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Synergetic formulation of Cyanex 272/Cyanex 302 for hexavalent chromium removal from electroplating wastewater

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Abstract−Hazardous hexavalent chromium (Cr(VI)) released from the electroplating industry beyond the discharge concentration limit has created great concern worldwide. Solvent extraction (SX) is an effective method for metal separation from an aqueous system. Throughout this work, novel synergistic solvent extraction of Cr(VI) from rinsed electroplating wastewater was performed using a mixture of two organophosphorus acidic extractants containing di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) and di-2,4,4-trimethylpentyl mono-thio-phosphinic acid (Cyanex 302) in kerosene. The results showed almost 99±0.816% of Cr(VI) was synergistically reduced and extracted to the less toxic trivalent chromium (Cr(III)) using the total mixture concentration of 0.1 M (0.04 M Cyanex 272+0.06 M Cyanex 302). For recycling, the organic phase was recycled or reused up to 11 times for excellent extraction (99±0.471%) and stripping (99±0.942%) and became stable afterwards until a certain time. The total concentration of the mixture system was reduced by 50% (0.05 M) using 0.01 M Cyanex 272 and 0.04 M Cyanex 302, with almost 100% of Cr(VI) extraction as less toxic Cr(III). The Cr(III) in the loaded organic phase was completely recovered using 7.0 M hydrochloric acid (HCl). It is concluded that the synergistic extraction using Cyanex 272/Cyanex 302 system improved the Cr(VI) extraction and reduced the chemical consumption in the organic phase.

Keywords: Synergistic Formulation, Solvent Extraction, Cr(VI), Electroplating Wastewater

INTRODUCTION

Metal processing industries are well known as high heavy metal dischargers of industrial effluents because they deal with various types of heavy metal ions in their processes [1]. Electroplating is one of the significant industrial contributors of heavy metal effluents into the environment because heavy metals are effectively utilized in electroplating. Chromium (Cr) is one of the most encountered metals in these industries. The release of industrial wastewater containing Cr, especially in the hexavalent state (Cr(VI)), is considered toxic compared to its less toxic form of trivalent chromium (Cr(III)). According to the Department of Environment Malaysia (DOE), the standard discharge limits of Cr(VI) and Cr(III) are 0.05 and 0.20 ppm, respectively [2]. Hence, removing Cr(VI) from wastewater has become the greatest priority for these industries. Cr(VI) has been successfully extracted or removed using several conventional methods, including membrane separation, adsorption, precipitation, and solvent extraction (SX). Previously, Hosseini et al. [3] effectively removed Cr (~80%) from electroplating wastewater using fabricated nanofiltration membrane. Muthumareeswaran et al. [4] successfully removed Cr (>90%) from wastewater using ultrafiltration membrane. However, these methods usually suffer from high operating costs and energy consumption. Liquid membrane technology for Cr removal has been reported by previous studies with higher extraction percentages within the range of 90%-99% [5-7]. However, this technology seems to be limited by the instability of emulsion and membrane support. Dognani et al. [8] reported the effective removal of Cr from wastewater using adsorption, which could be successfully recycled and reused for at least five cycles. Adsorption highly depends on the adsorbent used, which is sometimes produced from expensive materials, such as activated carbon [9]. Meanwhile, precipitation is one of the well-known methods applied in the industry due to its simplicity and low cost. However, sludges are produced through precipitation, which requires further handling and treatment [10].

Solvent extraction is one of the simplest separation techniques widely applied to remove various metals from wastewater [11]. Through this method, the organic phase containing an extractant in the diluent (organic liquid) can selectively extract the targeted metal ion from aqueous wastewater [12,13]. The successful removal of Cr(VI) through SX applied various types of basic and neutral extractants, including tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), trioctylamine (TOA), and Aliquat 336 [14-19]. Synergistic extraction of heavy metals through SX has attracted considerable attention as the method is proven to synergistically improve the extraction performance of the targeted solute and simultane-

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Table 1. Summary of synergistic extraction of chromium using various mixture of extractants

Metal	Extractants	Type of mixture	Reference
Cr(III)	D2EHPA+Cyanex 272	Acidic-acidic	[28]
	D2EHPA+Isooctanol	Acidic-neutral	[19]
Cr(VI)	Triethanolamine+Trioctylamine	Basic-basic	[25]
	Alamine 300+Aliquat 336	Basic-basic	[26]
	Triisooctylamine+Tributylphosphate	Basic-neutral	[20]
	Cyanex 272+Cyanex 302	Acidic-acidic	Present work

ously reduce the amount of extractant used [19-24]. Table 1 presents a summary of the synergistic extraction of Cr using various mixtures of extractants, including basic-basic, basic-neutral, acidic-acidic, and acidic-neutral [20,25,26]. Due to the basic property of amine extractants, Cr(VI) can be extracted through ion-pair formation via anion exchange reaction between these amine extractants and the metal ions [27]. In contrast to Cr(VI), Cr(III) is more preferred to be extracted using acidic extractants through the cation exchange mechanism [20,21]. Another acidic hydroxy oxime extractant, LIX63, could also extract metals at a lower pH value of the aqueous phase [20]. The extractant contains an oxygen donor atom (hard base) that can form a complex with Cr(VI) (hard acid). Nevertheless, it is reported that LIX63 has slower extraction kinetics during metal extraction [21]. Neutral extractants are weakly basic and selectively extract neutral metal complexes by forming a solvate [27].

However, to date, there are no works concerning the synergistic extraction of Cr(VI) using a mixture of acidic-acidic extractants. Hence, through this work, the mixture of two organophosphorus acidic extractants as the novel synergistic extraction system was studied using a mixed extractant system containing di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) and di-2,4,4-trimethylpentyl mono-thio-phosphinic acid (Cyanex 302) for the removal of Cr(VI) from electroplating wastewater. The extraction behavior, composition and stoichiometric studies of the mixed extractant system, recovery of Cr from the loaded organic phase, and effect of carrier concentration were investigated. According to Senol [26], an extended matrix of distribution data for Cr(VI) removal produced using several mixtures of extractants achieved a larger optimal removal efficiency. This means that the selected mixed reagents are suitable as separating agents for Cr(VI) removal, hence showing excellent potential for a generalized application and optimization of the process. The derivative variation method proposed is applicable as an optimization tool towards complex non-linear phenomena, such as that in a reactive extraction system. Through this work, it is expected that an extended matrix of distribution data for Cr(VI) removal using the Cyanex 272/Cyanex 302 system can achieve the optimum removal efficiency and demonstrate excellent potential for a generalized application.

EXPERIMENTAL

1. Materials

Industrial plating wastewater containing Cr(VI) was supplied by a local electroplating company in Pasir Gudang, Johor, Malaysia. The electroplating wastewater was analyzed as shown in Table 2. As can be noted, the highest concentration was recorded for Cr(VI) (42.26 ppm) compared to other metals in the acidic electroplating wastewater. Besides chromium, other metals present in the sample included cadmium, Cd (0.04 ppm), Arsenic, As (0.14 ppm) and Iron, Fe (0.027 ppm). In terms of the selectivity, As, Fe and Cd existed at a very low concentration (<0.5 ppm) and almost negligible. This indicates that the influence of other metals present in the feed phase probably did not disturb the chromium ions removal process in the system. Moreover, instead of acidic extractant, the extraction of Cd and As mostly uses basic extractant such as Tri-iso-octyl amine (TIOA), trioctylamine (TOA) and Aliquat 336 [29-31]. The organic formulation for synergistic Cr extraction was formulated using organophosphorus acidic extractants, Cyanex 272 (95%), Cyanex 302 (99%), and bis-2-ethylhexyl phosphoric acid (D2EHPA) (≥95% assay) procured from Sigma-Aldrich. Meanwhile, 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX63) was supplied from Cognis, Australia. Kerosene as diluent was purchased from Sigma-Aldrich. Diphenylcarbazide (DPC) obtained from Sigma-Aldrich was employed for the analysis of chromium concentration. All chemicals and raw materials were directly utilized without further purification.

Table 2. Analysis of Cr electroplating wastewater [32]

Physical properties	
Viscosity	0.83 cP
Density	1.008 g/ml
pH	3.0
Ions	Concentration (ppm)
Cadmium, Cd^{2+}	0.04
Chromium(VI), $Cr_2O_7^{2-}$	42.62
Arsenic, As^{5+}	0.14
Iron, Fe^{2+}	0.027
Sulfate, SO_4^{2-}	4.45

2. Solvent Extraction (SX) Process

Solvent extraction was performed by shaking equal volumes of liquid organic (extractants in organic diluent) and aqueous phases (chromium electroplating wastewater) using a mechanical shaker at 320 rpm for 18 h in order to reach the equilibrium. After settling or phase separation of the aqueous and organic phases for about 30 min, the concentration of chromium in electroplating wastewater was diluted and analyzed via reaction with DPC in acidic solution, wherein the red-violet solution of unknown composition was produced. This solution was analyzed using an ultraviolet-visible (UV-Vis) spectrophotometer at a wavelength of 540 nm. The concentration of chromium in the organic phase was calculated using mass balance principles. For the back extraction or stripping, the chromium-loaded organic phase was shaken with an equal volume of stripping solution using the above-mentioned similar conditions to achieve the equilibrium. Similarly, after separation, the concentration of chromium in the electroplating wastewater was analyzed using a UV-Vis spectrophotometer. All experiments were carried out at room temperature (26±1 °C). The experiments were conducted in triplicate with standard deviation less than 5%. Fourier transform infrared (FTIR) spectroscopy was performed to analyze the complex formation in the organic solution containing chromium loaded with the extractant.

3. Data Analysis

In SX, the efficiency of extraction and stripping was calculated by means of Eqs. (1) and (2), respectively. The distribution ratio, D, and synergistic enhancement factor, R_f, were determined by means of Eqs. (3) and (4), respectively [21,33]. D represents the ratio of the chromium concentration present in the organic phase to the aqueous phase at equilibrium. R_f is the ratio of the distribution ratio of mixed-extractant system to the distribution ratio of single extractants.

$$\text{Extraction, }\% = \frac{C_i - C_{aq}}{C_i} \times 100 \tag{1}$$

$$\text{Stripping, }\% = \frac{C_s}{C_{org}} \times 100 \tag{2}$$

$$\text{Distribution ratio, } D = \frac{C_{org}}{C_{aq}} \tag{3}$$

$$\text{Synergistic enhancement factor, } R_f = \frac{D_{mix}}{(D_A + D_B)} \tag{4}$$

where C_i represents concentration of chromium in electroplating wastewater (ppm), C_{aq} represents concentration of chromium in electroplating wastewater after extraction (ppm), C_s signifies concentration of chromium stripping phase after extraction (ppm), C_{org} denotes the concentration of chromium in organic phase. Meanwhile, D_{mix}, D_A and D_B denote the distribution ratios of a Cr ion with mixtures and single extractants, respectively, in the binary liquid system.

RESULTS AND DISCUSSION

1. Extraction of Cr(VI) using Acidic Extractants

Table 3 illustrates the effect of several acidic extractants on the extraction efficiency of Cr(VI). It is noteworthy that Cyanex 302 provided the highest Cr(VI) extraction (68±0.816%), followed by LIX63 (43±1.247%), D2EHPA (17±0.471%) and Cyanex 272 (15±0.471%). Both Cyanex 302 and Cyanex 272 are regarded as phosphinic acids. D2EHPA and LIX63 are phosphoric and chelating acids, respectively. Metal extraction using an acidic extractant is highly pH-dependent, based on the nature of the donor atom [34]. In terms of the phosphinic group, Cyanex 302 seems suitable for the extraction of Cr(VI) from acidic electroplating wastewater. Prior works have reported that a sulfur-containing compound like Cyanex 302 is a strong acidic extractant and capable of extracting the metal at a lower pH of aqueous solution [34,35]. Sole and Hiskey [34] discovered that the acidity of the organophosphorus extractants increased with respect to the lower acid dissociation constant (pK_a) based on the following order: Cyanex 302 (pK_a=5.63)>Cyanex 272 (pK_a=6.37). Also, Cyanex 302 is one of the sulfur-based reducing agents for Cr(VI) to Cr(III) [35]. Electrons are more readily shared in a metal-sulfur bond than in a metal-oxygen bond, hence introducing a greater degree of covalency and increasing the strength of the bond [36]. According to Lanagan and Ibana [11], in terms of the oxidation state, significant extraction of Cr(VI) did not occur at a slightly acidic pH condition when using Cyanex 272. Although Cyanex 272 contains oxygen and is regarded as a hard base that can form a stable complex with Cr, Cyanex 272 is more preferred for the cation exchange mechanism with Cr(III). Besides, its high pK_a value is not suitable for extracting Cr(VI) from acidic solution. LIX63 offers slower kinetics for metal extraction [20]. Meanwhile, the acidic extractant of D2EHPA is more suitable for Cr(III) extraction [19].

Table 3. Effect of acidic extractants on Cr(VI) extraction (Experimental conditions: [Extractant]: 0.10 M; diluent: kerosene; agitator speed: 320 rpm; agitation time: 18 h; temperature= 26±1 °C)

Extractant	Extraction (%)
Cyanex 302	68±0.816
LIX63	43±1.247
D2EHPA	17±0.471
Cyanex 272	15±0.471

2. Effect of Different Mixed Extractant System on Cr(VI) Extraction

Fig. 1 demonstrates the influence of several different mixed extractant systems on Cr(VI) extraction using various combinations of Cyanex 302, LIX63, D2EHPA, and Cyanex 272. Table 4 tabulates the data for the distribution ratios (D) and synergistic factors (R_f) for all the mixed extractant systems considered. The mixed extractants of 0.05 M Cyanex 272+0.05 M Cyanex 302 were advantageous over other mixed extractant systems with the highest Cr(VI) extraction (95%). Additionally, this system yielded the highest D (19.50±0.450) and R_f (7.73±0.021). A high D indicates the high capacity loading of Cr into the organic phase using the Cyanex 272/Cyanex 302 system. Zaheri et al. [37] reported that synergistic extraction occurs when R_f>1, whereas R_f<1 represents antagonistic extraction. The Cyanex 272/Cyanex 302 system exhibits a synergistic effect that accelerates the extraction performance of Cr from acidic electroplating wastewater. Subsequently, 95±1.247% of Cr(VI) was extracted using 0.1 M of the mixture system (0.05 M Cyanex 302+0.05 M Cyanex 272), which was higher than the previous individual system of 0.1 M Cyanex 302 (68±0.816%) and 0.1 M Cyanex 272 (15±0.471%). Therefore, the binary mixture system containing Cyanex 302 and Cyanex 272 can improve the extraction efficiency of Cr(VI).

The dominance of chromate ions ($HCrO_4^-$ and $Cr_2O_7^{2-}$) in Cr-contaminated water is recognized by the yellow or orange color im-

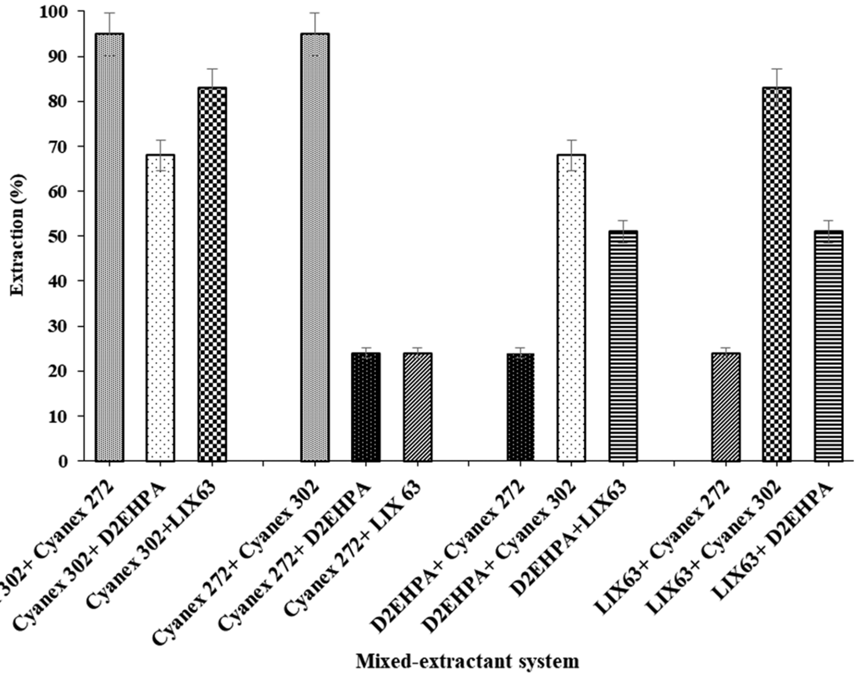

Fig. 1. Effect of mixed extractant system on Cr(VI) extraction (Experimental condition: [Base extractant]: 0.05 M; [synergist extractant]: 0.05 M; diluent: kerosene; agitator speed: 320 rpm; agitation time: 18 h; temperature=26±1 °C).

Table 4. Distribution ratio, D, and synergistic enhancement factor, R_f, of mixed-extractant system on Cr(VI) extraction

Synergist extractant	Base extractant							
	Cyanex 302		Cyanex 272		D2EHPA		LIX63	
	D	R_f	D	R_f	D	R_f	D	R_f
Cyanex 302	1.16±0.022	1.00±0.041	19.50±0.450	7.73±0.021	1.41±0.045	0.58±0.045	4.85±0.082	2.05±0.041
Cyanex 272	19.50±0.450	7.73±0.021	0.17±0.012	1.00±0.041	0.30±0.047	0.46±0.005	0.30±0.014	0.52±0.013
D2EHPA	1.41±0.045	0.58±0.045	0.30±0.047	0.46±0.005	0.21±0.012	1.00±0.041	1.05±0.012	2.14±0.026
LIX63	4.85±0.082	2.05±0.041	0.30±0.014	0.52±0.013	1.05±0.012	2.14±0.026	0.78±0.037	1.00±0.041

parted to the water in the concentration above 1 mg/L. In this work, the aqueous solution containing Cr is orange; hence, dichromate ($Cr_2O_7^{2-}$) seems to be dominant [31]. $HCrO_4^-$ dimerizes to form $Cr_2O_7^{2-}$, as represented by Eq. (5). Regarding the synergistic mechanism, Liu et al. [38] found that the synergistic extraction system highly depends on the nature of the metal ions and the phase medium. Cyanex 302 has a dual function. In terms of the phase medium, the stronger acidic Cyanex 302 can reduce the pK_a value of Cyanex 272 for the maximum extraction of Cr(VI) from acidic aqueous solution [39]. Besides controlling the acidity of organic phase medium, Cyanex 302 is a sulfur-based reducing agent, which reduces Cr(VI) to Cr(III) [34,36]. An equilibrium equation showing the reduction of chromic acid, CrO_4^{2-} to Cr^{3+} after reaction with ($R_2P(S)OH$) (Cyanex 302) is presented in Eq. (6). It is assumed that further oxidation of Cyanex 302 does not occur in this reduction reaction as the pH of the aqueous phase is not strongly acidic [19,36,39]. Using the slope analysis method, Fig. 2(a) shows the mole ratio of Cyanex 302 : Cr in the extracted complex of approximately 2 : 1, representing one mole of Cr complexes that reacted with two moles of Cyanex 302 during extraction.

$$2\,HCrO_{4\,(aq)}^{-} \rightarrow Cr_2O_{7\,(aq)}^{2-} + H_2O_{(aq)} \quad (5)$$

$$Cr_2O_{7\,(aq)}^{2-} + H_2O_{(aq)} + 2(R_2P(S)OH)_{2\,(org)} \rightarrow 2(R_2P(OH)S^-)_2\text{-}Cr(OH)_2^+)_{(org)} + 3O_{2(g)} \quad (6)$$

According to the hard-soft acid-base (HSAB) theory, hard acids form stronger bonds with hard bases, whereas soft acids interact more strongly with soft bases. Thus, the most stable complexes are hard-hard and soft-soft interactions [38]. The molecules of Cyanex 272 contain an oxygen donor atom and behave as a hard base extractant for stable complexation with Cr(III) (hard acid element). Hence, Cyanex 272 is responsible for the stable complexation with the reduced Cr(III) ions [28]. Using the slope analysis method, a stoichiometric study of Cyanex 272 was performed by plotting the graph of log D_{mix} vs. log [Cyanex 272] at a fixed concentration of Cyanex 302, as shown in Fig. 2(b). The result indicates the slope value of 0.2, hence implying the mole ratio of Cyanex 272 : Cr in the extracted complex of 1 : 5. Eq. (7) represents the reaction of Cyanex 272 with the reduced chromium:

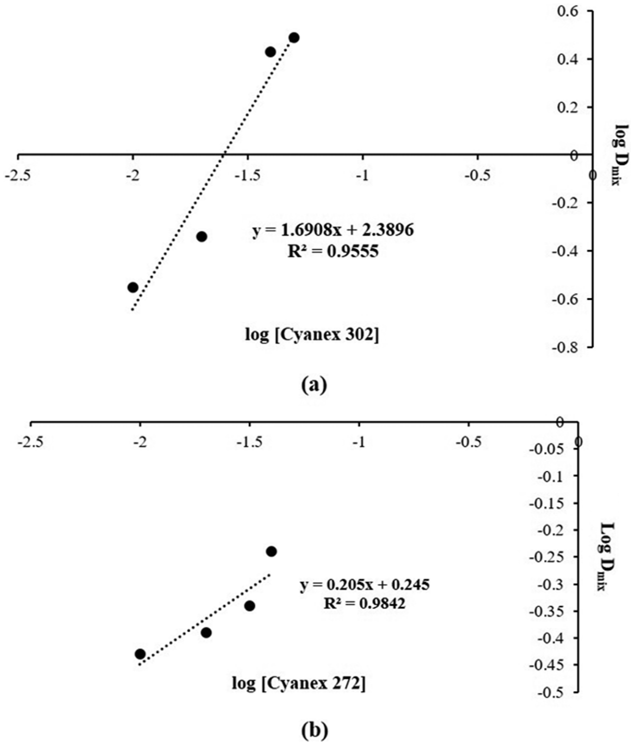

Fig. 2. Effect of concentration of Cyanex 272 (a) and Cyanex 302 concentrations (b) on the distribution ratio of Cr. Experimental conditions: [Cr]: 41 ppm; diluent: kerosene; agitator speed: 320 rpm; agitation time: 18 h; temperature=26±1 °C).

$$2(R_2P(OH)S^-)_2\text{-}Cr(OH)_2^+)_{(org)}+5(R_2P(O)OH)_{2(org)} \rightarrow 2(R_2P(O)O^-)_2\text{-}Cr(OH)^+_{2\,(org)}+ 2R_2P(S)OH\ldots({}^-OOPR_2)_{3\,(org)}+10H^+ \qquad (7)$$

On the other hand, other mixed extractant systems showed a synergistic reaction towards Cr(VI) extraction, including Cyanex 302/LIX63 (83±1.247%) and D2EHPA/LIX63 (51±0.471%) with R_f>1 of 2.05±0.041 and 2.14±0.026, respectively. For the Cyanex 302/LIX63 system, LIX63 acts as the base extractant due to the lower extraction efficiency (43±1.247%). The presence of Cyanex 302 enhances the protonation of LIX63 in acidic media, hence increasing the complexation of Cr with LIX63 [40]. Meanwhile, for the D2EHPA/LIX63 system, there was only a slight increment in the Cr(VI) extraction (51±0.943%). This could be due to the lower acidity of phosphoric acid compared to phosphinic acid, hence lowering the protonation of LIX63 and their complexation with Cr.

In contrast, the mixed extractant systems that exhibited antagonist relationships with R_f<1 are Cyanex 302/D2EHPA (68±0.816%), Cyanex 272/D2EHPA (24±1.247%) and Cyanex 272/LIX63 (24±0.816%) with the R_f values of 0.58±0.045, 0.46±0.005 and 0.52±0.013, respectively. For the mixed extractant systems of Cyanex 302/D2EHPA and Cyanex 272/D2EHPA, D2EHPA as phosphoric acid seems to suppress the activity of phosphinic acids by increasing the pK_a value of the mixture system in the organic phase, thus making the systems unsuitable for Cr extraction from acidic solution. Besides, for the Cyanex 272/LIX63 system, the addition of Cyanex 272 with low acidity disrupts the protonation degree of LIX63, hence reducing the extraction efficiency of Cr(VI). Thus, the mixed synergistic extractant system of 0.05 M Cyanex 272+0.05 M Cyanex 302 was selected for subsequent experiments.

3. Fourier Transform Infrared Spectra Analysis

Fig. 3 exhibits the FTIR spectra analysis of the organic phase with fresh Cyanex 272 (a), the mixture of Cyanex 272 and Cyanex 302 (b), and Cr loaded with the mixed extractant system (c), respectively. The structure of Cyanex 272 and Cyanex 302 is shown

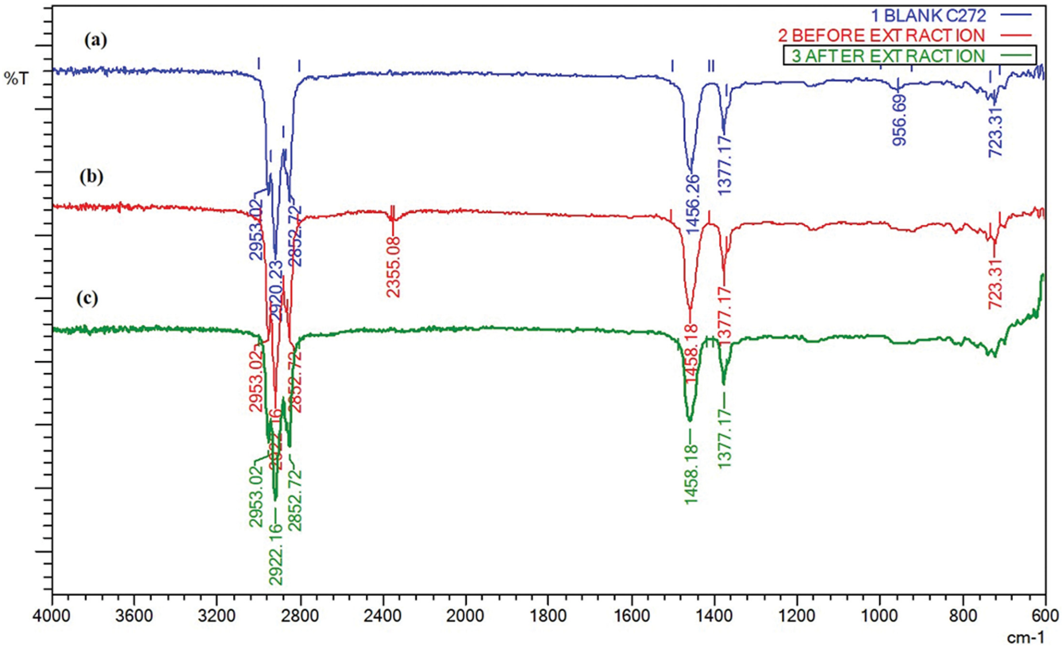

Fig. 3. FT-IR spectra of the organic phases with fresh Cyanex 272 (a), Cyanex 272/Cyanex 272 mixture system (b) and Cr loaded with Cyanex 272/ Cyanex 302 system (c).

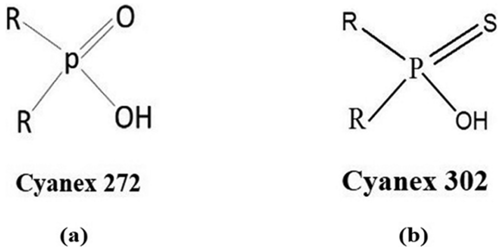

Fig. 4. Structure of Cyanex 272 (a) and Cyanex 302(b) where R= C_8H_{17}.

in Fig. 4. As observed in Fig. 3(a), the spectrum of fresh Cyanex 272 shows several bands at 723.31, 1,377.17, and 1,456.26 cm^{-1}, which represent the long-chain methyl rock, methyl rock, and C-H scissoring of alkanes (R) in the Cyanex 272 structure, respectively. Also, the bands at 2,852.72 and 2,920.23 cm^{-1} signify the asymmetric and symmetric CH_2 in the alkane group of Cyanex 272, respectively [41]. These bands appeared in all samples as the R group of both Cyanex 302 and Cyanex 272 is similar. Meanwhile, the band of 956.69 cm^{-1} represents the bending vibration of P-O-H bond of Cyanex 272 [42,43]. Upon mixing with Cyanex 302 in Fig. 3(b), the P-O-H band (i.e., bending vibration) of Cyanex 272 shifts to the stretching vibration at a new band of 2,355.08 cm^{-1} [35,36]. This occurrence is due to the hydrogen bonding interaction between Cyanex 272 and Cyanex 302 structures. According to Fig. 3(c), the stretching vibration of P-O-H band for the dimer formation disappeared after the extraction with Cr in the synergistic system, hence indicating the formation of P-O-Cr.

4. Effect of Different Fractions of Cyanex 272/Cyanex 302 System on the Synergistic Extraction of Cr(VI)

Fig. 5(a) presents the effect of the concentration of a single system of Cyanex 272 and Cyanex 302 towards the distribution ratios and extraction percentages of Cr, respectively. Obviously, upon increasing the concentration from 0.01 to 0.10 M, the single system containing Cyanex 302 shows higher extraction and distribution ratio of Cr than a single system of Cyanex 272. The single system of Cyanex 302 clearly shows a strong affinity towards Cr(VI) than the single-system Cyanex 272. Hence, it can be inferred that Cyanex 272 and Cyanex 302 behave as the base and synergistic extractants, respectively, for Cr(VI) extraction using the present synergistic extraction system. Meanwhile, Fig. 5(b) presents the effect of various mole fractions of Cyanex 272, $X_{Cyanex\,272}$ towards the values of D and R_f of Cr(VI). It is observed that at 0.0 of $X_{Cyanex\,272}$ (0.1 M Cyanex 302), both D and R_f values are only 2.15±0.041 and 1.00±0.041, respectively. Interestingly, a significant increase in the value of D (40±0.450) was observed upon increasing the $X_{Cyanex\,272}$ from 0.1 to 0.4. These results indicate that the maximum synergistic effect was obtained within the studied ranges of the Cyanex 272/Cyanex 302 system. These results also agree with the R_f values, which increased gradually until reaching the maximum values of $X_{Cyanex\,272}$ at 0.4 (R_{max}=27.6±0.041). Essentially, upon increasing the $X_{Cyanex\,272}$ (base extractant), the mole fraction of Cyanex 302 (synergist extractant) was also reduced. The concentration of Cyanex 272 can be used up to 0.04 M, whereas the concentration of Cyanex 302 can be reduced to 0.06 M in the mixed extractant system. At this stage, 0.04 M Cyanex 272 is sufficient to completely extract the Cr(VI) ions from the aqueous phase. Likewise, 0.06 M Cyanex 302 can provide the maximum acidity of the organic phase, which is suitable for the Cr(VI) transfer from acidic media [34]. Subsequently, the D of Cr(VI) decreased significantly beyond 0.4 of $X_{Cyanex\,272}$ (D=19.5±0041), and very low D values (~1.0) were observed with a further increment of $X_{Cyanex\,272}$ from 0.6 to 1.0. Similarly, a significant drop in the synergistic factor (R_f=~1.0) was observed with the increase of $X_{Cyanex\,272}$ from 0.6 to 1.0. These results indicate that the higher Cyanex 272 concentration predominantly affects the shifting in the higher pK_a value of the organic phase, which subsequently inhibits the transfer of Cr into the organic phase [34]. Using the distribution data from a single system of Cyanex 272 and Cyanex 302 and compared with the mixture system of Cyanex 272/Cyanex 302 helps in achieving the optimum removal efficiency of Cr(VI) and shows excellent potential for a generalized application and optimization of the process. Thus, the optimal synergistic mixture of 0.04 M Cyanex 272+0.06 M Cyanex 302 was employed for the subsequent investigation.

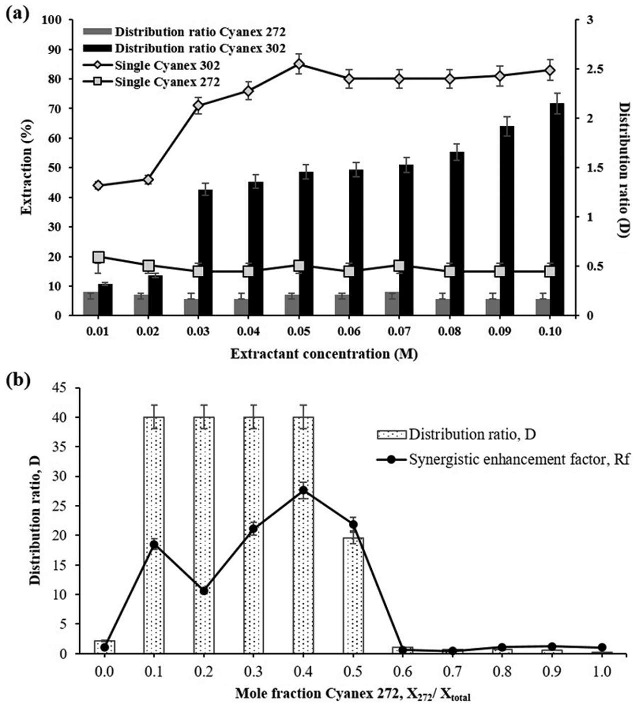

Fig. 5. Effect of concentration of single system on the distribution ratio and extraction of chromium (a) Different composition of Cyanex 272/Cyanex 302 system on the distribution ratio and synergistic factor of Cr(VI) (b) Experimental conditions: diluent: kerosene; agitator speed: 320 rpm; agitation time: 18 h; temperature=26±1 °C.

5. Recovery of Chromium from Loaded Mixture System of Cyanex 272/Cyanex 302

Mineral acids are typically employed for the recovery or stripping of metal ions from the loaded acidic extractant [19]. Throughout this work, the back extraction of Cr(III) from the loaded Cyanex 302/Cyanex 272 system was performed using various concentrations of hydrochloric acid (HCl) as a stripping agent, as demon-

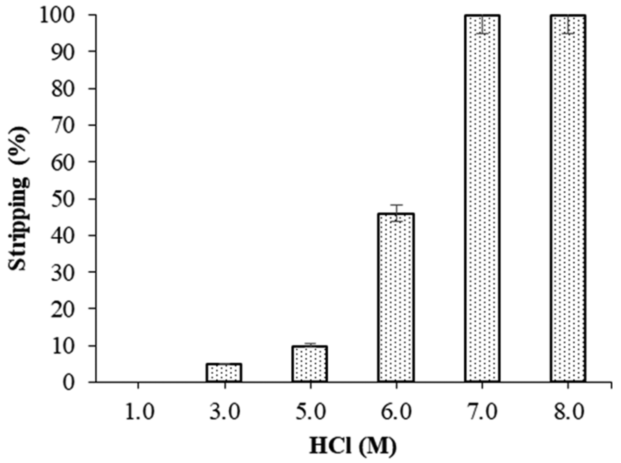

Fig. 6. Stripping of Cr(III) loaded with organic phase containing the mixture of Cyanex 272 and Cyanex 302 using different HCl concentrations. Experimental conditions: [HCl]: 1.0-8.0 M; [Cyanex 272-Cyanex 302]: 0.04-0.06 M; diluent: kerosene; agitator speed: 320 rpm; agitation time: 18 h; temperature= 26±1 °C).

strated in Fig. 6. According to the results obtained, upon increasing HCl concentration from 1.0 to 8.0 M, the stripping performance of Cr(III) increased steadily from 0 to 100%. These results reveal that it is difficult to strip out Cr(III) from the loaded mixture system as Cr(III) is regarded as a hard acid, whereas Cyanex 272 is a hard base extractant. Thus, the interaction between Cr(III) and Cyanex 272 is extremely strong and hard to destabilize, hence requiring the complete extraction of Cr(III) using the high HCl concentration up to 7.0 M. Besides, Pandey et al. [44] claimed that the difficulty in Cr stripping is probably due to the Cr complexation with an organophosphorus acidic extractant (polymeric species), which is difficult to strip. Beyond 7.0 M HCl, the decomposition of extractant occurs due to the noticeable brownish color in the stripping phase. A similar observation was reported in a previous work that employed up to 8.0 M HCl for metal ion extraction [45]. Thus, 7.0 M HCl is sufficient to avoid the decomposition of extractant and provide 100% stripping of Cr(III) from the loaded mixture system. Meanwhile, to determine the stoichiometry of stripping reaction, the number of moles of the stripping agent involved was obtained from the plot of log D vs. log [HCl], as presented in Fig. 7. Based on the graph, the slope of 2.3 represents about two moles of HCl involved during the stripping reaction.

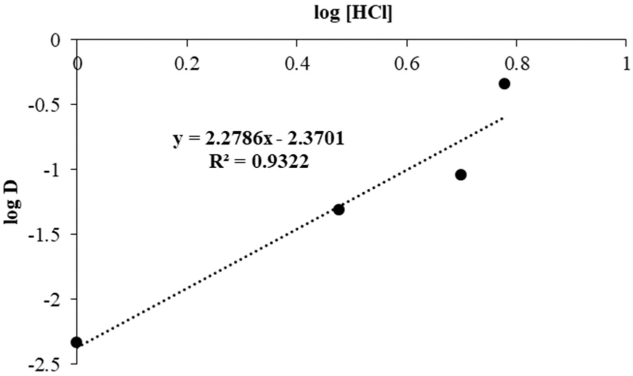

Fig. 7. Effect of HCl concentration on the distribution ratio of Cr. Experimental conditions: [Cr]: 41 ppm; diluent: kerosene; agitator speed: 320 rpm; agitation time: 18 h; temperature=26± 1 °C).

Table 5. Results of several consecutives runs of extraction and stripping of Cr with respect to the regeneration of organic phase containing of Cyanex 302 and Cyanex 272 in kerosene

No of run	Extraction (%)	Stripping (%)
1	99±0.471	99±0.816
2	99±0.816	99±0.471
3	99±1.700	99±0.943
4	99±0.943	99±1.414
5	99±1.247	99±1.247
6	99±1.414	99±0.816
7	99±0.942	99±1.700
8	99±0.816	99±0.471
9	99±0.471	99±0.471
10	99±0.816	99±0.816
11	99±0.471	99±0.942

$$2(R_2P(O)O^-)_2\text{-}Cr(OH)^+_{2\,(org)}+2HCl_{(aq)}\rightarrow$$
$$\bullet 2Cr(OH)Cl_{(aq)}+2(R_2P(O)OH)_{2\,(org)} \qquad (8)$$

6. Regeneration of Organic Phase Towards Extraction and Stripping of Chromium

Organic phase regeneration is one of the main advantages of liquid-liquid extraction [2]. Table 5 tabulates the results of several consecutive runs of extraction and stripping of chromium in response to the regeneration of the organic phase containing the mixed extractant system. In this part, the reusability of the organic phase was evaluated for the extraction and stripping of chromium using the abovementioned best conditions of 0.04 M Cyanex 272+0.06 M Cyanex 302 in kerosene for 18 h (for the first cycle). For the subsequent cycles, the extraction and stripping were conducted using 40 ppm of chromium and 7.0 M HCl as the feed and stripping solutions, respectively, together with the remaining organic phase from the previous cycle. Based on the results obtained, the organic phase could be recycled or reused up to 11 times with excellent extraction (99±0.471%) and stripping (99±0.942%). Therefore, the organic phase is expected to be stable for several more cycles. Nevertheless, there is a possibility of declining performance when the stripping process starts to diminish the extraction of chromium from the chromium-loaded organic phase. Hence, the liquid organic phase will accumulate with unstripped chromium and the contaminated organic phase will disturb the chromium extraction from the feed phase during recycling.

7. Effect of Carrier Concentrations

Theoretically, through a synergistic extraction system, the carrier concentration in the organic phase is reduced and the extraction efficiency is improved [46]. The effect of different concentrations of the mixture system containing Cyanex 272 and Cyanex 302 was

Table 6. Percentages of extraction of Cr with respect to the different concentration mixture of Cyanex 272 and Cyanex 302

Cyanex 272 (M)	Cyanex 302 (M)	Total mixture (M)	Extraction (%)
0.01	0.03	0.04	72±1.699
	0.04	0.05	99±0.816
	0.05	0.06	99±0.942
	0.06	0.07	99±1.247
0.04	0.00	0.04	15±0.471
	0.01	0.05	21±1.247
	0.02	0.06	25±1.247
	0.03	0.07	29±1.247

studied towards the percentage of Cr extraction, and the results are shown in Table 6. By fixing the Cyanex 272 concentration at 0.01 M, almost 99±0.816% of Cr was extracted as the Cyanex 302 concentration increased from 0.03 to 0.04 M. This indicates that the presence of Cyanex 302 in the organic phase had synergistically improved the extraction efficiency of Cr. Upon increasing the Cyanex 302 concentration up to 0.06 M, the extraction efficiency of Cr became plateau (99±1.247%). Such a phenomenon is attributed to the excess Cyanex 302 concentration in the mixture system [16]. Through the synergistic extraction, 0.01 M Cyanex 272 (base extractant) is sufficient for complete extraction of Cr from the electroplating wastewater. Chemically, the presence of an oxygen donor atom (hard base) in Cyanex 272 molecules produces stable complexation with chromium (hard acid) [28]. The presence of Cyanex 302 in the mixture system predominantly influences the extraction of Cr due to the highly acidic nature, which can reduce the pK_a value of Cyanex 272 for the maximum extraction of Cr(VI) from acidic aqueous solution [32]. The higher concentration of Cyanex 302 than Cyanex 272 in the mixture system offers a highly acidic organic phase medium, which promotes high chemical potential between the organic and aqueous feed phases [42]. This condition acts as a driving force that leads to the high extraction of chromium.

Conversely, a similar total mixture of 0.05 M (0.04 M Cyanex 272+0.01 M Cyanex 302) achieved low extraction efficiency of Cr. The reduction in the Cyanex 302 concentration provides low acidity in the organic phase, which limits the protonation of Cyanex 272 for complexation with chromium [32]. It can be inferred that the present total mixture system of 0.05 M (0.01 M Cyanex 272+0.04 M Cyanex 302) can be used instead of the previously applied total mixture system of 0.10 M (0.04 M Cyanex 272+0.06 M Cyanex 302). This result signifies that the total mixture system can be reduced to 0.05 M (50%) in the mixture system and can simultaneously provide an excellent extraction efficiency of chromium (99±0.816%).

8. Effect of Agitation Time on Chromium Extraction

The effect of agitation time towards synergistic chromium extraction is illustrated in Fig. 8. The finding revealed that the extraction efficiency increased up to 100±1.247% upon increasing the agitation time to 60 min. The percentage of chromium extraction remained unchanged with a further increase in the extraction time above 60 min, thus indicating the equilibrium time of extraction was achieved. This means the system equilibrium was attained after 60 min of extraction. It can be inferred that through the synergistic extraction, the system achieved the extraction equilibrium early due to the fast reaction during synergism. Zhang et al. [19] also reported that the synergistic extraction of Cr occurred within 20 min of extraction time. It can be concluded that the synergistic extraction system offers fast reaction and simultaneously reduces the chemical consumption and improves the extraction efficiency.

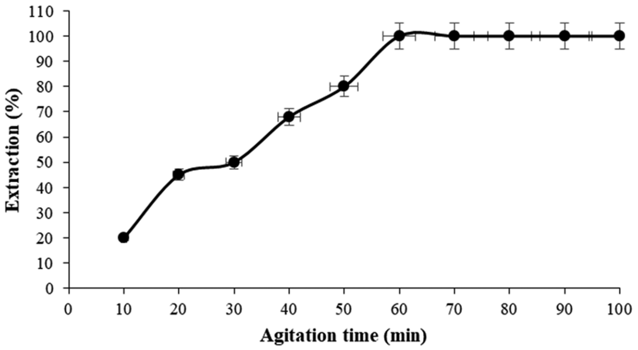

Fig. 8. Effect of agitation time on chromium extraction.

9.Future Prospective in Synergetic Liquid-liquid Extraction

The optimization of two or more parameters in a liquid-liquid extraction study is suggested for future work as the approach is easier, more statistically correct, and more functional using several multivariate methods, such as experimental design, chemometrics, and others. Additionally, the proper functioning of the system can consider all relevant variables and their interactions, as well as find the best experimental conditions. For instance, Begum et al. [47] optimized two factors in liquid-liquid extraction by applying Taguchi full-factorial design using statistical software MINITAB 18. These multivariate methods have also been applied in other studies, such as in dye-sensitized solar cells, sensors, and supported liquid membrane [48-53]. On the other hand, the derivative variation method is also applicable for optimization study which can quantify experimentally and analytically the optimum extraction conditions [26]. The mass-action law methodology also can be developed to accurately represent the properties of an extraction system involving a mixed carrier. Senol [26] showed that all the extraction data provide good compliance with the proposed mass action law model structures involving several physical variables.

CONCLUSIONS

Cyanex 272 and Cyanex 302 can be an excellent combination to synergistically increase the extraction efficiency of Cr(VI) from electroplating wastewater. Both Cyanex 272 and Cyanex 302 play a role as base and synergist extractants, respectively. Cyanex 272 contains an oxygen donor atom responsible for stable complexation with Cr(VI), whereas Cyanex 302 reduces the pK_a value of Cyanex 272 for the maximum extraction of Cr(VI) from the acidic electroplating solution. Cyanex 302 is also one of the sulfur-containing compounds that can act as a reducing agent for the reduction of Cr(VI) to the less toxic Cr(III). In terms of recycling, the organic phase could be recycled or reused up to ten times with excellent extraction and stripping (~100%) and seemed to be stable afterwards. Almost 100% of Cr(VI) was loaded into the organic phase when employing the total mixture system of 0.01 M (0.04 M Cyanex 272+0.06 M Cyanex 302). The total mixture system could be reduced by 50% (0.05 M) using 0.01 M Cyanex 272 and 0.04 M Cyanex 302 with excellent Cr extraction. Meanwhile, the recovery of the extracted Cr(III) showed that Cr(III) was completely stripped by 7.0 M HCl as a stripping agent in 18 h.

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