

REMOVAL OF HEXAVALENT CHROMIUM BY EMULSION LIQUID MEMBRANE TECHNIQUE

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ABSTRACT

Chromium is a very harmful metal, highly toxic and carcinogenic in nature. Its removal from effluents like electroplating rinse waters and tannery effluents is of primordial importance. This paper deals with the removal of hexavalent chromium ions from aqueous solutions and industrial effluents by using emulsion liquid membrane (ELM) technique. The effect of surfactant concentration, carrier concentration, agitating speed and emulsification time on the emulsion stability has been studied. The effects of emulsion phase to the external phase (M/E) ratio and impeller speed on the percentage reduction of Cr (VI) ions in three types of effluents viz. synthetic effluent, electroplating effluent, and tannery effluent have been reported. Emulsion liquid membrane is observed as a very effective process by which the Cr (VI) ions can be removed successfully. A generalised mathematical equation to determine the percentage recovery of metal ions is obtained by regression analysis using the experimental data and is found to predict the percentage recovery with in an average error of 15 percent.

Keywords: Emulsion, liquid membrane, chromium(VI), tannery effluent, electroplating effluent.

INTRODUCTION

With the wake of plethora on the environment, the world emphasises the need for cleaner technologies in industrial production with minimum pollution [2]. Consumption of heavy metals and their usage is increasing steeply while their availability is diminishing drastically. Even the low quantities of heavy metals discharged in effluents cause serious environmental and health problems [3]. Hence, recovery of heavy metals like chromium, zinc, nickel, copper and mercury from effluents is of great importance to the society.

Conventional treatment techniques like precipitation (pyrometallurgical) and filtration generate solid wastes. Electrochemical processes [4, 5] are also used for metal ions recovery which are less efficient and uneco-

nomical for dilute streams [6, 7]. Liquid – liquid extraction for metals recovery from effluent [8] is another option. Though this operation extracts solute, it releases a waste solution or stream which has the contaminant metals and this has to be stripped by another operation to avoid disposal problems. Separation techniques based on liquid membranes offer high scope and potential [9-17] due to its characteristics such as ease of operation, lesser energy requirement and high selectivity. Compared to supported liquid membranes, ELM also offers other advantages of large interfacial area, low cost factors and a single stage operation of both extraction and stripping. It finds more applications in the industrial effluent treatments [18] and in waste water treatments [19-21].

Wide spectrum of systems, comprising gases [22], organic solvents, amino acids [23, 24], electrolytes and

metal ions can be separated or enriched using liquid membranes.

The recovery of chromium was studied in a variety of membranes using anionic carriers. It was found that SLM was the most efficient and BLM had the lowest permeability [25, 26] Flat sheet cyanex membranes were also used to study the recovery of chromium [27]. Mathematical Models for the Extraction of chromium from an aqueous acidic solution were also reported [28]. Mass transfer models for the extraction of chromium using aliquat 336 were also reported [29].

EXPERIMENTAL

Materials

The membrane phase used is a homogeneous mixture of commercial grade kerosene as organic solvent, SPAN 80 as the surfactant, Bis-(2-ethyl hexyl)-phosphate as the carrier. The internal stripping phase is an aqueous solution of sulphuric acid. The three types of feeds chosen for study are synthetically prepared feed containing Cr (VI) ions of 10 mg dm^{-3} , electroplating and tannery effluents collected from the near by industries containing Cr (III) ions. The industrial effluents are then converted to Cr (VI) ions of 10 mg dm^{-3} for throughout our studies. The properties of the raw industrial effluents used are given in Table 1.

Experiments

The emulsion used in the study is of water-oil-water (w/o/w) type. It is formed by mixing 50 % by volume of aqueous 1 M sulphuric acid, as internal stripping phase, with 50 % by volume of organic phase. The

Table 1. Characterization of industrial effluents.

Properties	Electroplating Effluent	Tannery Effluent
pH	4.5	2.5
Cr (III), mg dm^{-3}	3000	3000
COD, mg dm^{-3}	2700	2200
BOD, mg dm^{-3}	945	800
Odour	Very high	Very high
Colour	Dark brown	Dark brown

organic phase initially contains 0.2-1.6 % (v/v) surfactant, 0-4 % carrier and the rest solvent. The mixture is then stirred at different speeds ranging from 3000 – 6500 rpm with various emulsification times from 10 min to 1 hour to optimise the process conditions for obtaining stable emulsion.

A one litre capacity batch extractor, 12.5 cm in diameter and 20 cm in height with a variable speed agitator of paddle type is used. It is charged with a desired ratio of emulsion to external phase (effluent to be treated) and stirred well at a particular speed for 30 minutes. During the contact between aqueous solution and emulsion, solute transport occurs through the membrane phase in to the internal stripping phase where it is concentrated. Extraction and stripping are carried out in a single stage and the mixture is allowed to separate. The treated effluent is then separated from the emulsion and analysed for the chromium concentration (in the external phase) using a UV Jasco spectrophotometer, at 540 nm in the UV wave length range. The experiments are repeated for different emulsion to external phase (M/E) ratios of 0.25, 0.33, 0.5, 0.75, 1.0 and 1.5 (v/v), impeller speeds of 200, 300, 400 and 500 rpm and with various carrier concentrations of 0, 2 and 3 % (v/v). The experiments are repeated twice to check the reproducibility of the results.

RESULTS AND DISCUSSION

Effect of parameters on emulsion stability

Emulsion instability is mainly caused by membrane breakage and membrane swelling. The effect of various operating parameters like surfactant concentration, carrier concentration, mixing time and emulsification speed on the stability of emulsion is shown in Figs. 1 to 4. It is observed that increase in concentration of surfactant upto 1.2 % (v/v), increases the stability of emulsion to 3.0 hours. Further increase in concentration of surfactant reduces the stability time. Similarly, an increase in mixing time beyond 15 minutes and an increase in agitation speed beyond 6000 rpm reduce the stability of emulsion as shown in Figs. 1, 2 and 3.

Fig. 4 indicates that increase in concentration of carrier decreases the stability, but too low carrier concentration decreases the solute transfer rate. Hence, an intermediate carrier concentration of 2 and 3 % (v/

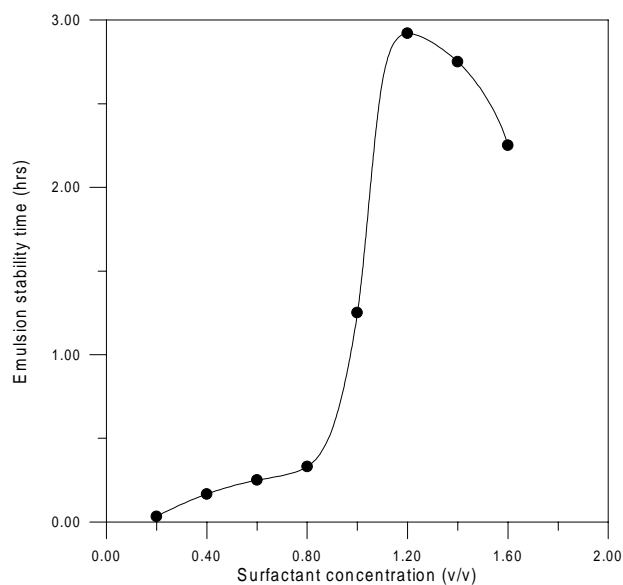


Fig. 1. Effect of surfactant concentration on emulsion stability.

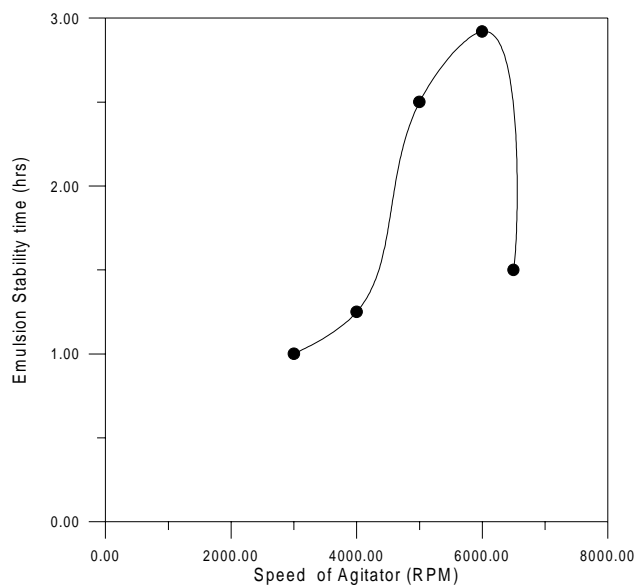


Fig. 3. Effect of agitator speed on stability of emulsion.

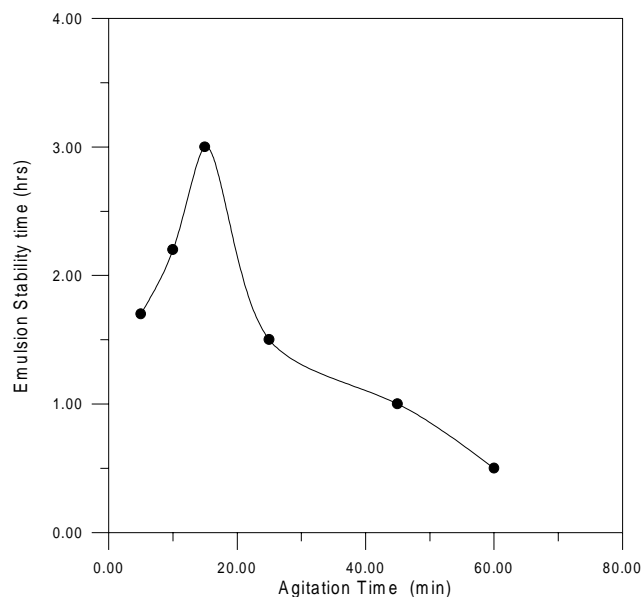


Fig. 2. Effect of agitation time on stability of emulsion.

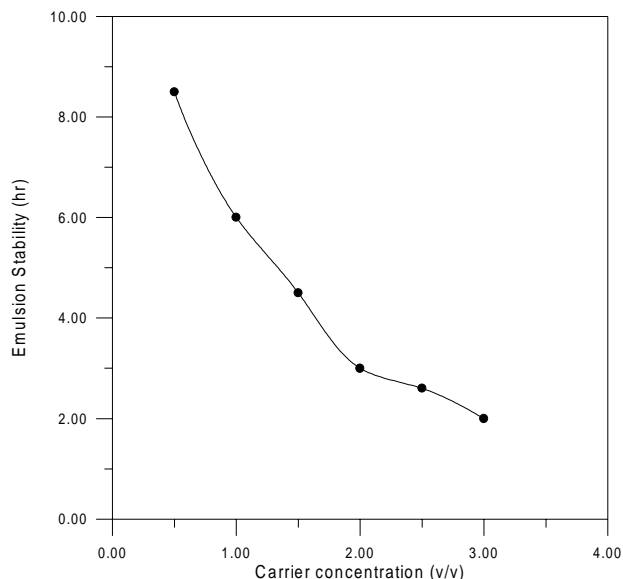


Fig. 4. Effect of carrier concentrations on emulsion stability.

v) is taken in order to maintain both stability and solute transfer rate.

After several trials, it is found that the emulsion containing 1.2 % (v/v) surfactant, 2-3 % (v/v) carrier and the rest solvent prepared at 6000 rpm and 15 minutes is very stable.

Effect of operating parameters on synthetic effluent

Experimental studies were carried out at various impeller speeds for different M/E ratios and carrier con-

centrations in-order to study the effect of operating conditions on the recovery of Cr (VI) ions from the synthetic effluent as external phase and the results obtained are shown in Figs. 5-10.

1. Effect of Agitation speed

The effect of agitation speed on percentage Cr removal in the synthetic effluent as external phase is

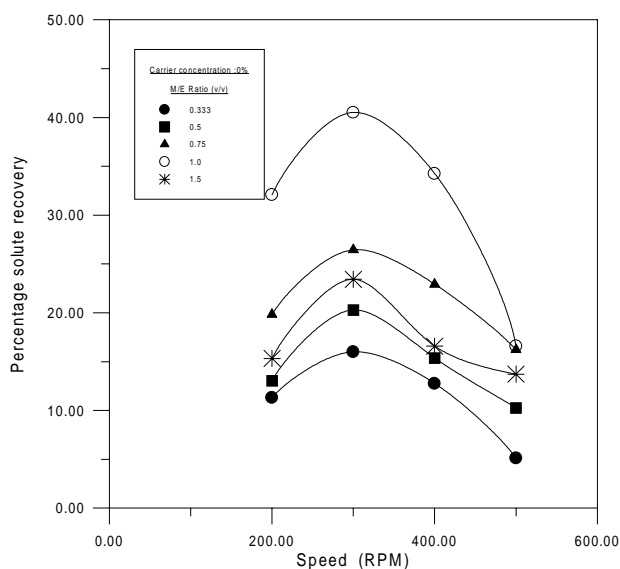


Fig. 5a. Effect of speed on percentage of solute recovery.

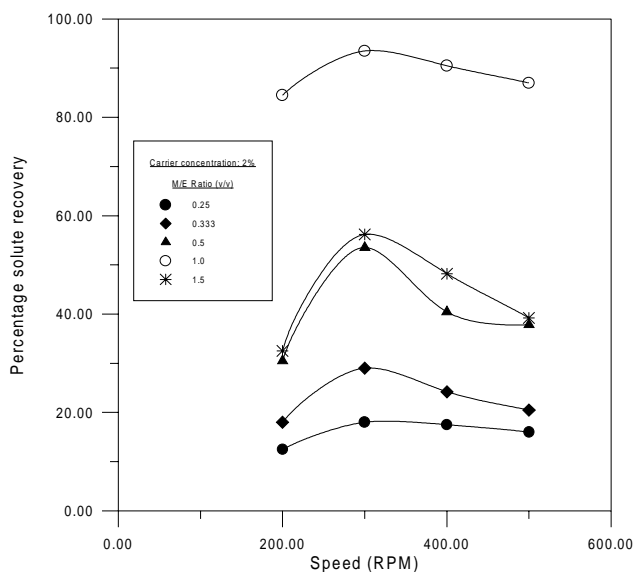


Fig. 6a. Effect of speed on percentage solute recovery.

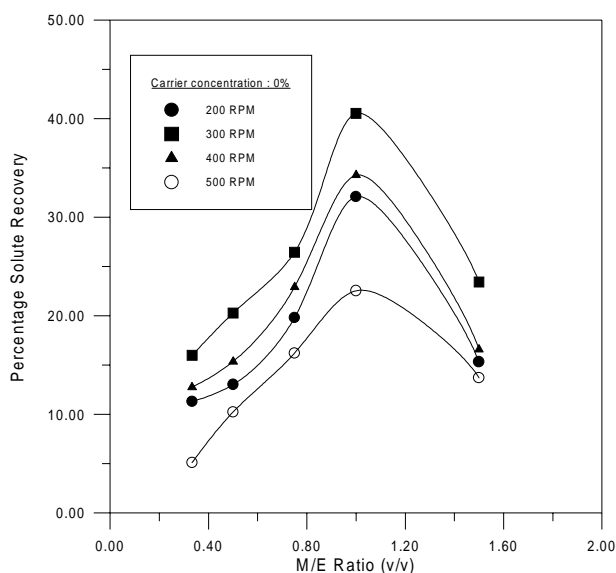


Fig. 5b. Effect of M/E ratio on percentage of solute recovery.

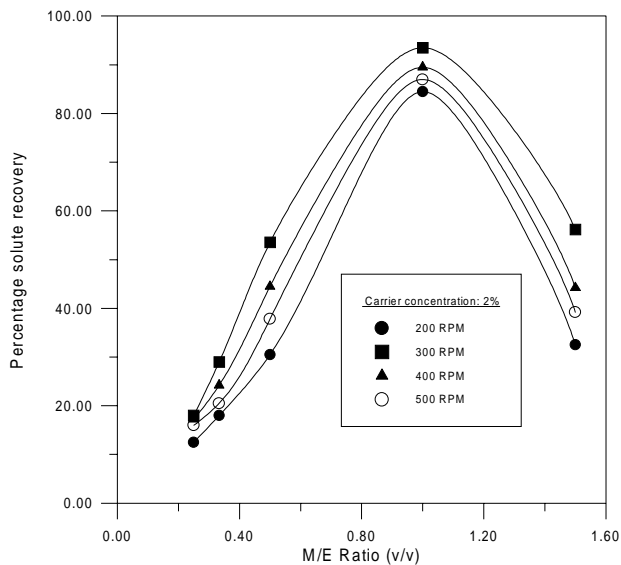


Fig. 6b. Effect of M/E ratio on percentage of solute recovery.

shown in Figs. 5a, 6a, 7a and 8a. It is observed from these Figures that as the speed is increased from 200 to 500 rpm, the percentage solute recovered from external phase increased and decreased at a specified M/E ratio for 0, 2, 3, and 4 % carrier concentrations. The similar results have been found for various M/E ratios at different carrier concentrations. The agitation speed at 300 rpm is found to be the most effective to recover 40.53 %, 93.5%, 96 % and 68.57 % of solute from external phase for 0, 2, 3 and 4 % carrier concentrations respectively at 1:1 M/E ratio. The reason for the drop in percentage of metal ions extracted from external phase be-

yond 300 rpm is due to either de-emulsification induced by higher shear of the impeller or due to leakage from internal stripping phase.

2. Effect of M/E ratio

From Figs. 5b, 6b, 7b and 8b, it is observed that when the M/E ratio is varied from 0.25 to 1.5 (v/v), the percentage of solute recovered from external phase initially increased and then decreased beyond the ratio of 1:1. The same trend of results is observed for various carrier concentrations at different impeller speeds. This

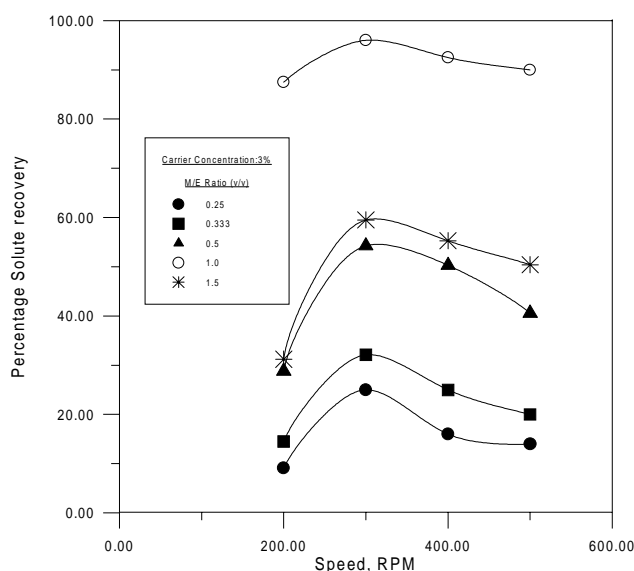


Fig. 7a. Effect of speed on percentage solute recovery.

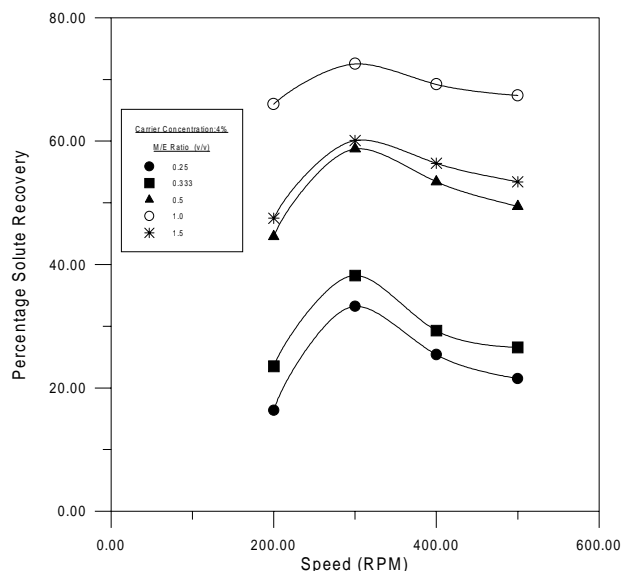


Fig. 8a. Effect of speed on percentage solute recovery.

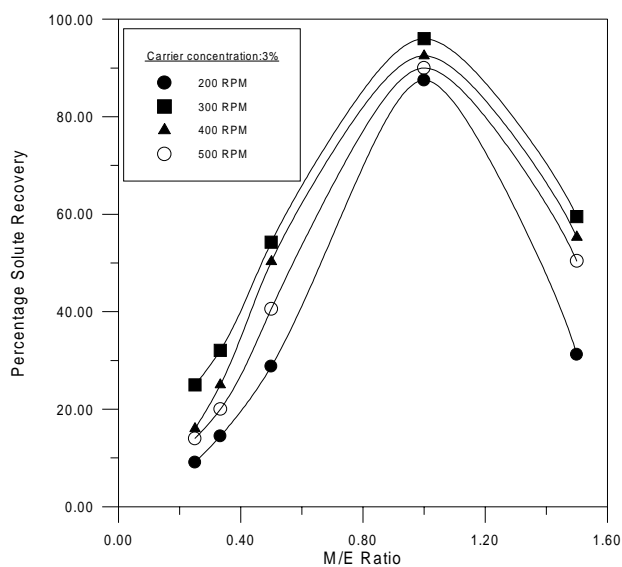


Fig. 7b. Effect of M/E ratio on percentage solute recovery.

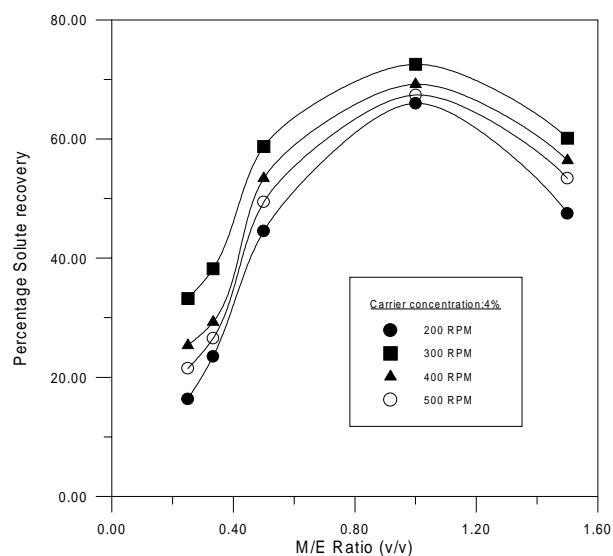


Fig. 8b. Effect of M/E ratio on percentage solute recovery.

is due to the reduction in interfacial area of contact between external phase and emulsion phase due to high intensity of micelle concentration, (nothing but the dense micelle interfacial layer formed) at the membrane phase which resists the solute transfer.

3. Effect of carrier concentration

Increasing the amount of carrier has two effects. The viscosity of membrane phase, which limits the extraction rate, decreases on increasing the carrier concentration and hence the carrier acts as a thinner for

the membrane phase and enhances the rate of solute transport through membrane for extraction. At the same time, increasing the carrier concentration over a certain limit decreases the stability of the emulsion. The maximum recovery of Cr (VI) ions is found at a carrier concentration of 3 % (v/v) based on emulsion phase as shown in Fig. 9.

4. Effect of Feed Concentration

The effect of feed concentration on percentage solute recovered in the synthetic effluent at optimised

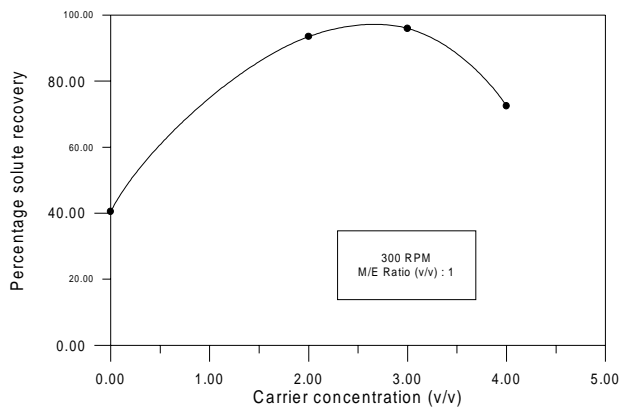


Fig. 9. Effect of carrier concentration on percentage of solute recovery.

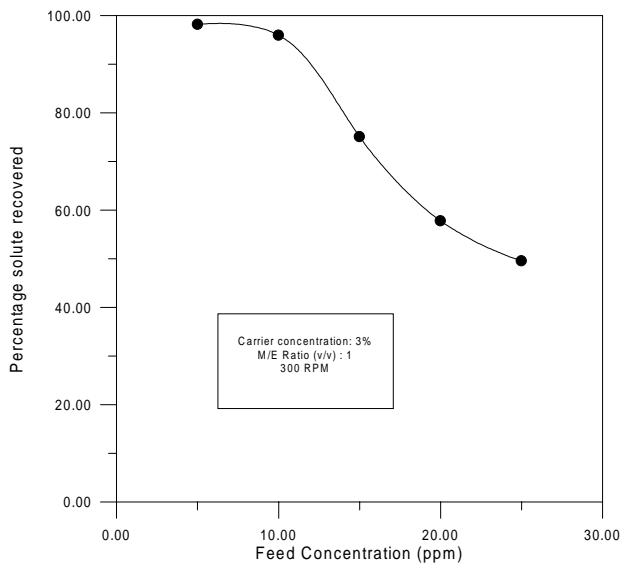


Fig. 10. Effect of feed concentration on percentage of solute recovery.

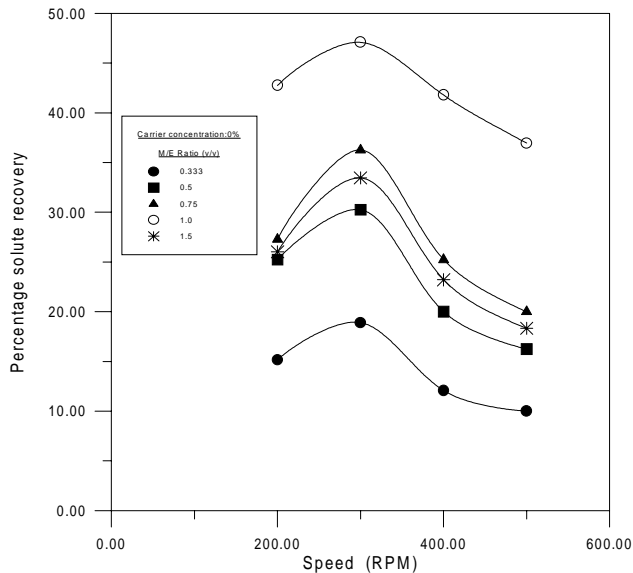


Fig. 11. Effect of speed on percentage solute recovery.

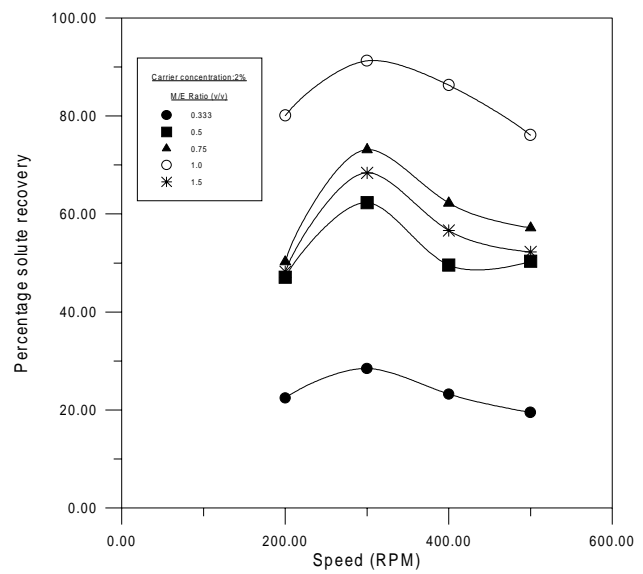


Fig. 12. Effect of speed on percentage solute recovery.

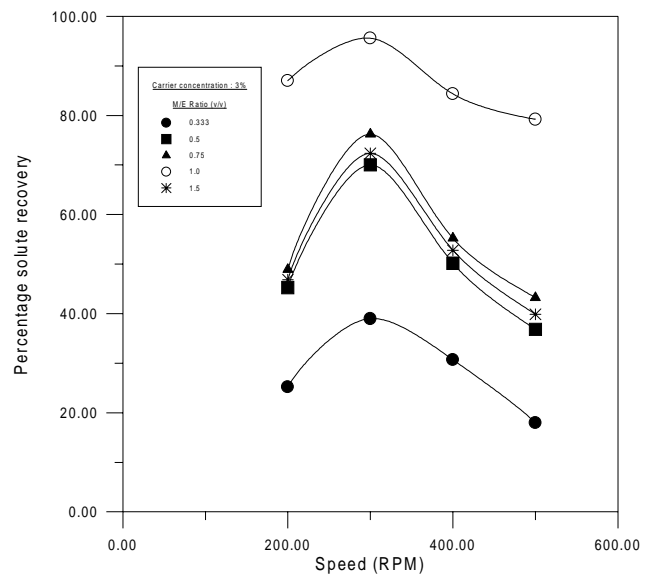


Fig. 13. Effect of speed on percentage solute recovery.

conditions of 300 rpm, 1:1 M/E ratio and 3 % carrier concentration is shown in Fig.10. It is observed that increase in feed phase concentration decreases the percentage of solute recovered. This also confirms that this technique is more effective to treat dilute streams.

Effect of operating parameters on electroplating effluent

Experimental studies were carried out at various impeller speeds for different M/E ratios and carrier concentrations to optimize the operating conditions on the

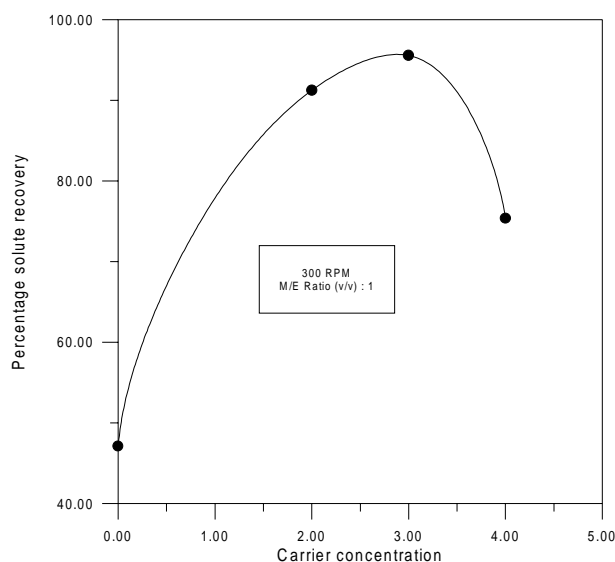


Fig. 14. Effect of carrier concentration on percentage of solute recovery.



Fig. 16. Effect of speed on percentage solute recovery.

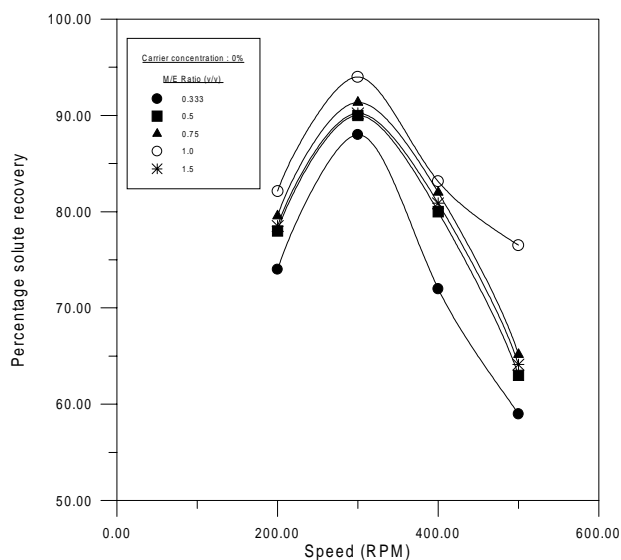


Fig. 15. Effect of speed on percentage solute recovery.

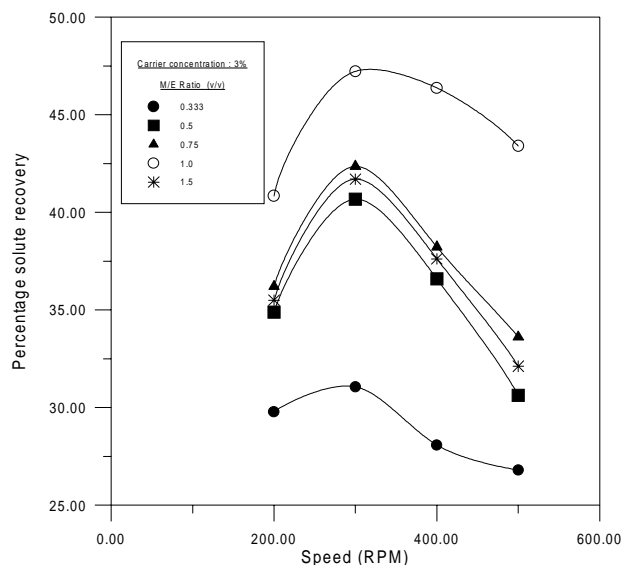


Fig. 17. Effect of speed on percentage solute recovery.

recovery of Cr (VI) ions from the electroplating effluent as external phase and the results are shown in Figs. 11-14. Results indicate that a similar trend of solute recovery for various agitation speeds (200 to 500 rpm), M/E ratio (0.33 to 1.5 v/v) and carrier concentrations (0 to 4 %) as that of synthetic effluent. When the speed is increased beyond 300 rpm, the percentage solute recovered is reduced at different M/E ratios. The agitation speed of 300 rpm is found to be the most effective one and the recovery of Cr (VI) ions is 47.1 %, 91.26 %, 95.59 % and 75.36 % from electroplating effluent at 0 %, 2 %, 3 % and 4 % carrier concentrations respec-

tively at an M/E ratio of 1:1 as shown in Figs. 11-13. From Fig. 14 it is found that the carrier concentration of 3 % (v/v) based on emulsion phase is the optimum for the maximum recovery of Cr (VI) ions in the effluents from Electroplating Industry.

Effect of operating parameters on Tannery Effluent

The effect of operating conditions on percentage recovery of Cr (VI) ions from the tannery effluent as external phase as shown in Figs. 15-17. They indicate that the agitation speed at 300 rpm is found to be the

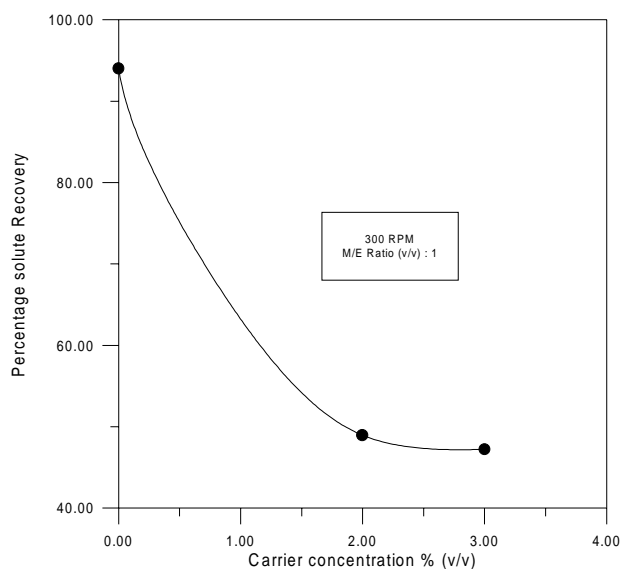


Fig. 18. Effect of carrier concentration on percentage of solute recovery.

most effective to recover 94 %, 48.93 % and 47.23 % of Cr (VI) ions using 0 %, 2 % and 3 % carrier concentrations respectively at an M/E ratio of 1:1.

The effect of carrier concentration in the membrane phase on percentage solute recovery from external phase at 300 rpm and 1:1 M/E ratio is shown in Fig. 18. It is clearly seen that in the absence of carrier, the percentage solute recovery is maximum (the highest). Increasing the carrier concentration decreases the percentage solute recovery which is an anomalous situation. This is due to the suppression of ionization of Bis-2-ethylhexyl phosphate by the highly acidic tannery effluent containing hexavalent chromium which has a pH of 1.45.

Mathematical equation predicted by Regression Analysis

The percentage of solute recovered from external phase (R) is dependent on Speed (N), Membrane to external phase ratio (M/E) and Carrier concentration (C). By regression analysis of all the above experimental results, the following relation was arrived for the solute recovery in terms of operating parameters.

$$R = 17.7868 + 0.0144485N + 51.7283 (M/E) - 1.43319 C.$$

The above equation fits the experimental data within an average error of 15 %.

CONCLUSIONS

From the studies conducted it is concluded that the emulsion prepared for the removal of Cr (VI) ions at 6000 rpm with an agitation for 15 minutes containing 1.2 % (v/v) surfactant and 2-3 % (v/v) carrier is very stable.

- The maximum solute recovery of 96 % is obtained for the M/E ratio (v/v) of 1:1 at an extraction speed of 300 rpm and 3 % carrier concentration for the synthetic effluent containing Cr (VI) ions.

- The maximum solute recovery of 95.59 % is obtained for the M/E ratio (v/v) of 1:1 at an extraction speed of 300 rpm and 3 % carrier concentration for the effluent from electroplating industry containing Cr (VI) ions.

- The maximum solute recovery of 94 % is obtained for the M/E ratio (v/v) of 1:1 at an extraction speed of 300 rpm and 0 % carrier concentration for the effluent from tannery industry containing Cr (VI) ions.

It is found that the extraction performance decreases beyond 300 rpm and M/E ratio of 1 due to membrane leakage and reduction in interfacial area, respectively. As far as the carrier concentration is concerned, in the case of tannery effluent the ionization is suppressed due to the acidic nature of the effluent which leads to decrease in solute recovery.

A mathematical equation has been developed from the experimental data by Regression Analysis, the equation is validated, and it is found to fit with a deviation of 15 %. Based on the above laboratory results it has been concluded that ELM technique has a great potential to be utilized for the recovery of chromium from electroplating and tannery effluents. The work on continuous extraction column using ELM technique for the recovery of Cr (VI) ions is in progress.

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