr(VI), within a short period but the complex hindered the rate of mass transfer through the membrane phase to stripping phase. Moreover at pH 6.5, the Cr(III) ion is precipitated as $Cr(OH)_3$ and it is easier to maintain the pH of the effluent.

Effect of Changes of Ratio of Organic Phase with External Feed Phase

The experiment was done with a different volume ratio of kerosene (organic phase) with aqueous feed phase. The percent recovery of Cr(VI) ion with different kerosene/feed ratio in various pH conditions are described in Fig. (3). The sonicator was used at 100% amplitude (i.e., 30 KHz). The internal striping phase volume was 25 ml of 1 (N) NaOH. It was observed that in acidic medium (i.e., in pH 2.4 and 6.5) the removal of chromium ion from

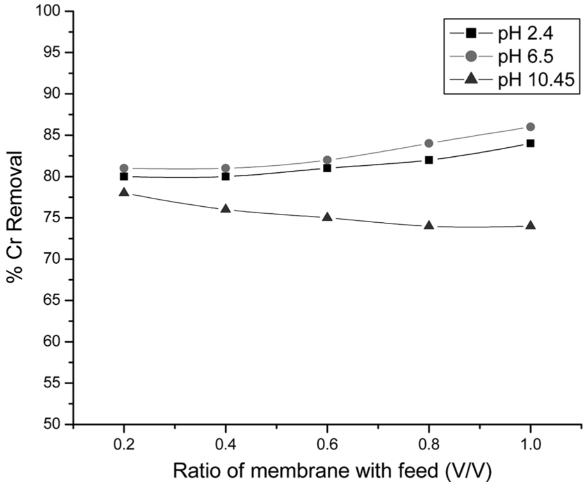


FIG. 3. Ratio of membrane/feed ratio with % of removal.

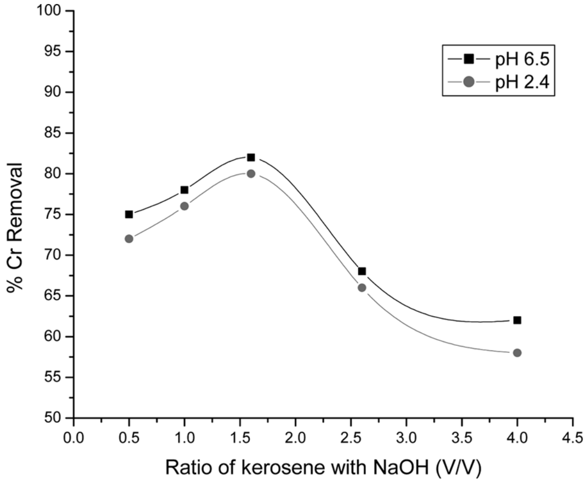


FIG. 4. Effect of change of internal stripping phase.

the feed phase is increased with increasing the ratio of the organic phase to the feed phase from 0.2 to 1. With increase in volume of the organic phase the total interfacial area in the system is gradually increased, which leads to the higher removal efficiency. The stability of emulsion in alkaline medium is significantly low compared to acidic medium. The separation efficiency reduced at pH 10.45 with an increasing volume ratio of organic to aqueous phase in alkaline medium. This may be due to the fact that the swelling phenomenon becomes remarkably fast in alkaline medium. In the presence of NaOH, all dichromate was converted to Na-chromate or precipitated as $Cr(OH)_3$. The color of the solution became straw yellow to greenish blue. As a result the chromium removal efficiency was also reduced.

Effect of Internal Phase Concentration

Figure (4) describes the removal of chromium with the ratio of organic membrane phase to internal striping phase in different pH. From the figure it is clear that with increase in volume of the internal aqueous phase, the stability of the emulsion decreases accompanied by a corresponding decrease of the removal of chromium ion. The results may be attributed to the leakage of emulsion globule as stated earlier. The unstable and larger emulsion globule significantly reduces the recovery efficiency of the system.

Effect of Carrier Concentration

The effect of changes of ratio of volume of carrier to feed is described in Fig. (5). The volume of the feed was kept constant in 200 ml. The volume of Aliquat 336 was changed in each run. The volume of the surfactant and kerosene (membrane phase) were kept constant throughout the experiment. The sonicator was used at 100% amplitude (i.e., 30 KHz). It was observed that, increasing the carrier concentration over a certain limit, the stability of emulsion decreased and reduced the removal of the chromium ion. This may be due to the increase of viscosity of the membrane phase with an increase in carrier concentration (25), which reduces the contact area with the external continuous phase. Also, increase in carrier concentration in the system might result in increase of the swelling effect with consequent decreases of the efficiency of the process (26).

Effect of Surfactant Concentration

The experiments were performed with 200 ml feed solution (at pH 2.40 and 6.50) with 40 ml Kerosene, 5 ml Aliquat 336, and 25 ml NaOH. The sonicator was used at 100% amplitude (i.e., 30 KHz). Figure (6) showed the effect of surfactant concentration on the removal of Cr(VI) ion from the reaction medium. The removal of metal ion was

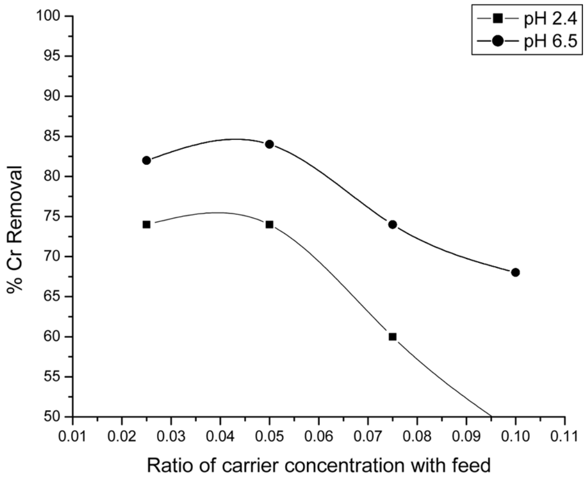


FIG. 5. Effect of carrier concentration in different pH.

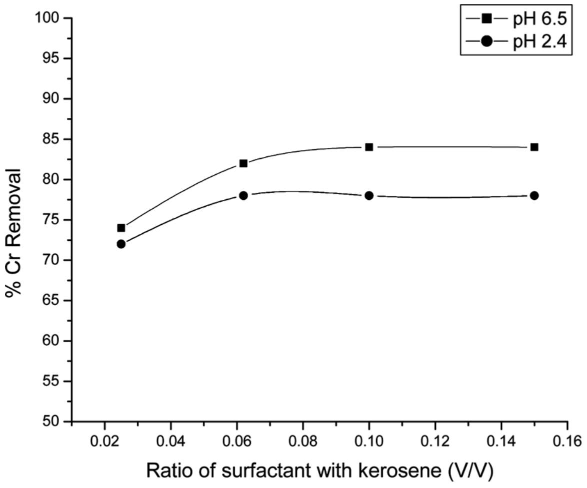


FIG. 6. Effect of surfactant conc. with organic membrane (V/V).

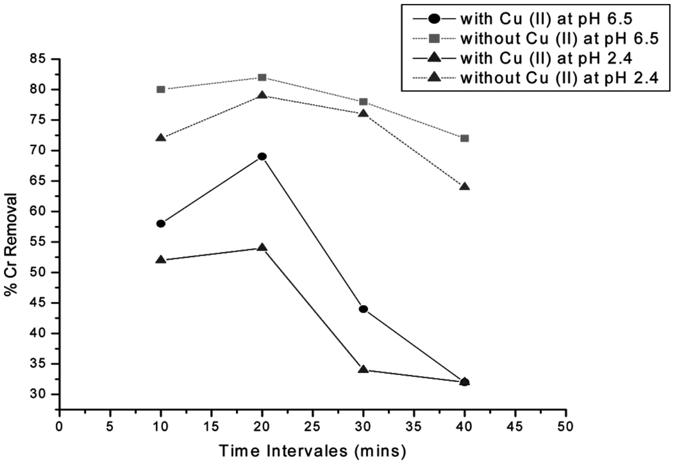


FIG. 8. Effect of metal ion copper (+2) in feed solution.

increased with increase in surfactant concentration. But after a critical value of concentration of the surfactant the removal rate of metal ions became constant. The fact may be due to the degree of stability of emulsion increases with increase of concentration of the surfactant. But after a critical concentration of surfactant the degree of stability of emulsion becomes nearly constant due to the saturation of the surfactant in the organic phase.

Effect of Feed Concentration

The metal ion concentration was varied in 200 ml feed solution (i.e., 80 ppm, 90 ppm, 100 ppm, 110 ppm, 120 ppm of Cr(VI)) only at pH 6.5. The other experiments parameter were 40 ml Kerosene, 5 ml Aliquat 336, and 25 ml NaOH. The sonicator was used at 100% amplitude (i.e., 30 KHz). The results are described in Fig. (7). From the figure it is cleare that with an increase in metal ion concentration in the feed, the efficiency of the removal of metal ion becomes low. So the process is applicable in case of the removal of metal ion from feed of low concentration.

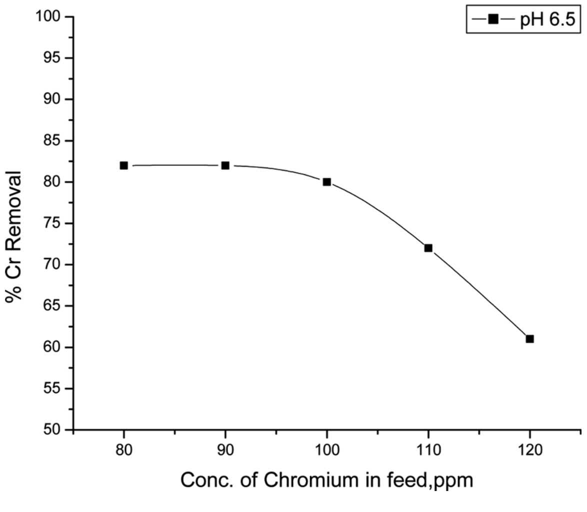


FIG. 7. Effect of feed concentration with % removal of chromium.

Effect in the Presence of Cu(II) Ion

A 200 ml feed solution having concentration of 100 ppm Cr(VI) and 100 ppm Cu(II) ion were taken as external phase. The pH of the solution was fixed at 2.40 or 6.5 for two different runs. The other parameter was the same. The total recovery efficiency of Cr(VI) with time is described in Fig. (8). It is observed that the presence of the other cation i.e., Cu(+2) (equal amount) reduces the efficiency of the removal of chromium ion. The organic membrane phase is going to be dispersed in the external aqueous phase to form an emulsion. In this case, in the feed solution the Cr ions were present in different oxidation states in anion form. During the mixing of the external phase to the organic phase, the Cu(+2) ions were present in the boundary of the aqueous phase due to its high mobility in the aqueous phase compared to chromate anion. As a result the compatibly large chromate ion could not come in contact with the membrane phase due to sterric effect. Moreover, due to the smaller size of Cu(+2) compared with $Cr_2O_7^{-2}$, the transport of Cr(VI) ion through the organic membrane hindered. As a result the removal of Cr ion reduced.

CONCLUSION

The following conclusions may be drawn based on this study:

- To reduce metal ion in ELM process, it is required to enhance gradually the stirring rate, thus the shearing forces arising from the sonicator do not break the emulsion.

- The pH of the feed solution is an important parameter which affects the removal efficiency throughout the ELM process. The pH 2.4 or 6.5 of the feed solution are favored in the removal process to an almost equal extent. It is known that the pH value of the external phase in ELM affects the rate of mass transfer because of the driving force that results from the transport of H+ions from the internal to the external phase, which is inverse in the metal ions. But a faster extraction rate reduces the stability of the membrane. From this study it is concluded that the pH of the feed solution up to 6.5 may be favorable for the system. So pH 6.5 of the feed solution is considered as optimum pH condition of the system. It also helps to control the pH of the effluent water in sewerage.
- Span 80 is a good emulsifier and has low resistance to mass transfer (Ho and Sirkar, 1992). The surfactant gives the stability of the emulsion globules. If the concentration of this surfactant is not optimized, then the membrane can break down due to low stability. Then Span 80 and the other ingredients in the membrane phase can permeate into the wastewater. The optimum surfactant value will be 5% V/V with membrane for ELM.
- The carrier concentration and Membrane to External Phase ratio is optimized. The carrier concentration and organic membrane concentration is 10% V/V and 40% V/V of the total organic phase. 1 (N) NaOH is optimized as stripping phase.
- It is observed that from a time period of 10–15 minutes the removal efficiency is maximum. After that the stability of emulsion is affected due to swelling or leakage of the emulsion globule. So the time period plays a very important role. A separate study can be done to evaluate the emulsion stability in ELM. The parameters which reduce the stability of the emulsion are continuous stirring, a high pH value of the feed solution, more carrier concentration, and a higher metal ion concentration. But no effect has been observed with increase in surfactant concentration.
- The ELM process could be a cost-effective and less hazardous separation process, which is effective for the removal of metal ion in a low concentration. The system can be continued to recover the pollutant from the stripping phase followed by recycling the organic phase for further use. More efforts are needed to develop a specific ELM system for specific industrial aqueous waste stream.

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