

Emulsion breakage behaviour on chromium (VI) removal using emulsion liquid membrane containing quaternary ammonium compounds

Norul Fatiha Mohamed Noah ^a, Norasikin Othman ^{a,b,*}, Norela Jusoh ^a

^a Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^b Centre of Lipids Engineering & Applied Research (CLEAR), Ibnu Sina Institute for Scientific and Industrial Research (ISISIR), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

* Corresponding author: norasikin@cheme.utm.my

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Abstract

Environmental pollution caused by heavy metals such as chromium, nickel, and lead has become a serious worldwide issue due to their threats to humans, animals and plants as well as to the stability of the overall ecosystem. Its removal from effluents such as electroplating rinse wastewater and tannery effluents is of primordial importance. In this study, the emulsion liquid membrane (ELM) technology was employed as a remediation technique that capable of removing Cr (VI) efficiently from wastewater where extraction and stripping processes are performed in a single operation. The ELM is consists of trioctylmethylammonium chloride (Alamine 336) as an extractant, palm oil as an organic diluent, sodium hydroxide (NaOH) as a stripping solution and sorbitan monooleate (Span-80) as a surfactant to stabilize the emulsion phase. The effect of operational parameters such as the agitation speed, phase contact time, extractant concentration and stripping agent concentration were studied to optimize the conditions for emulsion stability and maximum removal of chromium. The best removal efficiency was obtained at 350 rpm of agitation speed and 3 minutes of phase contact time with 0.04 M Alamine 336 as extractant and 0.1 M NaOH as stripping agent. In this condition, the maximum removal efficiency of 98% was obtained with a minimum breakage rate of 10%.

Keywords: Emulsion liquid membrane, chromium, electroplating wastewater, chromium

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INTRODUCTION

Chromium is one of the heavy metals that are non-degradable and their presence in wastewater inhibits the microbial digestion processes which can lead to biomagnification when released into the environment via discharge waters. Along with the development of manufacturing industries, the amount of chromium ions in wastewater which were direct and indirectly discharged to the environment have tremendously increased[1]. In industrial wastewater treatment, chromium are considered as more toxic and receiving more attention from researchers [2].

Cr exists in various oxidative forms in wastewater; however, two stable oxidation states which are Cr (III) and Cr (VI) are considered more significant in term of environmental pollution point of view. Owing to its high carcinogenic and resistant properties, Cr (VI) compounds are approximately 100 times more harmful and toxic than Cr (III) salts[3][4]. There are many Cr contamination sources such as metal plating industry, mining operations, tanneries, batteries, electroplating and metallurgy[5]. Cr (VI) pollution is mainly caused by excessive discharging of wastewater from electroplating industries in which Cr (VI) concentrations are ranged from 42.8 to 3950.0 mg/L.

The U.S. Environmental Protection Agency has identified Cr (VI) as one of the heavy metals that can be a threat to humans, and set enforceable standards in drinking water and wastewater discharge which are <50 µg/L and 0.1–0.5 mg/L, respectively[6]. Ingestion of Cr (VI) beyond the permissible limits can cause severe gastric damage,

liver, kidney and lung cancer, and other health related complications[7]. Over the past few years, there have been numerous new methods and techniques developed focusing on the removal of Cr ions from industrial wastewater such as oxidation[8][6], reduction[9], reverse osmosis, electrodialysis[10], biosorption[11], ion exchange[12], and ultrafiltration [13]. However, these methods have inherent limitations such as large amount of sludge generation, less efficiency, sensitive operating conditions and costly disposal. Obviously, it is of great importance to find an eco-friendly removal process for Cr (VI) due to the growing awareness of the environmental protection problems.

One of the promising methods to remove Cr (VI) from wastewater is emulsion liquid membrane (ELM). ELM technique is widely investigated in the field of wastewater treatment to remove heavy metal ions [14][15][16], organic pollutants[17][18][19][20], and other contaminants. Li invented the ELM separation technique in 1968 [21], which was based on selective permeation through a liquid surfactant membrane. An ELM is a three-phase dispersion system, where a primary emulsion is dispersed in a continuous effluent phase, which is the phase to be treated. In this system, the extraction and stripping steps take place simultaneously and therefore, the system do not usually meet the equilibrium making it a very efficient separation technique.

Unfortunately, stability problem is the most serious problems in the application of the emulsion liquid membrane to industrial separation process. The membrane breakage includes rupture of the emulsion, leading to loss of internal phase. The main factors affect the emulsion stability encompass membrane formation, emulsion

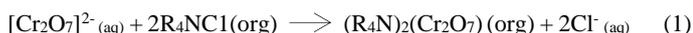
preparation methods and condition under which emulsion is contacted with reactant phase. Breakup of the emulsion and subsequent release of the internal receptor phase to the external donor phase would nullify the extraction process [12]. In the meantime, the membrane breakage occurs when portions of the internal phase spill into the external phase. During breakage, the stripping agent and previously extracted solute is leaked into the external phase [22].

Nowadays, there are very few studies that use palm oil as a diluent in the ELM process. Yet, among nine types of commercially available vegetable oils in India, Venkateswaran and Palanivelu [15], found that palm oil is the best LM with permeability of 8.5×10^{-6} m/s in acidic feed of pH 2.0 with 0.2 M sodium hydroxide as an effective stripping agent. Since palm oil is easily available in Malaysia at a low cost, it is a suitable substitute for the common petroleum-based diluents such as kerosene, toluene, heptane and n-dodecane.

The main focus of this research is to utilize a quaternary ammonium compound (Alamine 336) as extractant to extract Cr (VI) from the electroplating rinse wastewater by ELM using palm oil as ecofriendly solvent. The effect of various operating conditions such as concentration of extractant, speed of agitation, phase contact time and stripping agent concentration were studied on the emulsion stability and extraction efficiency of Cr (VI) from aqueous solutions.

Mechanism of chromium extraction process

The mechanisms of Cr extraction and stripping processes involving $[\text{Cr}_2\text{O}_7]^{2-}$ ion Alamine 336 and NaOH are illustrated in Figure 1. In this mechanism the extractant, Alamine 336 presented in the membrane phase chemically reacts with Cr anionic complex in palm oil (liquid membrane phase) to form complexes of Cr-Alamine 336 at the membrane-external interphase as represented by Equation 1 [12].



Then, the complex $(\text{R}_4\text{N})_2(\text{Cr}_2\text{O}_7)$ diffused through the liquid membrane phase from the membrane-external interphase to the membrane-internal interphase. Then, the Cr-Alamine 336 complexes at the membrane-internal interphase were stripped by reacting it with NaOH from the internal phase as shown in Equation 2. The Cr-sodium complexes were released to the internal phase and the extractant diffused back to the membrane-external interphase to react with other Cr [12].

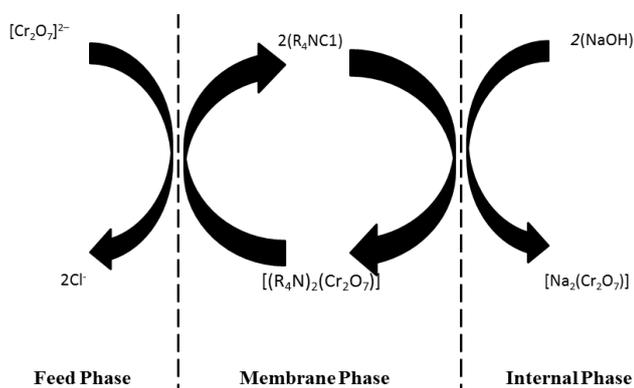
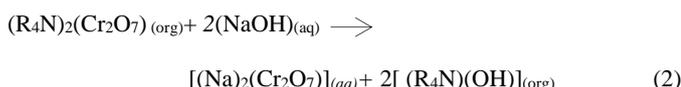


Figure 1 Extraction and stripping mechanism of Cr by Alamine 336.

EXPERIMENTAL

Materials

There are four components in ELM system namely extractant, surfactant, stripping agent and diluent. All four components were manufactured for laboratory grade and were used as received. Alamine 336 as an extractant for Cr was obtained from Sigma Aldrich. Palm oil

and Span 80 as a diluent and surfactant were purchased from Buruh and Fluka, respectively. NaOH was purchased from Merck (M) Sdn. Bhd. Real rinse electroplating process wastewater sample contained 40ppm Cr (VI) was obtained from the Electroplating Company at Masai, Johor.

Analytical method

The apparatus used includes Homogeniser Heidolph Silent Crusher-M. Perkin Elmer Flame Atomic Absorption Spectrometer (AAS) was used for Cr (VI) measurements at $\lambda=540$ nm. The extraction experiments were carried out using a digital mixer system (Cole-parmer EW-50006-00).

Rinse electroplating wastewater characterization

Ion Chromatography (IC) model LC20 with electric chemical detector model ED40 was used to measure anion contents in the rinse electroplating wastewater samples. Contents of metals in the rinse electroplating wastewaters were measured using the Atomic Absorption Spectroscopy (AAS). Cyber scan 100 pH meter model was used to measure the pH. A hydrometer was used to measure the densities (ρ) of the electroplating wastewater samples. The programmable Rheometer Brookfield Model DV-III at room temperature was used to determine the kinematic viscosity, ν .

Experimental procedures

The organic solution was prepared by dissolving an appropriate concentration of extractant (Alamine 336) and surfactant (Span 80) in a diluent (palm oil). The internal aqueous phase was a NaOH solution. An equal volume of 5mL portions of organic phase and aqueous phase were stirred continuously at 10,000 rpm for about 3 min using a motor driven emulsifier to obtain stable water in oil emulsion. The emulsion must be freshly prepared before each experiment of extraction study. The prepared emulsion was then dispersed into external phase containing Cr in the agitated vessel and stirred at 250 rpm for a few min. The aqueous phase was filtered in order to remove the entrainment and the raffinate phases were analysed by AAS. The volume of emulsion before and after extraction was measured for emulsion stability study. The range of parameter used in the ELM extraction of Cr from simulated liquid waste is listed in Table 1. All experiments were performed at room temperature (26 ± 1 °C).

Table 1: Experimental conditions used for the preparations of ELMs.

Operating conditions	Ranges
Volume of NaOH (ml)	5
Volume of Alamine 336 in palm oil (ml)	5
Emulsifying time (min)	3
Span 80 concentration (% w/v)	3% w/v
Homogenizer speed (rpm)	10000
Agitation speed (rpm)	150-450
NaOH concentration (M)	0.05-1.0
Alamine 336 concentration (M)	0.004-0.1
Treat ratio (emulsion to external ratio)	1:3
Phase contact time (min)	1, 3, 5, 7

The percentage of Cr extraction and swelling or breakage were determined using Equation 3 and 4:

$$\text{Extraction (\%)} = \frac{[\text{Cr}]_i - [\text{Cr}]_f}{[\text{Cr}]_i} \times 100 \quad (3)$$

$$\text{Swelling/Breakage (\%)} = \frac{V_f - V_i}{V_i} \times 100 \quad (4)$$

where, $[\text{Cr}]_i$ is the initial concentration of Cr ion in aqueous before extraction, $[\text{Cr}]_f$ represents the final concentration of Cr ion in aqueous after extraction, V_i is the initial volume of emulsion before extraction, and V_f is the final volume of emulsion after extraction process. Positive value give swelling meanwhile negative value give breakage percentage.

RESULTS AND DISCUSSION

Rinse electroplating wastewater characterization

The properties of the rinse electroplating wastewater are presented in Table 1. Both physical and chemical characterizations towards rinse electroplating wastewater were carried out including the analysis of ions compositions, density, pH, and viscosity. Chromium used in the electroplating process is Sodium dichromate (NaCr_2O_7). Generally, hexavalent chromium ions exist in aqueous solution as various forms of chromate such as hydrochromate (HCrO_4^-), chromate (CrO_4^{2-}), and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ionic species. The proportion of each ion in solution is pH dependent. In acidic condition, the dichromate ($\text{Cr}_2\text{O}_7^{2-}$) species predominate. In this experiment, pH of the chromium (VI) stock solution prepared was around 3.0 and, thus, hydrochromate dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions predominated and involved in most of the reactions. Results showed that chromium ions appeared in high concentrations (43 ppm) while the other metal ions such as As, Cd and Fe existed in a very low concentration (<0.5 ppm) and almost negligible. While, the low concentrations of sulphate ions at 4.45 ppm in the exit waste indicate that it may not compete with chromium ions extraction in the system.

Table 1: Physical and chemical properties of real rinse electroplating wastes solution.

Cations	Concentration (ppm)	Anions	Concentration (ppm)
Cr	42.62	SO_4^{2-}	4.45
As	0.14		
Fe	0.027	Physical properties	
Cd	0.04	Viscosity	0.83 cP
		Density	1.008 g/ml
		pH	3

Effect of agitation speed

The influence of agitation speed towards the performance of Cr extraction and emulsion breakage is depicted in Figure 2. The result shows that at low agitation speed of 150 rpm, the percentage of membrane breakage is higher which is around 40%. At the same time, low Cr extraction percentage which is around 60% is observed. This indicates that lower speed offers weak dispersion of emulsion in the treated feed solutions, hence leading to the formation of larger globules. As a result, the emulsion will simply break during an extraction process. This result is in agreement with Kumbasar[23], stating that due to the low agitation speed, the ELM globules cannot be well-dispersed in the external solution and formations of large globules were observed during the experiment. Then, there is an increment of the membrane stability from 40% to 20% breakage percentage with increasing agitation speed from 150 to 350rpm, respectively.

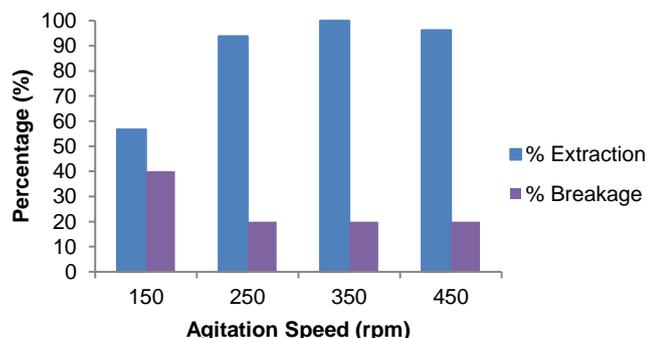


Figure 2: Effect of agitation speed on Cr extraction and emulsion stability (Experimental conditions: [Alamine 336] = 0.04 M, [NaOH] = 0.05 M in distilled water, Aqueous/Organic = 5mL/5mL, Treat ratio = 1:3, Span 80 concentration = 3 % w/v, emulsifying time= 3 minutes, homogenizer

speed = 10000 rpm, Phase contact time = 3 min, and initial pH of waste = 3).

Meanwhile, the extraction performance drastically increases from 60% to 100%. This is due to the smaller emulsion globules formed as a result of shear force from the agitation speed. This condition will provide more mass transfer area leading to higher Cr extraction and emulsion stability. Further increment up to 450 rpm resulted in no significant effects on the breakage percentage which remains constant at 20%. However, the extraction percentage has slightly decreased from 100% to 98%. Higher mixing speed may results in breaking the emulsion droplets. At the same time, some globules also tend to swell. Therefore, this indicates that the increase in mass transfer area resulted by the formation of smaller globules at higher speeds of agitation cannot compensate the effect of internal phase reagent release through emulsion breakup. Consequently, above a critical speed of agitation, the overall rate of extraction decreases and the extraction efficiency decreases considerably [12]. Thus, 350 rpm is an appropriate speed for further extraction process.

Effect of phase contact time

Figure 3 illustrates the effect of various phase contact time towards the performance of Cr ion extraction and emulsion breakage. According to Figure 3, 30% of emulsion breakage was observed at the first 1 min. Insufficient contact time leads to the formation of larger size of emulsion globules that easily ruptures, thus causing the stripping agent to leak into the external phase. The result demonstrates that Cr extraction increases on increasing contact time from 1 to 3 minutes while at the same time, the breakage decreases. It seems that this period of contact time is adequate for satisfactory extraction efficiency. As the phase contact time was further increased up to 7 min, the extraction remain unchanged while emulsion breakage increased. This is due to the instability of the emulsion over longer contact times. This can be explained by the fact that the hydration surfactant significantly increases the co-transport of water molecules into the internal phase. Due to the equal amount of organic phase and internal phase, this amount of organic is unable to retain the increased amount of water inside the phase properly hence leading to the emulsion breakage. Thus, 3 min of contact time were the best condition for Cr ion extraction and chosen for the next experiment.

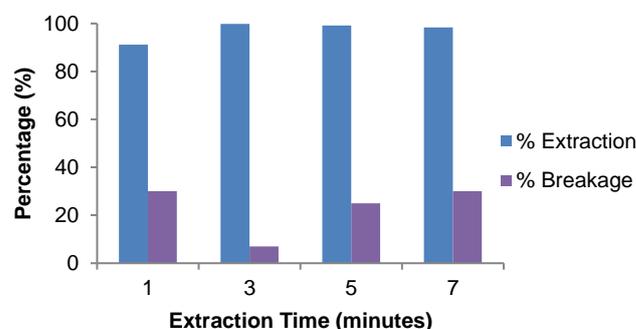


Figure 3: Effect of phase contact time on Cr extraction and emulsion stability (Experimental conditions: [Alamine 336] = 0.04 M, [NaOH] = 0.05 M in distilled water, Aqueous/Organic = 5mL/5mL, Treat ratio = 1:3, Span 80 concentration = 3 % w/v, emulsifying time= 3 minutes, homogenizer speed = 10000 rpm, Agitation speed= 350rpm and initial pH of waste = 3).

Effect of extractant concentration

The variation of extraction percentage and membrane breakage with Alamine 336 concentration is presented in Figure 4. In the concentration range of 0.004 to 0.04 M, the percentage of Cr extraction increases from 70 to 100%. Theoretically, a good extraction performance will be obtained at high concentration of Alamine 336 as more Cr-Alamine 336 complexes existed in the liquid membrane phase. Therefore, more Cr is extracted within the time. This theory is in agreement with León et al [24] stating that the increase in the extractant concentration enhances the extraction of metals as a higher number of extractant molecules are associated to the metal ions. At the same time, increasing the extractant concentration from 0.004 to 0.01 M results to no significant changes in the emulsion breakage due to some globules

that tend to swell and break at the same time. Therefore, a trade-off between these two effects exists. Furthermore, the emulsion breakage decreases by increasing the extractant concentration from 0.01 to 0.04 M. This can be attributed to the membrane phase that tends to be more viscous at higher extractant concentration as shown in Figure 5. This condition creates resistance for water molecules transportation from the feed phase into the internal phase, hence decreasing the emulsion breakage. This is supported by Lee et al. [25] that higher concentration of extractant leads to high viscosity effect which resists the mass transfer of water molecules into the internal phase [25].

At 0.04 to 0.1 M of Alamine 336 concentrations, there are no significant changes observed in Cr extraction and emulsion breakage. This indicates that 0.04 M Alamine 336 is enough for extraction of Cr. Also, this can be ascribed to the increase in the membrane viscosity with increasing extractant concentration which leads to a lower diffusion of metal complexes through the membrane phase, as noted by other authors [26]. This is in agreement with Björkegren et al. [27] that excess in extractant concentration leads to high osmotic swelling and high rates of membranes breakdown. Then, a trade-off between these two effects exists. According to these data, 0.04 M Alamine 336 concentration is selected as the best condition with the lowest percentage of breakage.

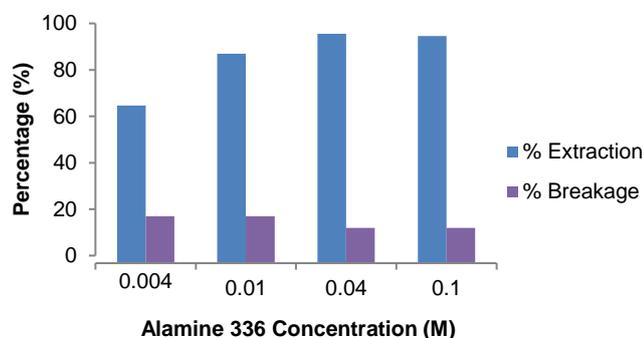


Figure 4: Effect of Alamine 336 concentration on Cr extraction and emulsion stability (Experimental conditions: [NaOH] = 0.05 M in distilled water, Aqueous/Organic = 5mL/5mL, Treat ratio = 1:3, Span 80 concentration = 3 % w/v, emulsifying time= 3 minutes, homogenizer speed = 10000 rpm, Phase contact time = 3 min, Agitation speed= 350rpm and initial pH of waste = 3).

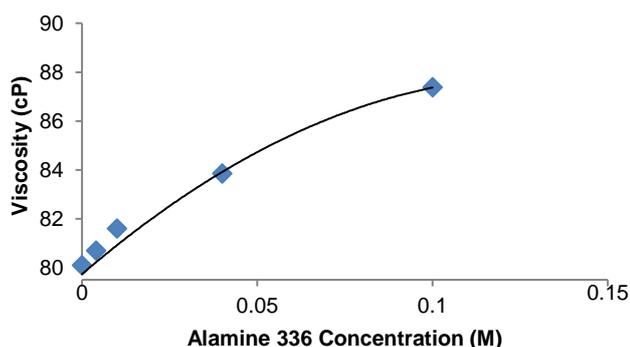


Figure 5 Effect of extractant concentration on viscosity of liquid membrane (Experimental conditions: Diluent = palm oil).

Effect of stripping agent concentration (NaOH)

Figure 6 illustrates the effect of stripping agent concentrations on the extraction of Cr ion performance and emulsion stability. The result demonstrates that 98% of Cr ion is extracted with NaOH concentration in between 0.05M to 0.5 M. This indicates that 0.05M is enough for facilitated transport of Cr. However, the degree of break-up was found to be scarcely dependent indicating that the range of NaOH concentration added (<0.5M) as a stripping reagent in the internal phase does not affect the stability of liquid membranes.

Subsequently, there is a decrease of the Cr extraction from 95 to 80% with increasing NaOH concentration from 0.5 to 1.0 M, respectively. At the same time, the membrane breakage increases from

5 to 20%, respectively. This can be explained by the fact that the NaOH concentration beyond 0.5 M created a stronger pH gradient that leads to the occurrence of osmotic pressure gradient between the external liquid phase and the W/O emulsion phase, allowing transportation of more water molecules from the feed phase into stripping phases. Accumulation of water inside the W/O emulsion globules will cause globule swelling and eventually break-up, leading to a loss in the liquid membrane extraction efficiency [15]. Furthermore, an increase in NaOH can cause hydrolysis of the ester bonds of Span-80 [24], leading to a decrease in the W/O emulsion stability. Hence, an increase in NaOH concentration will adversely affect the extraction efficiency. Similar trends were reported previously by Othman et al. [12] indicating that higher concentration of stripping agent will lead to reactions with surfactant and reduces the number of surfactant in the membrane causing emulsion destabilization. The saturation of the driving force for diffusion through ELM also exists owing to the increase of metal complexes concentration at the membrane-stripping solutions interface [28]. Therefore, further increase of the NaOH concentration from 0.5 to 1.0 M only significantly reduced the Cr extraction and increased the breakage percentages. The stripping agent concentration is important with respect to the emulsion stability, as concentrations higher than 0.5 M NaOH results in decreased removal efficiency.

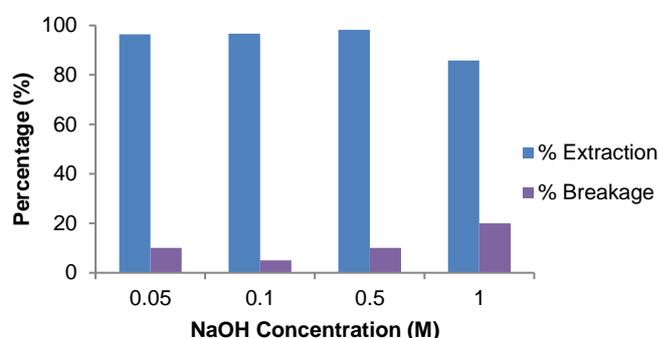


Figure 6: Effect of NaOH concentration on Cr extraction and emulsion stability (Experimental conditions: [Alamine 336] = 0.04 M, Aqueous/Organic = 5mL/5mL, Treat ratio = 1:3, Span 80 concentration = 3 % w/v, emulsifying time= 3 minutes, homogenizer speed = 10000 rpm, Phase contact time = 3 min, Agitation speed= 350rpm and initial pH of waste = 3).

CONCLUSION

As a conclusion, a system of emulsion liquid membranes was developed in order to remove Cr ions from wastewater. The best conditions to obtain the stable emulsion was at the 350 rpm of agitation speed, 3 minutes of phase contact time, 0.04 M Alamine 336 as extractant and 0.1 M NaOH as stripping agent with values of extraction yields of 100%.

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