SUTHAPAT SATHITYATIWAT

RECOVERY OF ZINC FROM METAL-PLATING INDUSTRIAL WASTEWATERS BY LIQUID-LIQUID EXTRACTION

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Declaration of Authorship

I declare that I am the author of this work, which is original. The work cites other authors and works, which are adequately referred in the text and are listed in the bibliography.

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(Suthapat Sathityatiwat)

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Abstract

The extraction of zinc(II) from zinc-plating wastewater by liquid-liquid extraction was studied using the commercial extractants di-(2-ethylhexyl)phosphoric acid (D2EHPA) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex® 272), as well as the ionic liquids, Trihexyltetradecylphosphonium bromide (Cyphos® 102), Trihexyltetradecylphosphonium decanoate (Cyphos® 103) and Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® 104), diluted in organic solvents. First, the commercial extractants and the ionic liquids with the most potential were selected based on the results from diluents, modifiers and stripping solution screening tests. Then, the optimization of extraction and re-extraction (stripping) conditions for each extractant was achieved either by effluent pre-treatment (pH adjustment) to remove iron prior to liquid-liquid extraction or by adjusting the extractant-to-zinc ratio. Afterwards, one commercial extractant and one ionic liquid were selected for further evaluation based on the following parameters: reusability, contact time (kinetic studies), and loading capacity.

Of the two commercial extractants, the most promising results were obtained with 20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP (tributyl phosphate) as the modifier after a contact time of only five minutes. The extraction efficiency for zinc was 98%, with co-extraction of iron which can be resolved by pre-treating the effluent to pH 5.5 to precipitate iron prior to liquid-liquid extraction. Selective stripping of zinc from the loaded organic phase was achieved using 0.6 M H_2SO_4. Under these optimized conditions, the reusability of the organic phase was successfully tested in three cycles of zinc extraction and re-extraction without loss of efficiency.

Regarding ionic liquids, 0.08 M Cyphos® 102 in kerosene exhibited superior selectivity for zinc extraction (83%), with little to no co-extraction of iron. Despite this high efficiency, an issue of insolubility of Cyphos® 102 in the diluent was observed, with the ionic liquid being in a layer below kerosene. This insolubility issue made decantation difficult, which affected the reusability of the extraction system. However, the issue can be solved with the addition of 3% (v/v) decanol as modifier, but resulting in the decrease in zinc extraction efficiency to 40%. A raise of the concentration to 0.24 M Cyphos® 102 in kerosene with 3% (v/v) decanol allowed a 95% extraction efficiency of zinc with no insolubility being observed. On the other hand, the stripping of zinc from this loaded organic phase was obtained using a high concentration of HNO_3 of 2M. Nevertheless, the problem of reusability of the organic phase remained, whereby

zinc extraction decreased to 54% and re-extraction decreased to 5% in the second cycle. Therefore, time and effort need to be devoted to future studies to evaluate the application of Cyphos®102 in liquid-liquid extraction of zinc from zinc-plating wastewaters.

Keywords: liquid-liquid extraction, zinc electroplating effluent, solvent extraction, ionic liquids, Cyphos® 102, Cyphos® 104, D2EHPA, Cyanex® 272, zinc extraction, metal-plating wastewaters

RESUMO

A extração de zinco (II) de água residual da indústria de zincagem por extração líquido-líquido foi estudada utilizando-se os extratantes comerciais Ácido di- (2-etilhexil) fosfórico (D2EHPA) e Ácido bis (2,4,4-trimetilpentil) fosfínico (Cyanex® 272), e também os líquidos iónicos Brometo de triexiltridecilfosfónio (Cyphos® 102), Decanoato de triexiltriltecodecilfosfónio (Cyphos® 103) e Bis (2,4,4-trimetilpentil) fosfinato de tri-hexiltetradecilfosfónio (Cyphos® 104), diluídos em solventes orgânicos. Primeiro selecionaram-se o extratante e o líquido iónico com mais potencial numa triagem de diluentes e modificadores e em seguida fez-se uma otimização das condições de extração e re-extração de zinco, assim como um estudo de pré-tratamento por ajuste de pH para remoção prévia do ferro. Depois avaliou-se o potencial de cada um dos escolhidos através de estudos de reutilização do extratante em ciclos sucessivos de extração e re-extração, estudos de cinética para conhecimento do tempo de contacto necessário para extração e estudos de capacidade de carga da fase orgânica extratante.

Dos dois extratantes comerciais testados, os resultados mais promissores foram obtidos com 20% (p/p) D2EHPA em querosene com 3% (v/v) tributil fosfato (TBP) como modificador, após um tempo de contato de apenas cinco minutos. A eficiência de extração de zinco foi de 98%, mas com co-extração de ferro. No entanto isto pode ser resolvido por pré-tratamento do efluente ajustando o pH a 5.5 para precipitar o ferro antes da extração líquido-líquido. A re-extração seletiva de zinco da fase orgânica carregada foi obtida usando 0,6 M de H_2SO_4. Nestas condições otimizadas a reutilização da fase orgânica foi testada com sucesso em três ciclos de extração e re-extração de zinco sem perda de eficiência.

Em relação aos líquidos iônicos, 0.08 M Cyphos® 102 em querosene exibiu seletividade superior em relação à extração de zinco (83%), com pouca ou nenhuma co-extração de ferro. Apesar desta eficiência elevada observou-se um problema de insolubilidade, ficando este líquido iónico numa camada inferior à querosene, o que dificultou a separação da fase orgânica e afetou a sua reutilização. Este problema de insolubilidade foi resolvido com adição de 3% (v/v) decanol como modificador, no entanto a eficiência de extração de zinco diminuiu para 40%. Um aumento da concentração para 0.24 M de Cyphos® 102 em querosene com 3% (v/v) decanol permitiu uma eficiência de 95% de extração de zinco sem o problema da insolubilidade. Por outro lado, a re-extração de zinco desta fase orgânica carregada foi obtida usando 2 M de HNO_3. Ainda assim, manteve-se o problema da reutilização da fase orgânica:

num segundo ciclo a extração de zinco baixou para 54% e a sua re-extração baixou para 5%. Portanto, serão necessários tempo e esforço dedicados a estudos futuros para avaliar a aplicação de Cyphos®102 na extração líquido-líquido de zinco de águas da indústria de zincagem.

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GENERAL INTRODUCTION

1. Introduction

Zinc is a limited resource that plays a crucial role in many industries. However, consuming zinc from primary sources alone is no longer sustainable, and developments of new methods to recover this metal from secondary sources are necessary for the future of the zinc industry. Therefore, the objective of this work, which is part of the METALCHEMBIO* project, is to explore the possibilities of utilizing liquid-liquid extraction (also called solvent extraction, SX) using both commercial (D2EHPA and Cyanex® 272) and innovative extractants, such as ionic liquids (Cyphos® 102, Cyphos® 103 and Cyphos® 104) to extract zinc from zinc-plating wastewater, particularly from zinc electroplating process using acidic baths. It is also important to report that, to the best of our knowledge, all ionic liquids mentioned have never been tested on zinc-plating wastewater.

2. Zinc industry

Zinc is an important commodity in the metal industry which is used to coat steel products (60%) as well as die casting in the form of zinc base alloys (15%), brass and bronze (14%) as well as compounds comprising of zinc sulfate and zinc oxide (8%) (International Zinc Association [IZA], 2019). While the annual consumption of zinc is estimated to be 16 million tonnes (see Fig. 1.1), the production of refined zinc from primary resources is about 12 million tonnes, making up to 75% of total zinc production (IZA, 2019).

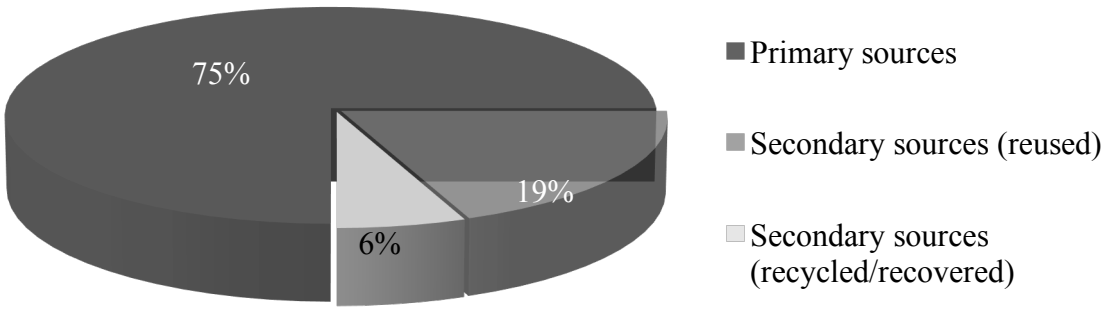


Figure 1.1. Sources of zinc production

The remaining 4 million tonnes are derived from recycled zinc which can be categorized based on the purity of the zinc: refining before use not required (3 million tonnes or 19%) and refining required (1 million tonnes or 6%) (IZA, 2015). Selling for US$2,555/tonne as of mid-December of 2018 (Tibballs, 2018), zinc is a limited resource and its recovery from secondary sources such as industrial wastes has become a subject of interest. Modern technology manages to recover zinc from secondary sources but in small amounts compared to primary sources. Therefore, it is of high interest to learn from the traditional methods of zinc recovery and explore new alternatives that may be more efficient and greener for the environment as well as more economically viable.

3. Zinc electroplating production process

The process of zinc plating typically involves coating products, such as that made of steel, by immersing in molten zinc at 450-460 ◦C (hot-dip galvanizing) or by applying electrical current (electroplating) (Rusynyk, 2012). According to Kobya et al. (2017), typical plating baths used in the zinc-plating process can be categorized as alkaline cyanide zinc, alkaline non-cyanide zinc, and chloride or acidic zinc. The alkaline cyanide zinc bath is made of sodium cyanide, 7.5–34 g/L zinc cyanide and proprietary additives. On the other hand, a zinc-plating process which employs alkaline non-cyanide zinc baths uses zinc in the form of sodium zincate (6-23 g/L), water conditioner, caustic soda, and organic additives. Acidic zinc or chloride zinc baths are made of zinc ions in the form of zinc chloride (15-38 g/L), ammonium chloride, potassium chloride or boric acid along with proprietary additives. Water in the cleansing bath can be contaminated by zinc, cyanide and other toxic chemicals during the plating or cleaning process via ‘drag-outs’ from prior processes. As a result, 0.112-252 mg/L of zinc, 0.005–150,000 mg/L of cyanide (for alkaline cyanide zinc baths) and metal ions, such as iron and nickel, can be found in electroplating wastewater effluents in concentrations above the permissible levels for neutralized industrial wastewaters in which, according to European and national standards, are 10 mg/L Fe, 2 mg/L Zn and 1 g/L Cl^- at pH range of 6-9 (Kobya, Demirbas, Ozyonar, Sirtbas, & Gengec, 2017; Regel-Rosocka & Wisniewski, 2011).

4. Traditional zinc recovery techniques for zinc electroplating wastewaters

The typical method used in the industry for the purification of zinc is precipitation with hydroxides such as soda, lime or a mixture of both (Ríos *et al.*, 2010). In this treatment,

iron and also cadmium are precipitated out of the solution as residues, while zinc is then recovered by electrowinning (Ríos *et al*., 2010) –an electrolytic process used in the recovery of metals from aqueous solutions, or electrolyte, containing positively charged metals and a negatively charged anion (Evans, 2003). Additionally, the treatment process may involve several additional steps namely: (1) oxidation of Fe^{2+} to Fe^{3+} with hydrogen peroxide (H_2O_2), (2) reduction of Cr^{6+} to Cr^{3+} in an acidic solution of pH 2-3 by addition of iron chloride ($FeCl_2$), sodium sulfide (Na_2S) or sodium bisulphite ($NaHSO_3$), (3) pH adjustment to approximately 7.0-8.5 with hydroxides to induce the precipitation of metals, (4) induce coagulation and flocculation and (5) filtration of wastewater for further treatment from hazardous suspended sludge (Ríos *et al.*, 2010).

5. Liquid-liquid extraction

Solvent extraction or liquid-liquid extraction is a well-known and explored method of separation of metals such as Zn, Fe, Co, Cr, Cu, Ni, and rare earth metals (Mansur, Rocha, Magalhães, & Benedetto, 2008). Furthermore, the technique also has applications in the reprocessing of nuclear fuels and purification of phosphoric acid media, etc. (Mansur *et al*., 2008). Although various combinations of extractants, diluents and modifiers can be used, the solvent extraction technique typically involves three main steps: extraction, scrubbing, and stripping (Mansur *et al*., 2008). Figure 1.2 depicts the typical liquid-liquid extraction process with zinc as the target metal. In the extraction stage, the aqueous metal-bearing effluent (feed solution) is contacted and agitated with an extractant diluted in an organic diluent, such as kerosene (Mansur *et al*., 2008). An extractant, or extracting agent is responsible for the transfer of a solute from one phase to the other (McNaught *et al*., 2006). Due to the differences in the polarities of the aqueous (feed solution) and the organic phase (extractant dissolved in the diluent), the target metal is transferred from the former to the latter phase (loaded organic phase) (Mansur *et al*., 2008). Depending on the selectivity of the extractant, the loaded organic phase will then either undergo stripping or scrubbing. If the selectivity of the extractant is low and co-extraction of non-target metals is high, scrubbing may be necessary to remove the co-extracted metals to ensure high purity of the metal of interest (Mansur *et al*., 2008). On the other hand, the metal of interest is stripped from the loaded organic phase by an aqueous solution, resulting in a concentrated solution of the target metal (Mansur *et al*., 2008), which undergo further refining processes such as crystallization, evaporation, electrolysis or electrowinning (Dreisinger, 2009).

Figure 1.2. Liquid-liquid extraction process with zinc as the target metal.

Many advantages contribute to the interest in solvent extraction as an alternative strategy to the traditional precipitation method: metal separation and recovery from low concentrated wastewater and leachates from secondary sources, availability of technological and technical solutions, selectivity by design to achieve high metal purity and a commonly known mechanism of mass transport and reaction (Ríos *et al*., 2010). However, it is also important to mention the challenges that may arise from the liquid-liquid extraction technique for future improvements and innovations: the physical, environmental and health hazard of diluents (the most popular being flammable kerosene) and other organic solvents, the formation of unfavorable third phases, transport of impurities to the interface, the lack of a simple and universal method of recovery of various metals, as well as the scalability of the technique to the industrial scale (Ríos *et al*., 2010; Regel-Rosocka & Alguacil, 2013).

6. Zinc electroplating effluent

Several characteristics of the effluent should be considered prior to the selection of the appropriate extractant for solvent extraction including pH, the concentration of metals, accompanying metals, the presence of complexing anions, ionic strength and the type of aqueous media (*i.e.* nitric acid, sulfuric acid, hydrochloric acid, etc.) (Regel-Rosocka & Alguacil, 2013). Depending on these parameters, the most promising extractants can be

selected from four main species of organic compounds categorized as acidic, basic, chelating and solvating extractants, which interact with the metals in the aqueous solutions through different mechanisms. Furthermore, mixtures of extractants (synergetic mixtures) can also be used to improve the efficiency and specificity of the system (Regel-Rosocka & Alguacil, 2013).

The zinc-plating effluent used in this work, obtained from Industrial Goñabe, Valladolid, Spain, were rinse-waters derived from electroplating process using chloride zinc baths (see Fig. 1.3). Water in the cleansing bath in the chloride zinc electroplating process can be contaminated by zinc and other toxic chemicals during the plating or cleaning process via 'drag-outs' from prior processes. Characterization of the wastewater samples were carried out and discussed in the Results and Discussion section.

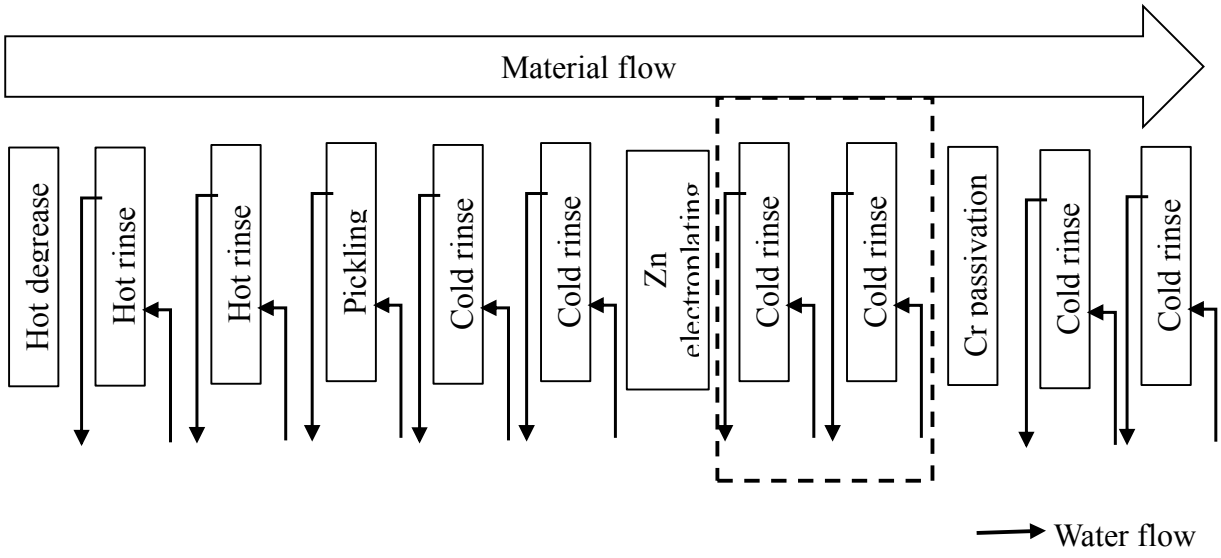


Figure 1.3. Zinc electroplating process flow. Adapted from "Zinc Coatings," 2006, *Midwest Metal Products*. Retrieved June 3, 2019, from http://anglerings.com/Value-Added/Zinc-Coatings. Copyright 2019 by Midwest Metal Products.

7. Commercial Extractants

The use of commercial extractants is a widely explored and reported strategy in liquid-liquid extraction. Some of these extractants and the specific characteristics of effluents in which they were tested can be found in Table 1.1.

Table 1.1. Commercial extractant and their respective liquid-liquid extraction conditions

EXTRACTANT	Diluent		Target Metal	Aqueous Media	Yield	Reference
	Name	Molarity				
Versatic 10 acid + LIX 63 (aka. CSIRO DSX system)	Orfom SX80 CT (mixture of naphtalene and ethylbenzene)	6.25% Versatic 10 13.2% LIX 63	Co and Zn	HNO3 leached liquor	99%	Regel-Rosocka, M., & Alguacil, F. J. (2013). Recent trends in metals extraction. Revista De Metalurgia, 49(4), 292-316. doi:10.3989/revmetalm.1344
Cyanex® 272		30%	Zn		Zn:Co ratio of 4000:1	
		30%	Co		~100%	
		5%	Zn		99.90%	
LIX 860 N LIX 84 I	kerosene	N/A	Cu	Pregnant leach solution from oxide and sulphide ore	N/A	Regel-Rosocka, M., & Alguacil, F. J. (2013). Recent trends in metals extraction. Revista De Metalurgia, 49(4), 292-316. doi:10.3989/revmetalm.1344
D2EHPA	N/A	N/A	Mn	Oxidation with air/SO2 mixture or SX	N/A	
Acorga M5640	ShellSol D70	10%	Cu (present as chalcopyrite)	Real leach solution with tap water or deionized water	98-99%	Ferreira, A. E., Agarwal, S., Machado, R. M., Gameiro, M. L., Santos, S. M., Reis, M. T., . . . Carvalho, J. M. (2010). Extraction of copper from acidic leach solution with Acorga M5640 using a pulsed sieve plate column. Hydrometallurgy, 104(1), 66-75. doi:10.1016/j.hydromet.2010.04.013
LK-C2	kerosene	15% vol	Cu	HNO3 solution	99.98%	Zhang, X., Li, X., Cao, H., & Zhang, Y. (2010). Separation of copper, iron (III), zinc and nickel from nitrate solution by solvent extraction using LK-C2. Separation and Purification Technology, 70(3), 306-313. doi:10.1016/j.seppur.2009.10.012
		20% vol	Fe	HNO3 solution	96.14%	
		20% vol	Ni	HNO3 solution	99.53%	
LIX 984N	kerosene	50% (v/v) A/O phase ratio of 1:1.5	Cu	HNO3 solution	99.70%	Long Le, H., Jeong, J., Lee, J.-C., Pandey, B. D., Yoo, J.-M., & Huyunh, T. H. (2011). Hydrometallurgical Process for Copper Recovery from Waste

						Printed Circuit Boards (PCBs).
LIX84	kerosene	50%	Cu(II)	Ammonia-ammonium sulfate leached liquor	99.60%	Yang, J., Wu, Y., & Li, J. (2012). Recovery of ultrafine copper particles from metal components of waste printed circuit boards
LIX84-IC	kerosene	25%	Cu	HNO3 leached liquor	99.99%	Kumari, A., Jha, M. K., & Singh, R. P. (2016). Recovery of metals from pyrolysed PCBs by hydrometallurgical techniques.
Cyanex® 923	kerosene	0.2 M	Au(III) and Fe(III)	pH 0.7 leach solution diluted with HCl solution of the same acidity	99.5% Au(III) 91.70% Fe(III)	Nguyen, T. H., Wang, L., & Lee, M. S. (2017). Separation and Recovery of Precious Metals from Leach Liquors of Spent Electronic Wastes by Solvent Extraction. *Korean Journal of Metals and Materials,55*(4), 247-255. doi:10.3365/kjmm.2017.55.4.247
Cyanex® 272	kerosene	0.6 M	Fe	Sulfuric acid leach liquor from spent household batteries	>95%	Provazi, K., Campos, B. A., Espinosa, D. C., & Tenório, J. A. (2011). Metal separation from mixed types of batteries using selective precipitation and liquid–liquid extraction techniques. Waste Management, 31(1), 59-64. doi:10.1016/j.wasman.2010.08.021
			Zn		99%	
			Ni		85%	
OPAP	kerosene	0.95 F	Fe	hot-acid leach solution (HAL)	N/A	Principe, F., & Demopoulos, G. (2004). Comparative study of iron(III) separation from zinc sulphate–sulphuric acid solutions using the organophosphorus extractants, OPAP and D2EHPA. Hydrometallurgy, 74(1-2), 93-102. doi:10.1016/j.hydromet.2004.01.004
D2EHPA		1.25 F			N/A	
TBP	Kerosene (Exxsol D-80)	100% v/v TBP A/O ratio=1:1 T=25◦C	Zn	spent hydrochloric acid pickling liquors	92.5%	Mansur, M. B., Rocha, S. D., Magalhães, F. S., & Benedetto, J. D. (2008). Selective

				from metal plating containing 70.2 g/L of Zn, 92.2 g/L of Fe		extraction of zinc(II) over iron(II) from spent hydrochloric acid pickling effluent by liquid-liquid extraction. Journal of Hazardous Materials, 150(3), 669-678. doi:10.1016/j.jhazmat.2007.05.019
Cyanex® 301	Kerosene (Exxsol D-80)	1.5 mol/L A/O ratio = 1:1 T=25◦C		spent hydrochloric acid pickling liquors from metal plating containing 33.9 g/L of Zn, 203.9 g/L of Fe and 2 M HCl	80-95%	
Cyanex® 272	Kerosene (Exxsol D-80)				70%	
D2EHPA	Kerosene + 3% (v/v) TBP	20% (w/w) A/O = 1:1	Zn	Zinc leach residue from industrial filter cake	98.3%	Vahidi, E., Rashchi, F., & Moradkhani, D. (2009). Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA. *Minerals Engineering,22*(2), 204-206. doi:10.1016/j.mineng.2008.05.002

These extractants can be categorized into four main categories: neutral (solvating), chelating, acidic and basic extractants. Solvating (or neutral) extractants, extract metal by replacing the hydration sheath of the neutral ion-pairs with solvent molecules (Mansur *et al.*, 2008). For example, the commercially available Cyanex® 923 (a mixture of trialkylphosphine oxides) was used to extract Fe(III) and Au(III) in leach solutions of HCl and pH 7.0 which also contain accompanying metals such as Pd(II), Pt(IV), Cu(II) and Cr(III) (Nguyen, Wang, & Lee, 2017). Another commercially available solvating extractant, tributyl phosphate (TBP) was reported to be effective in the selective extraction of Zn(II) over Fe(II) and Fe(III) from metal plating wastewater (spent hydrochloric acid pickling liquor) with 92.5% yield for Zn(II) and only 11.2% co-extraction of Fe(II) (Mansur *et al.*, 2008). However, several drawbacks were noted such as the high concentration of extractant, 80-100% (v/v), required to achieve the reported extraction efficiency and the transfer of a significant amount of water to the organic phase (Mansur *et al.*, 2008).

Chelating agents act as ligands that bind to metal cations by forming metal-extractant chelates and releasing hydrogen ions in the process ("Chelate," 2007). Ketoxime and aldoxime species such as LIX 54 (dodecylphenylmethyl-β-diketone), LIX 63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime), LIX 64 (2-hydroxy-5-nonylbenzophenone oxime), LIX 84-IC

(2-hydroxy-5-nonyl acetophenone oxime), LIX 860N-I (5-dodecylsalicylaldoxime), Acorga M5640 (active substance 2-hydroxy-5-nonylbenzaldehyde oxime) are some chelating agents commercially available today (Regel-Rosocka & Alguacil, 2013). Additionally, LIX 84, LIX 984N and LIX 84-IC are known to achieve extraction efficiencies higher than 99% for copper in printed circuit boards (PCBs) wastewater containing high concentrations of Fe and Pb with lower concentrations of Sn, Zn, and Ni (Le et al., 2011; Yang, Wu, & Li, 2012).

Acidic (or liquid-cation exchange) extractants, exchange their hydrogen ions with metal cations to form metal salts. One of the most widely known extractants of this class is di-(2-ethylhexyl) phosphoric acid (D2EHPA) which shows an extractive selectivity towards zinc from Cu(II), Co(II), Ni(II) and other bivalent transition metals (Mansur *et al.*, 2008). Other commercially available acidic extractants includes phosphinic acids such as bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex® 272) and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex® 301) which were selected as extractants for the extraction of Zn(II) over Fe(II) and Fe(III) from spent hydrochloric acid pickling liquor generated from the metal plating industry. The result shows that Cyanex® 301 was more effective in extracting Zn(II) (80-95%) with less co-extraction of Fe(II) (less than 10%) than Cyanex® 272 (70% Zn(II) and 20% Fe(II)) (Mansur *et al.*, 2008). Furthermore, many studies reported the viability of Cyanex® 272 as extractant for zinc and cobalt from nitric acid leached liquor with the selectivity of the two target metals controllable by pH adjustments (pH 2.6-2.9 for zinc and pH5.2-5.5 for cobalt) (Dreisinger, 2009).

On the other hand, basic (or liquid-anion exchange) extractants, extract anions or anionic metal complexes (Gallacher, 1981). Amines and quaternary ammonium salts such as Primene 81R, Primene TOA, Primene JMT, Amberlite LA-2, Alamine 336 and Aliquat 336 are typically used as basic extractants (Regel-Rosocka & Alguacil, 2013). The loaded organic phase of this type of extractants typically undergoes stripping with aqueous salts or bases for better phase separation (Regel-Rosocka & Alguacil, 2013). Tertiary amines, like Alamine 336, are used to extract uranium, in the form of uranyl sulfate complexes, as well as the extraction of chloride complexes. In the latter case, extraction selectivity of different metals can be achieved by varying the concentration of chloride. For example, solvent extraction with Alamine 336 at 40℃ and pH 2 is selective towards ferric iron at a chloride concentration of 50 g/L, copper at approximately 100 g/L, and nickel at 250 g/L. Quaternary ammonium salts such as Aliquat 336 can be used over a wide pH range (Regel-Rosocka & Alguacil, 2013). However, due to the lack of proton that can be deprotonated, quaternary ammonium salts are more difficult to strip than amines (Gallacher, 1981).

8. Ionic liquids

An ionic liquid (molten salt) is a solvent system made of various combinations of oppositely charged ionic species whose asymmetry and charge dispersal results in a reduced packing of the solid-state –hence, the characteristically low melting points of less than 100°C (Hagiware & Ito, 2000). Some advantages pertinent to the application of ionic liquids in liquid-liquid extraction include: negligible vapor pressure, high thermal stability (which allows for operations over a wide range of temperature) and tunable miscibility in both organic and aqueous solvents (C. Trombini, personal communication, March 13, 2018). A list of several ionic liquids used in liquid-liquid extraction of various effluents and conditions can be found in Table 1.2. Despite their relatively high costs, some ionic liquids such as Cyphos® 101, Cyphos® 102, Cyphos® 103, Cyphos® 104 and urea-choline chloride are commercially available and can be utilized as extractants, with or without diluents (also called co-solvents), in the extraction of metals (Abbott, Capper, Davies, Rasheed, & Shikotra, 2005; Egorov *et al*., 2010; Regel-Rosocka & Wisniewski, 2011; Regel-Rosocka, Wisniewski, & Nowak, 2012).

Table 1.2. Ionic liquids and their respective liquid-liquid extraction conditions

Ionic Liquid	Target Metal	Diluent	A/O	Aqueous media	Yield (%)	Source
Cyphos ®101	Zn(II), Fe(II) and Fe(III)	toluene	50%	Chloride media. Aqueous feeds used for the determination of extraction isotherms contained 0.58 mol dm^{-3} (1.8 wt.%) HCl, 0.5–80 g dm^{-3} Zn(II), Fe (II) or Fe(III). Salts were introduced as chlorides and the concentration of chlorides was adjusted to 5 mol dm^{-3} with NaCl (POCh, Poland).	Zn(II) extraction from the feed containing only 5 g dm^{-3} exceeds 85% after the first extraction stage, reaching almost 100% after three stages. Meanwhile, iron(II) extraction also increases (after three stages it amounts to 40%).	Regel-Rosocka, M., & Wisniewski, M. (2011). Selective removal of zinc(II) from spent pickling solutions in the presence of iron ions with phosphonium ionic liquid Cyphos IL 101. Hydrometallurgy, 110(1-4), 85-90. doi:10.1016/j.hydromet.2011.08.012
Cyphos ® 101 (0.8 M)	Selective separation of Zn(II), Fe(II) and Fe(III)	toluene	1: 1	Model aqueous feeds contained 0.1–90 g/dm3 Zn(II) or Fe(II) or Fe(III); 1.8% (0.58 M) HCl; 5 M Cl (chloride content was adjusted with NaCl)..	~100%	Regel-Rosocka, M., Nowak, Ł, & Wiśniewski, M. (2012). Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids. Separation and Purification Technology, 97, 158-163. doi:10.1016/j.seppur.2012.01.035
Cyphos ®104 (0.2 M)	Selective separation of Zn(II), Fe(II) and Fe(III)	toluene	1:1	Model aqueous feeds contained 0.1–90 g/dm3 Zn(II) or Fe(II) or Fe(III); 1.8% (0.58 M) HCl; 5 M Cl (chloride content was adjusted with NaCl). Aqueous feed containing metal ions in 0.58 M HCl.	~100%	

Cyphos ® 102	Zn(II)	toluene	1:1	Zinc-plating mud solution containing hydrochloric acid	96.64%	Singh, R., Mahandra, H., & Gupta, B. (2017). Solvent extraction studies on cadmium and zinc using Cyphos IL 102 and recovery of zinc from zinc-plating mud. *Hydrometallurgy,172*, 11-18. doi:10.1016/j.hydromet.2017.06.017

As an example, Cyphos® 101 with toluene as co-solvent can be used to selectively extract zinc(II) over iron(II) in chloride media containing high concentrations of zinc(II) (Regel-Rosocka & Wisniewski, 2011). Cyphos® 102 was reported to be effective in the extraction of zinc(II) and cadmium from zinc-plating mud solution containing hydrochloric acid with 96.64% zinc extraction (Singh, Mahandra, & Gupta, 2017). To the best of our knowledge, while Cyphos® 103 has been studied in the removal of phenol from aqueous solutions in the form of supported liquid membrane (Pilli, Banerjee, & Mohanty, 2014), the application of Cyphos® 103 as potential extractant for liquid-liquid extraction of zinc has never been reported. Furthermore, 0.2 M Cyphos® 104 was reported to be effective in the extraction of Zn from model aqueous feeds containing 5 g/L of the metal and 0.58 M HCl with a percentage extraction of 94.2%. The same extractant was also reported to extract high concentrations of Fe(III) and less of Fe(II) (Regel-Rosocka & Wisniewski, 2011).

Since limited information was available, the objective of this set of experiment was to explore the potential and limitations of each ionic liquid in the application of zinc extraction from zinc-plating effluent in chloride media by carrying out screening tests and optimize as well as possible the conditions for the selected ionic liquid.

9. Diluents

Making up 70-95% of the organic phase, diluents are used to adjust the concentration of extractant to an optimum operational range, minimize aqueous-in-organic and organic-in-aqueous entrainment, as well as optimize transfer kinetics and phase disengagement (Bishop, Gray, Young, & Greene, 1996). Therefore, it is crucial that the extractant is miscible or soluble in the diluent of choice. Other parameters that should be taken into consideration in the selection of the ideal diluent for an extractant are pour point, flash point, phase break, transfer kinetics, diluent chemistry, diluent-extractant compatibility, selectivity, entrainment of organic in the aqueous phase, volatility, supplier's support, and price (Bishop *et al*., 1996). The most

popular diluent used in solvent extraction is kerosene, a flammable mixture with varying compositions of hydrocarbons such as alkanes, alkenes, alkynes and aromatic compounds which is commonly used for combustion purposes but is less volatile than traditional gasoline (Bishop *et al*., 1996).

10. Modifiers

The formation of a third phase is one of the major challenges in solvent extraction. A third phase can be formed during the phase separation stage whereby an insolubility issue occurs in the organic phase which leads to the formation of an additional third phase between the organic and the aqueous phase. Several factors can lead to a third phase formation: the presence of suspended solids, overloading of extractant and temperature (Olivier, 2011). Additionally, the formation of the third phase in solvent extraction often occurs with aliphatic diluents (Olivier, 2011). The issue can typically be resolved by increasing the operating temperature or the addition of modifiers, substances that have the ability to increase the solubility of an extractant in the diluent, modify the interfacial properties or reduce adsorption losses (McNaught *et al*., 2006). Some commonly used modifiers include 2-ethylhexanol, isodecanol, *p*-nonyl phenol and TBP (tributyl phosphate) which is typically added into the organic phase at 2-5 % (v/v) (Olivier, 2011).

However, adding a high amount of modifier into the organic phase not only mean the increase in the overall expense of the operation but it can also lead to a decrease in the extraction efficiency of the system (Al-Siddique, Adeler, & Huwyler, 1980). This may occur when the modifier completely dissolves the third phase into the organic phase to a point where increasing the modifier no longer result in the increase of the target metal in the organic phase, while the concentration in the aqueous phase increased. This phenomenon results in the decrease in the extraction efficiency of the extraction system
(Al-Siddique *et al*., 1980).

11. Stripping

Depending on the purity or the concentration of co-extracted metals in the loaded organic phase, solvent extraction may be followed by either stripping or scrubbing. Typically, stripping (see Fig. 1.4) is done in order to recover the metal of interest through a transfer of the target metal specie from the loaded organic phase to the aqueous stripping phase. This can be

performed by using relatively strong acid solutions such as H_2SO_4, HCl or HNO_3 to replace the metal ion attached to the extractant by hydrogen ions, allowing for the organic reagent to be recycled for the consecutive solvent extraction cycles (Olivier, 2011). Other acids such as oxalic acid have also been studied as potential stripping agents for the stripping of iron(III) which binds strongly to D2EHPA, making stripping and recovery of the metal from the extractant difficult even with high concentrations of H_2SO_4 (D. Singh, Mishra, & H. Singh, 2006).

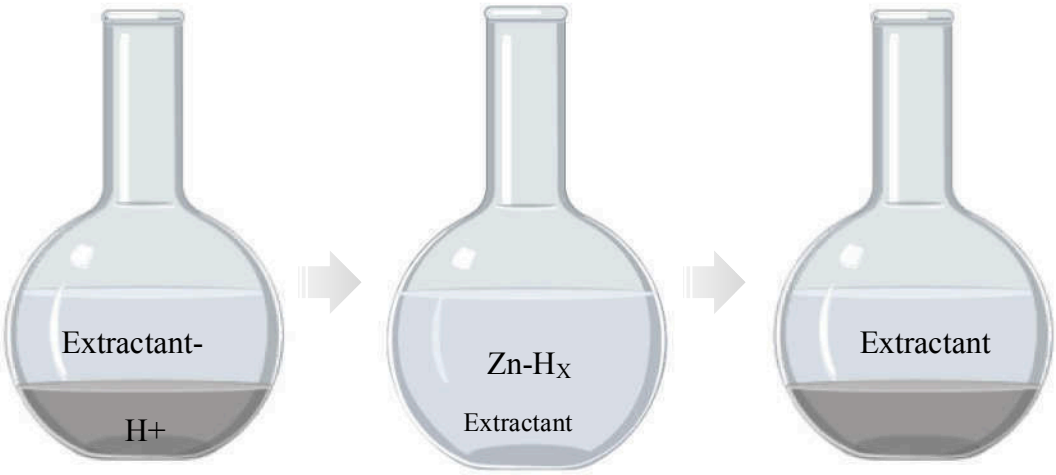


Figure 1.4. Stripping of loaded organic phase from liquid-liquid extraction process

12. Iron removal

In many cases, undesired metals are co-extracted along with the metal of interest (see Fig. 1.5) and, depending on the difference in the affinities of the extracted metals, directly stripping of the loaded organic phase may result in the transfer of the co-extracted metal along with the metal of interest in the final stage of recovery.

In such cases, selective removal of co-extracted metal from the loaded organic phase is necessary (Inezédy, Lengyel, & Ure, 1997). This can be achieved by removing unwanted metal from the loaded organic phase with aqueous solutions such as strong alkaline solutions (sodium carbonate or hydroxides), high concentrations of hydrochloric acid (i.e. 6 M), demineralized water and spent electrolyte or oxalic acid (U.S. patent No. US4235713A, 1980). This process, called scrubbing, are typically carried out prior to the stripping stage (Inezédy et al., 1997; SX Kinetics, n.d.). However, it was discovered that, depending on the selectivity of the stripping agent, the same technique can be applied after stripping of the

target metal. In this case, scrubbing was done with the objective to enhance the reusability of the organic phase.

Figure 1.5. Co-extraction of non-target metal (Fe) in liquid-liquid extraction

Alternatively, iron removal can also be carried out by metal precipitation as a form of effluent pretreatment. Figure 1.6 shows different solubilities of metal sulfides and metal hydroxides as function of pH. The data showed that within a certain pH range several metals can be removed by the addition of hydroxides or sulfides without affecting the solubility of some metals. Therefore, it is possible to remove Fe by adjusting the pH of the effluent within a pH range of 2-4 without affecting the solubility of Zn. Hence, in this research project, both scrubbing and pH pretreatment were tested for iron removal.

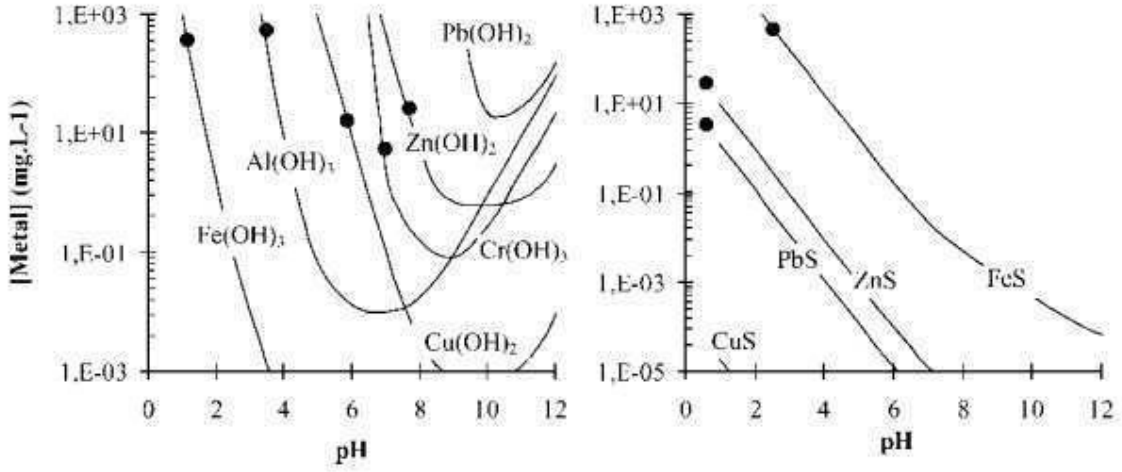


Figure 1.6. Solubilities of different metals as a function of pH. From "Heavy Metals Precipitation in Sewage Sludge" by M. M. Marchioretto, W. Rulkens, & H. Bruning, 2005, *Separation Science and Technology*, 40(16), 3393-3405. Copyright 2005 by Taylor & Francis LLC.

13. References

Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Shikotra, P. (2005). Selective Extraction of Metals from Mixed Oxide Matrixes Using Choline-Based Ionic Liquids. *Inorganic Chemistry, 44*(19), 6497-6499. doi:10.1021/ic0505450

Al-Siddique, F.R., Adeler, I., & Huwyler, S. (1980). Effect of pH and modifier-concentration on the solvent extraction of molybdenum with an alkyl amine (EIR--406). Switzerland

Bishop, M.D., Gray, L. A., Young, T. L., & Greene, M. G. (1996). Technical Developments Leading to Modern Solvent Extraction Diluents. *Society for Mining, Metallurgy, and Exploration, 96-49*. Retrieved from http://www.cpchem.com/bl/specchem/en-us/Documents/sme96-49.pdf

Chelate. (2007). In Encyclopedia Britannica. Retrieved from https://www.britannica.com/science/chelate

Dreisinger, D. (2009). Keynote address: Hydrometallurgical process development for complex ores and concentrates. *Journal of the Southern African Institute of Mining and Metallurgy, 109*(5), 253-271.

Egorov, V. M., Djigailo, D. I., Momotenko, D. S., Chernyshov, D. V., Torocheshnikova, I. I., Smirnova, S. V., & Pletnev, I. V. (2010). Task-specific ionic liquid trioctylmethylammonium salicylate as extraction solvent for transition metal ions. *Talanta, 80*(3), 1177-1182. doi:10.1016/j.talanta.2009.09.003

Evans, J. W. (2003). Metal Production: Electrometallurgy. Retrieved from https://www.sciencedirect.com/topics/chemistry/electrowinning

Gallacher, L. V. (1981). Liquid Ion Exchange in Metal Recovery and Recycling. In *Third Conference on Advanced Pollution Control for the Metal Finishing Industry: Presented at Orlando Hyatt House, Kissimmee, FL, April 14-16, 1980*. Cincinnati, OH: U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory.

Hagiwara, R., & Ito, Y. (2000). Room temperature ionic liquids of alkylimidazolium cations and fluoroanions. *Journal of Fluorine Chemistry, 105*(2), 221-227. doi:10.1016/s0022-1139(99)00267-5

Inezédy, J., Lengyel, T., & Ure, A. M. (1997). *Compendium of Analytical Nomenclature Definitive Rules 1997* (3rd ed.). IUPAC. Retrieved from https://media.iupac.org/publications/analytical_compendium/Cha09sec44.pdf.

International Zinc Association. (2015). "Zinc Recycling Material Supply." *Zinc Recycling Material Supply*. Accessed January 24. https://www.zinc.org/wp-content/uploads/sites/4/2015

International Zinc Association. (2019). "ZINC." *ZINC. International Zinc Association*. Accessed January 24. http://www.zinc.org/.

Kobya, M., Demirbas, E., Ozyonar, F., Sirtbas, G., & Gengec, E. (2017). Treatments of alkaline non-cyanide, alkaline cyanide and acidic zinc electroplating wastewaters by electrocoagulation. *Process Safety and Environmental Protection, 105*, 373-385. doi:10.1016/j.psep.2016.11.020

Le, H. L., Jeong, J., Lee, J., Pandey, B. D., Yoo, J., & Huyunh, T. H. (2011). Hydrometallurgical Process for Copper Recovery from Waste Printed Circuit Boards (PCBs). *Mineral Processing and Extractive Metallurgy Review, 32*(2), 90-104. doi:10.1080/08827508.2010.530720

Mansur, M. B., Rocha, S. D., Magalhães, F. S., & Benedetto, J. D. (2008). Selective extraction of zinc(II) over iron(II) from spent hydrochloric acid pickling effluent by liquid-liquid extraction. *Journal of Hazardous Materials, 150*(3), 669-678. doi:10.1016/j.jhazmat.2007.05.019

Marchioretto, M. M., Rulkens, W., & Bruning, H. (2005). Heavy Metals Precipitation in Sewage Sludge. *Separation Science and Technology,40*(16), 3393-3405. doi:10.1080/01496390500423748

McNaught, A. D., Wilkinson, A., Nic, M., Jirat, J., Kosata, B., & Jenkins, A. (2006). Extractant. *IUPAC Gold Book*. Retrieved from http://goldbook.iupac.org/html/E/E0229…

McNaught, A. D., Wilkinson, A., Nic, M., Jirat, J., Kosata, B., & Jenkins, A. (2006). Modifier. *IUPAC Gold Book*. Retrieved from https://goldbook.iupac.org/html/M/M03965.html

Nguyen, T. H., Wang, L., & Lee, M. S. (2017). Separation and Recovery of Precious Metals from Leach Liquors of Spent Electronic Wastes by Solvent Extraction. *Korean Journal of Metals and Materials,55*(4), 247-255. doi:10.3365/kjmm.2017.55.4.247

Nogueira, E. D., Abad, A. L. R., & Vega, J. M. R. (1980). *U.S. Patent No. US4235713A*. Washington, DC: U.S. Patent and Trademark Office. Process for the elimination of accumulated iron in organic phases of fluid-fluid extraction that contain di-2-ethyl-hexyl phosphoric acid

Olivier, M. C. (2011, December). Developing a solvent extraction process for the separation of cobalt and nickel from nickel sulfate solutions. Retrieved from http://scholar.sun.ac.za/handle/10019.1/17984

Pilli, S. R., Banerjee, T., & Mohanty, K. (2014). Performance of different ionic liquids to remove phenol from aqueous solutions using supported liquid membrane. *Desalination and Water Treatment,54*(11), 3062-3072. doi:10.1080/19443994.2014.907750

Regel-Rosocka, M. & Alguacil, F. J. (2013). Recent trends in metals extraction. *Revista De Metalurgia, 49*(4), 292-316. doi:10.3989/revmetalm.1344

Regel-Rosocka, M., Nowak, Ł, & Wiśniewski, M. (2012). Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids. *Separation and Purification Technology, 97*, 158-163. doi:10.1016/j.seppur.2012.01.035

Regel-Rosocka, M. & Wisniewski, M. (2011). Selective removal of zinc(II) from spent pickling solutions in the presence of iron ions with phosphonium ionic liquid Cyphos IL 101. *Hydrometallurgy, 110*(1-4), 85-90. doi:10.1016/j.hydromet.2011.08.012

Ríos, A. P., Hernández-Fernández, F. J., Lozano, L. J., Sánchez, S., Moreno, J. I., & Godínez, C. (2010). Removal of Metal Ions from Aqueous Solutions by Extraction with Ionic Liquids†. *Journal of Chemical & Engineering Data, 55*(2), 605-608. doi:10.1021/je9005008

Rusynyk, G. (2012, June 27). Hot-Dip Galvanizing vs. Zinc Plating. Retrieved from https://www.portlandbolt.com/technical/faqs/hot-dip-galvanizing-vs-electrogalvanizing-zinc-plating/

Singh, D., Mishra, S., & Singh, H. (2006). Stripping of iron (III) from the D2EHPA+TBP extract produced during uranium recovery from phosphoric acid by oxalic acid. *Hydrometallurgy, 81*(3-4), 214-218. doi:10.1016/j.hydromet.2005.12.006

Singh, R., Mahandra, H., & Gupta, B. (2017). Solvent extraction studies on cadmium and zinc using Cyphos IL 102 and recovery of zinc from zinc-plating mud. *Hydrometallurgy,172*, 11-18. doi:10.1016/j.hydromet.2017.06.017

SX Kinetics, Inc. (n.d.). Solvent Extraction Technology. Retrieved July 10, 2019, from http://www.sxkinetics.com/download/Technology.pdf

Tibballs, S. (2018, December 21). Zinc Outlook 2019: A Year That Has to Be Better | INN. Retrieved from https://investingnews.com/daily/resource-investing/base-metals-investing/zinc-investing/zinc-outlook/

Yang, J., Wu, Y., & Li, J. (2012). Recovery of ultrafine copper particles from metal components of waste printed circuit boards. *Hydrometallurgy, 121-124*, 1-6. doi:10.1016/j.hydromet.2012.04.01

Recovery of zinc from metal-plating industrial wastewaters by liquid-liquid extraction

Abstract

The extraction of zinc(II) from zinc-plating wastewater by liquid-liquid extraction was studied using the commercial extractants di-(2-ethylhexyl)phosphoric acid (D2EHPA) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex® 272), as well as the ionic liquids, Trihexyltetradecylphosphonium bromide (Cyphos® 102), Trihexyltetradecylphosphonium decanoate (Cyphos® 103) and Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® 104), diluted in organic solvents. First, the commercial extractants and the ionic liquids with the most potential were selected based on the results from diluents, modifiers and stripping solution screening tests. Then, the optimization of extraction and re-extraction (stripping) conditions for each extractant was achieved either by effluent pre-treatment (pH adjustment) to remove iron prior to liquid-liquid extraction or by adjusting the extractant-to-zinc ratio. Afterwards, one commercial extractant and one ionic liquid were selected for further evaluation based on the following parameters: reusability, contact time (kinetic studies), and loading capacity.

Of the two commercial extractants, the most promising results were obtained with 20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP (tributyl phosphate) as the modifier after a contact time of only five minutes. The extraction efficiency for zinc was 98%, with co-extraction of iron which can be resolved by pre-treating the effluent to pH 5.5 to precipitate iron prior to liquid-liquid extraction. Selective stripping of zinc from the loaded organic phase was achieved using 0.6 M H_2SO_4. Under these optimized conditions, the reusability of the organic phase was successfully tested in three cycles of zinc extraction and re-extraction without loss of efficiency.

Regarding ionic liquids, 0.08 M Cyphos® 102 in kerosene exhibited superior selectivity for zinc extraction (83%), with little to no co-extraction of iron. Despite this high efficiency, an issue of insolubility of Cyphos® 102 in the diluent was observed, with the ionic liquid being in a layer below kerosene. This insolubility issue made decantation difficult, which affected the reusability of the extraction system. However, the issue can be solved with the addition of 3% (v/v) decanol as modifier, but resulting in the decrease in zinc extraction efficiency to 40%. A raise of the concentration to 0.24 M Cyphos® 102 in kerosene with 3% (v/v) decanol allowed a 95% extraction efficiency of zinc with no insolubility being observed. On the other hand, the

stripping of zinc from this loaded organic phase was obtained using a high concentration of HNO_3 of 2M. Nevertheless, the problem of reusability of the organic phase remained, whereby zinc extraction decreased to 54% and re-extraction decreased to 5% in the second cycle. Therefore, time and effort need to be devoted to future studies to evaluate the application of Cyphos®102 in liquid-liquid extraction of zinc from zinc-plating wastewaters.

1. Introduction

Zinc is a limited resource that plays a crucial role in the metal industry. The metal is used to coat steel products (60%) as well as die casting in the form of zinc base alloys (15%), brass and bronze (14%) and compounds comprising of zinc sulfate and zinc oxide (8%) (International Zinc Association [IZA], 2019). While the annual consumption of zinc is estimated to be 16 million tonnes, only 6 % of the production comes from recycling or recovery (see Fig. 2.1). However, consuming zinc from primary sources alone is not sustainable and developments of new methods to recover this metal from secondary sources are necessary for the future of the zinc industry.

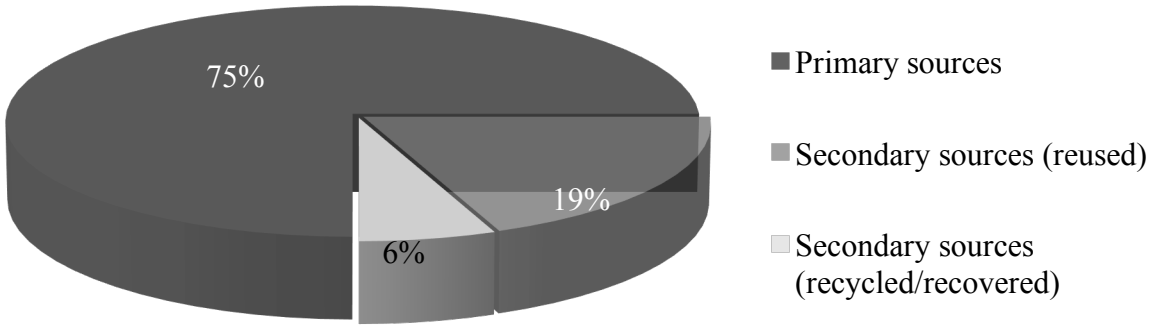


Figure 2.1. Sources of zinc production.

The process of zinc electroplating typically involves coating products, such as that made of steel, by immersing in molten zinc at 450-460 ◦C (hot-dip galvanizing) or by applying electrical current (electroplating) (Rusynyk, 2012). According to Kobya *et al.* (2017), typical plating baths used in the zinc-plating process can be categorized as alkaline cyanide zinc, alkaline non-cyanide zinc, and chloride or acidic zinc. The zinc-plating effluent used in this

work, obtained from Industrial Goñabe, Valladolid, Spain, were rinse-waters derived from electroplating process using chloride zinc baths which typically contains zinc ions in the form of zinc chloride (see Fig. 2.2). Water in the cleansing bath in the chloride zinc electroplating process can be contaminated by zinc and other toxic chemicals during the plating or cleaning process via 'drag-outs' from prior processes. As a result, metal ions can be found in electroplating wastewater effluent in concentrations above which neutralized industrial wasters were permissible by European and national standards for discharge (10 mg/L Fe, 2 mg/L Zn and 1 g/L Cl^- at pH range of 6-9) (Kobya *et al*., 2017; Regel-Rosocka, & Wisniewski, 2011).

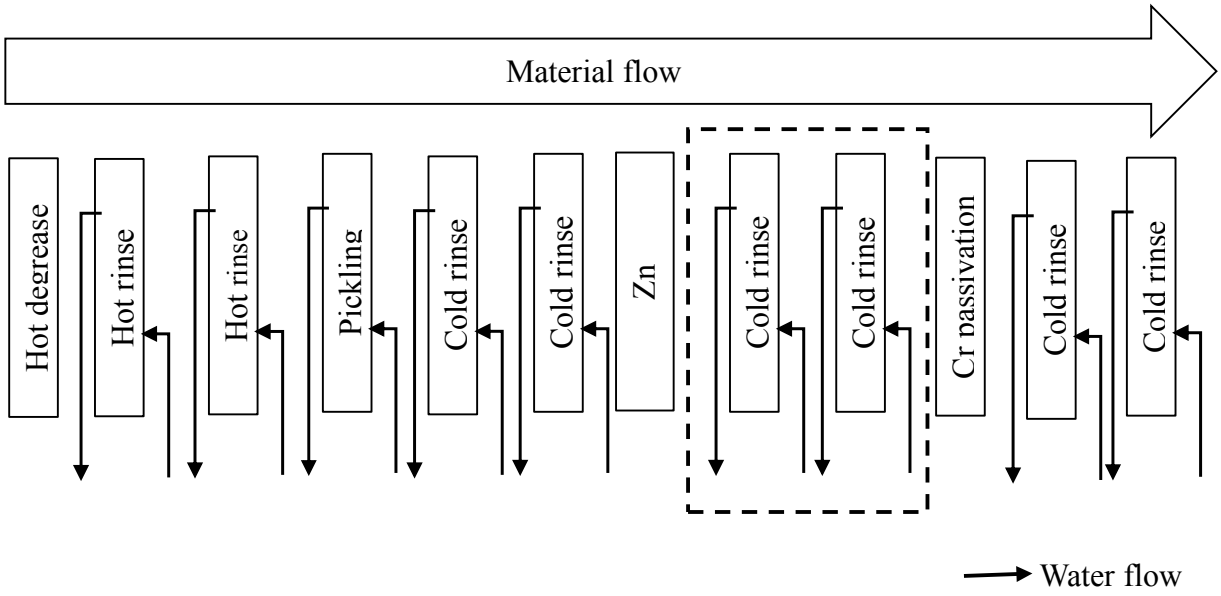


Figure 2.2. Zinc electroplating process flow. Adapted from "Zinc Coatings," 2006, *Midwest Metal Products.* Retrieved June 3, 2019, from http://anglerings.com/Value-Added/Zinc-Coatings. Copyright 2019 by Midwest Metal Products.

The typical method used in the industry for the purification of zinc is precipitation with hydroxides such as soda, lime or a mixture of both[7]. In this treatment, iron and also cadmium are precipitated out of the solution as residues, while zinc is recovered by electrowinning (Ríos *et al*., 2010). Additionally, the treatment process may involve several additional steps namely: (1) oxidation of Fe^{2+} to Fe^{3+} with hydrogen peroxide (H_2O_2), (2) reduction of Cr^{6+} to Cr^{3+} in an acidic solution of pH 2-3 by addition of iron chloride ($FeCl_2$), sodium sulfide (Na_2S) or sodium bisulphite ($NaHSO_3$), (3) pH adjustment to approximately 7.0-8.5 with hydroxides to induce the precipitation of metals, (4) induce coagulation and flocculation and (5) filtration of wastewater for further treatment from hazardous suspended sludge (Ríos *et al*., 2010).

Alternatively, solvent extraction or liquid-liquid extraction is a well-known and explored method of separation of metals such as Zn, Fe, Co, Cr, Cu, Ni, and rare earth metals (Mansur, Rocha, Magalhães, & Benedetto, 2008). Although various combinations of extractants, diluents and modifiers can be used, the solvent extraction technique typically involves three main steps: extraction, scrubbing, and stripping[12]. In the extraction stage, the aqueous metal-bearing effluent (feed solution) is contacted and agitated with an extractant diluted in an organic solvent, such as kerosene (Mansur *et al*., 2008). Due to the differences in the polarities of the aqueous (feed solution) and the organic phase (extractant dissolved in the diluent), the target metal is transferred from the former to the latter phase (loaded organic phase) (Mansur *et al*., 2008). Depending on the selectivity of the extractant, the loaded organic phase will then either undergo stripping or scrubbing. The metal of interest is stripped from the loaded organic phase by an aqueous solution, resulting in a concentrated solution of the target metal, which undergo further refining processes such as crystallization, evaporation, electrolysis or electrowinning (Dreisinger, 2009). On the other hand, if the selectivity of the extractant is low and co-extraction of non-target metals is high, scrubbing may be necessary to remove the co-extracted metals in the loaded organic phase prior to stripping to ensure high purity of the metal of interest (Mansur *et al*., 2008).

The use of commercial extractants is a widely explored and reported strategy in liquid-liquid extraction and can be categorized into four main categories: neutral (solvating), chelating, acidic and basic extractants. Solvating (or neutral) extractants extract metal by replacing the hydration sheath of the neutral ion-pairs with solvent molecules (Mansur *et al*., 2008). For example, the commercially available Cyanex® 923 (a mixture of trialkylphosphine oxides) was used to extract Fe(III) and Au(III), existing as $FeCl_3^-$ and $AuCl_3$, in leach solutions of HCl and pH 7.0, which also contain accompanying metals such as Pd(II), Pt(IV), Cu(II) and Cr(III) (Nguyen, Wang, & Lee, 2017). Another commercially available solvating extractant, tributyl phosphate (TBP), was reported to be effective in the selective extraction of Zn(II) over Fe(II) and Fe(III) from metal-plating wastewater (spent hydrochloric acid pickling liquor) with 92.5% yield for Zn(II) and only 11.2% co-extraction of Fe(II) (Mansur *et al*., 2008). However, several drawbacks were noted such as the high concentration of extractant, 80-100% (v/v), required to achieve the reported extraction efficiency and the transfer of a significant amount of water to the organic phase (Mansur *et al*., 2008).

Chelating agents act as ligands that bind to metal cations by forming metal-extractant chelates and releasing hydrogen ions in the process ("Chelate," 2007). Ketoxime and aldoxime species such as LIX 54 (dodecylphenylmethyl-β-diketone), LIX 63 (5,8-diethyl-7-hydroxy-6-

dodecanone oxime), LIX 64 (2-hydroxy-5-nonylbenzophenone oxime), LIX 84-IC (2-hydroxy-5-nonyl acetophenone oxime), LIX 860N-I (5-dodecylsalicylaldoxime), Acorga M5640 (active substance 2-hydroxy-5-nonylbenzaldehyde oxime) are some chelating agents commercially available today (Regel-Rosocka & Alguacil, 2013). Additionally, LIX 84, LIX 984N and LIX 84-IC are known to achieve extraction efficiencies higher than 99% for copper in printed circuit boards (PCBs) wastewater containing high concentrations of Fe and Pb with lower concentrations of Sn, Zn, and Ni (Le *et al*., 2011; Yang, Wu, & Li, 2012).

Acidic (or liquid-cation exchange) extractants exchange their hydrogen ions with metal cations to form metal salts. One of the most widely known extractants of this class is di-(2-ethylhexyl) phosphoric acid (D2EHPA) which shows an extractive selectivity towards zinc from Cu(II), Co(II), Ni(II) and other bivalent transition metals (Mansur *et al*., 2008). Other commercially available acidic extractants includes phosphinic acids such as bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex® 272) and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex® 301) which were selected for the extraction of Zn(II) over Fe(II) and Fe(III) from spent hydrochloric acid pickling liquor generated from the metal-plating industry. The result shows that Cyanex® 301 was more effective in extracting Zn(II) (80-95%) with less co-extraction of Fe(II) (less than 10%) than Cyanex® 272 (70% Zn(II) and 20% Fe(II)) (Mansur *et al*., 2008). Furthermore, many studies reported the viability of Cyanex® 272 as extractant for zinc and cobalt from nitric acid leached liquor with the selectivity of the two target metals controllable by pH adjustments (pH 2.6-2.9 for zinc and pH5.2-5.5 for cobalt) (Dreisinger, 2009).

On the other hand, basic (or liquid-anion exchange) extractants extract anions or anionic metal complexes (Gallacher, 1981). Amines and quaternary ammonium salts such as Primene 81R, Primene TOA, Primene JMT, Amberlite LA-2, Alamine 336 and Aliquat 336 are typically used as basic extractants (Regel-Rosocka & Alguacil, 2013). The loaded organic phase of this type of extractants typically undergoes stripping with aqueous salts or bases for better phase separation. Tertiary amines like Alamine 336 are used to extract uranium, in the form of uranyl sulfate complexes, as well as the extraction of chloride complexes (Regel-Rosocka & Alguacil, 2013). In the latter case, extraction selectivity of different metals can be achieved by varying the concentration of chloride. For example, solvent extraction with Alamine 336 at 40℃ and pH 2 is selective towards ferric iron at a chloride concentration of 50 g/L, copper at approximately 100 g/L, and nickel at 250 g/L (Regel-Rosocka & Alguacil, 2013). Quaternary ammonium salts such as Aliquat 336 can be used over a wide pH range (Regel-Rosocka & Alguacil, 2013). However, due to the lack of proton that can be

deprotonated, quaternary ammonium salts are more difficult to strip than amines (Gallacher, 1981).

Alternatively, forging a new landscape for innovation in liquid-liquid extraction is the use of ionic liquids as extractants. Ionic liquids (or molten salts) are solvents made of various combinations of oppositely charged ionic species whose asymmetry and charge dispersal results in a reduced packing of the solid-state which results in their characteristically low melting points of less than 100°C (Hagiwara & Ito, 2000). Some advantages pertinent to the application of ionic liquids in biphasic systems include negligible vapor pressure, high thermal stability (which allows for operations over a wide range of temperature) and tunable miscibility in both organic and aqueous solvents (C. Trombini, personal communication, March 13, 2018). Despite their relatively high costs, some ionic liquids such as Cyphos® 101, Cyphos® 102, Cyphos® 103, Cyphos® 104 and urea-choline chloride are commercially available and can be utilized as extractants, with or without diluents (also called co-solvents), in the recovery of metals (Regel-Rosocka & Wisniewski, 2011; Regel-Rosocka, Nowak, & Wisniewski, 2012; Abbott, Capper, Davies, Rasheed, & Shikotra, 2005; Egorov *et al.,* 2010). For example, Cyphos® 101 with toluene as co-solvent can be used to selectively extract zinc(II) over iron(II) in chloride media containing high concentrations of zinc(II) (Regel-Rosocka & Wisniewski, 2011). Cyphos® 102 was reported to be effective in the extraction of zinc(II) and cadmium from zinc-plating mud solution containing hydrochloric acid with 96.64% zinc recovery (Singh, Mahandra, & Gupta, 2017). To the best of our knowledge, while Cyphos® 103 has been studied in the removal of phenol from aqueous solutions in the form of supported liquid membrane (Pilli, Banerjee, & Mohanty, 2014), the application of Cyphos® 103 as potential extractant for liquid-liquid extraction of zinc has never been reported. Furthermore, 0.2 M Cyphos® 104 was reported to be effective in the extraction of Zn from model aqueous feeds containing 5 g/L of the metal and 0.58 M HCl with a percentage extraction of 94.2%. The same extractant was also reported to extract high concentrations of Fe(III) and less of Fe(II) (Regel-Rosocka & Wisniewski, 2011).

Many advantages contribute to the interest in solvent extraction as an alternative strategy to the traditional precipitation method: metal separation and recovery from low-concentrated wastewater and leachates from secondary sources, availability of technological and technical solutions, selectivity by design to achieve high metal purity and a commonly known mechanism of mass transport and reaction (Ríos *et al*., 2010). However, it is also important to mention the challenges that may arise with the technique so that future improvements and innovations can be explored: the physical, environmental and health hazard

of diluents (the most popular being flammable kerosene) and other organic solvents, the formation of unfavorable third phases, transport of impurities to the interface, the lack of a simple and universal method of recovery of various metals, as well as the scalability of the technique to the industrial scale (Ríos *et* al., 2010; Regel-Rosocka & Alguacil, 2013).

Therefore, the objective of this work, which is part of the METALCHEMBIO* project, is to explore the possibilities of utilizing liquid-liquid extraction (also called solvent extraction, SX) using both commercial (D2EHPA and Cyanex® 272) and innovative extractants, such as ionic liquids (Cyphos® 102, Cyphos® 103 and Cyphos® 104) to extract zinc from zinc-plating wastewater, particularly from zinc electroplating process using acidic baths. It is also important to report that, to the best of our knowledge, all ionic liquids mentioned have never been tested on zinc-plating wastewater.

2. Materials and methods

2.1 Zinc electroplating effluent

The zinc-plating wastewater used in this work was obtained from Industrial Goñabe, a Spanish company specialized in galvanization located in Valladolid, Spain. The sample is collected from the non-treated effluent of the wastewaters form the zinc electroplating line which uses electrodeposition baths with acidic zinc solutions.

Various physicochemical parameters were analyzed to characterize the zinc-plating effluent used in this work (Table 2.1). Redox potential (Eh) and pH were measured using a pH/E Meter GLP 21 (Crison). Sulphate concentration was determined by the sulfaVer4 procedure (Method 8051, Hach-Lange) using A UV-Visible spectrometer DR2800 (Hach-Lange) at 450nm. Determination of chloride concentration was done by using volumetric titration. Metal characterization of the zinc-plating effluent was done by diluting wastewater samples to 1:10, 1:100 and 1:1000 (v/v) with 5% nitric acid and analyzed using Flame Atomic Absorption Spectroscopy (FAAS) with a novAA 350 system (Analytik Jena) using standard calibration curves. The main iron specie was Fe(III), determined using AccuVac® Ampuls (Method 8146).

Table 2.1. Initial characterization of the zinc-plating effluent used in this work; supplied by Industrial Goñabe, Valladolid, Spain.

	Metals (mg/L)*	pH (Sorensen scale)	SO_4^{2-} (mg/L)	Eh (mV)	Cl^- (mg/L; media)
Zn	360 ± 7				
Fe	124 ± 8				
Cu	2.66 ± 0.03	2.10	49	501	1036
Cr	2.12 ± 0.06				
Mn	1.59 ± 0.02				

***** Concentrations are presented with technical standard deviations of three readings made for metals analysis with FAAS.

2.2 Reagents and solutions

Two commercial extractants diluted in organic solvents were tested as zinc liquid-liquid extractants in this study: Di-(2-ethylhexyl)phosphoric acid (D2EHPA, Acrōs Organics), Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex® 272, Solvay). In addition, three ionic liquids diluted in organic solvents were also tested as extractants, namely: Trihexyl(tetradecyl)phosphonium bromide (Cyphos® 102, Sigma-Aldrich), Trihexyl(tetradecyl)phosphonium decanoate (Cyphos® 103, Sigma-Aldrich), and Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® 104, Sigma-Aldrich). The organic solvents tested were: kerosene (Alfa Aesar, Thermo Fisher Scientific), SHELLSOL D70 (SHELL), SHELL GTL Solvent GS215 (SHELL), toluene (Panreac) and Escaid 102 (ExxonMobil). Tributyl phosphate (TBP, Sigma Aldrich), octanol (Acrōs Organics), decanol (Merck) and dodecanol (Merck) were tested as modifiers.

2.3. Experimental Scheme

The experimental scheme for the selection of commercial extractants and ionic liquids for liquid-liquid extraction of zinc-plating wastewater can be broken down into four main steps in the following sequence: (1) establishment of the initial experimental extraction conditions of all extractants selected from initial bibliographic search, (2) a set of screening tests to select the best diluents, modifiers and stripping agents, (3) optimization of extraction conditions for

the selected commercial extractant and IL(s), and (4) characterization of the performance of the selected commercial extractant and IL (Fig. 2.3). Optimization was customized to address the issues inherent in the selected candidates (iron removal or extractan-to-zinc ratio). Lastly, one commercial extractant and one ionic liquid were selected for the following performance tests: loading capacity, kinetics (contact time) and reusability. In the case of ILs, two candidates were optimized and final selection was done prior to performance tests.

The extraction conditions as well as the screening, the optimization and the characterization tests are described in greater detail in the Material and Methods section and discussed in the Results and Discussion section.

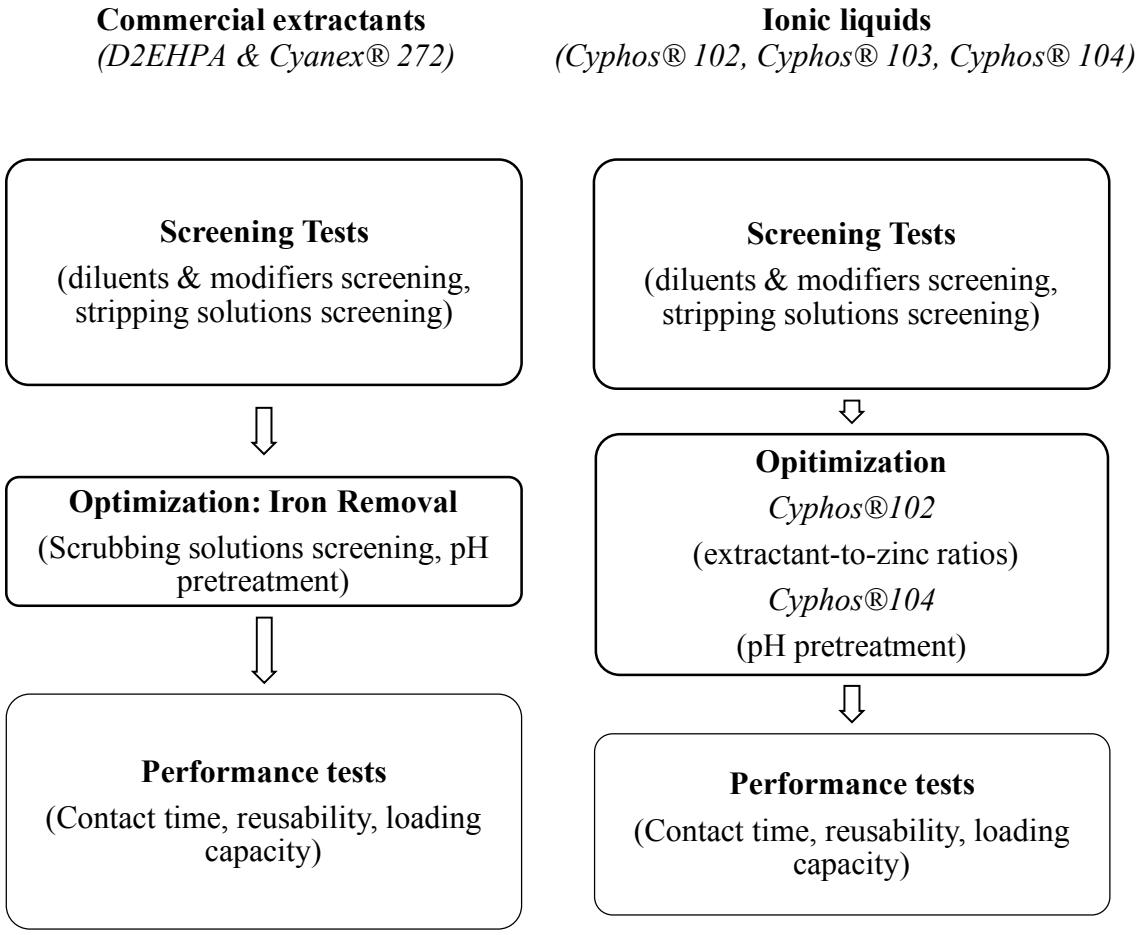


Figure 2.3. Experimental scheme for the selection and evaluation of commercial extractants and ionic liquids (ILs) for liquid-liquid extraction of zinc-plating wastewater

2.4. Standard procedures for liquid-liquid extraction

Unless stated otherwise, the standard procedures for liquid-liquid extraction, stripping and scrubbing employed in the entire research are as follow:

- An aqueous (*ie.* zinc-plating effluent, stripping solution or scrubbing solution) were contacted with equal volume (A/O = 1:1) of an organic phase (fresh or loaded).
- In the case of commercial extractants whereby the experiments were conducted in the winter, the room temperature was maintained at 21 ± 2 ℃. The aqueous-organic mixture was stirred at 400 rpm in a 100mL round-bottom open flask for 1 hour, and the two phases were decanted using a separatory funnel. The same conditions also apply for stripping and scrubbing experiments.
- In the case of ionic liquids whereby liquid-liquid extraction was conducted in the summer, the temperature was maintained at 25± 2 ℃. Due to the high cost of ionic liquids, the experiments were conducted in a smaller scale. Therefore, the organic phase and zinc-plating effluent were shaken in centrifuge tubes and shaken horizontally using an orbital shaker at 150 Mot/min for 30 minutes, in the case of liquid-liquid extraction, or 1 hour, in the case of stripping. The loaded organic and the aqueous phases were collected using transference pipettes.
- The initial and final pH of the zinc-plating effluent (aqueous phase) from all experiments were measured. The initial zinc-plating effluent as well as the decanted aqueous phase were diluted (1:10, 1:100, 1:500, and 1:1000) and the metals (zinc and iron) were analyzed using FAAS.

The extraction efficiency (see Equation 2.1) of metals was determined by calculating the final concentration of metal transferred to the organic phase $[M]^*_{(org,E)}$ after solvent extraction ($[M]^*_{(org,E)} = [M]_i - [M]^*_{(aq,E)}$), where $[M]_i$ is the initial concentration of the metal in the aqueous solution (zinc-plating effluent) and $[M]^*_{(aq,E)}$ is the concentration of the same metal remaining in the aqueous phase after extraction. The extraction efficiency was then calculated by dividing $[M]^*_{(org,E)}$ by the initial concentration of the metal $[M]_i$, and multiplying by 100 (see Equation 1):

Extraction Efficiency:

$$E = \left(\frac{[M]_i - [M]^*_{(aq,E)}}{[M]_i}\right) \times 100 \quad (2.1)$$

The ideal result is such that only zinc is extracted and transferred to the loaded organic phase while the other metals remain in the effluent.

The stripping efficiency was calculated according to the equation (2.2) in which S is the concentration of metal (mg/L) successfully removed and transferred from the loaded organic phase ($[M]^*_{(org,E)}$) to the aqueous stripping phase ($[M]^*_{(aq,S)}$).

Stripping Efficiency

$$S = \left(\frac{[M]^*_{(aq,S)}}{[M]^*_{(org,E)}}\right) \times 100\% \quad (2.2)$$

2.5. Liquid-liquid extraction with commercial extractants

D2EHPA and Cyanex® 272 are well-studied commercialized extractants known to be efficient for zinc extraction from metal-bearing wastewaters. Therefore, in this work they were selected for tests with a real zinc electroplating industrial wastewater.

2.5.1 Screening tests with D2EHPA

The chemical structure, chemical formula and physical properties of bis(2-ethylhexyl)phosphate (D2EHPA) can be found in Figure 2.4 and Table 2.2. The concentration of D2EHPA used in the experiment was 20% (w/w), or 0.52 M.

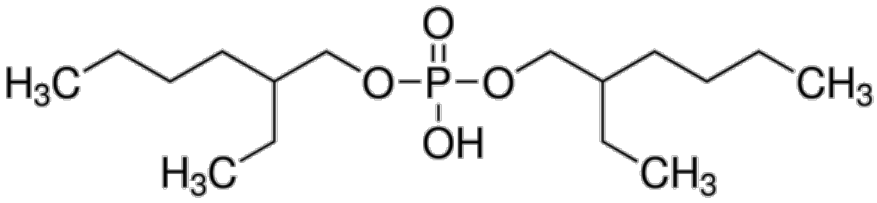


Figure 2.4. Chemical structure of Bis(2-ethylhexyl) phosphate (D2EHPA). *Note*. Retrieved from "Bis(2-ethylhexyl) phosphate" by Sigma Aldrich, 2019 (https://www.sigmaaldrich.com /catalog/product/aldrich/237825?lang=pt&region=PT&g..).Copyright 2019 by Merck KGaA.

Table 2.2. Chemical properties of D2EHPA. *Note*. Adapted from "Bis(2-ethylhexyl) phosphate" by Sigma Aldrich, 2019 (https://www.sigmaaldrich.com/catalog/product/aldrich/ 237825?lang=pt&region=PT&g..). Copyright 2019 by Merck KGaA.

Chemical formula	$C_{16}H_{35}O_{4P}$
Molar mass	322.43 g/mol
Density	0.965 g/mL at 25°C
Melting point	−60 °C (−76 °F)
Flash point	130 °C (266 °F)

2.5.1.1. Diluents and modifiers for D2EHPA

Diluents and modifiers screening for the solvent extraction of zinc-plating effluent was performed using 20% (w/w) D2EHPA in diluents of choice and different modifiers (octanol, decanol, dodecanol and tributyl phosphate (TBP)) with concentrations ranging from 0% to 7% (v/v). The diluents being tested were: kerosene, SHELLSOL D70 and SHELL GTL Solvent GS 215.

2.5.1.2 Stripping solutions for D2EHPA

To select the ideal solution for the stripping of loaded organic phase with zinc as the target metal, 0.2 M of HNO_3, HCl and H_2SO_4 solutions and deionized (DI) water were tested in 2 replicates.

2.5.2 Screening tests with Cyanex® 272

The chemical structure and physical properties of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex® 272) can be found in Figure 2.5 and Table 2.3. The concentration of the extractant used in the experiment was 20% (w/w), or 0.55 M (active compound).

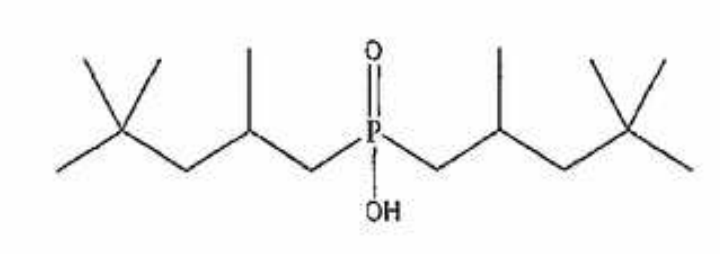


Figure 2.5. Chemical structure of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex® 272). *Note*. Retrieved from "Cyanex® 272" by Solvay, 2019 (https://www.solvay.com/en/product/cyanex-272). Copyright 2019 by Solvay.

Table 2.3. Chemical properties of Cyanex® 272. *Note*. Adapted from "Cyanex® 272" by Solvay, 2019 (https://www.solvay.com/en/product/cyanex-272). Copyright 2019 by Solvay.

Chemical formula	$C_{16}H_{35}O_2P$
Molar mass	290.428 g/mol
Density	0.9±0.1 g/mL
Boiling point	417.1±14.0 °C at 760 mmHg

2.5.2.1 Diluents and modifiers for Cyanex® 272

Diluents and modifiers screening for the solvent extraction of zinc-plating effluent was performed using 0.55 M (active compound) Cyanex® 272 in three diluents (SHELLSOL D70, SHELL GTL Solvent GS 215 and Escaid 102 (ExxonMobil). Based on the modifier screening result from prior experiments with D2EHPA, TBP was selected as the modifier and tested at 0%, 3%, and 7% (v/v).

2.5.2.2 Stripping solution for Cyanex® 272

The loaded organic phases from the diluents and modifier screening tests with Cyanex® 272 as the extractant were stripped with 0.2 M H_2SO_4 at room temperature (21± 2°C) and A/O = 1:1 for one hour.

2.5.3 Optimization with D2EHPA – iron removal

Due to the tendency of D2EHPA to co-extract iron which consequentially compromise the reusability of the extraction system, optimization was carried out with the focus on the removal of iron.

2.5.3.1 Iron scrubbing agents

Scrubbing of iron was tested using 1.3 M oxalic acid, 1.3 M ammonium sulfate, 6 M HCl and sea water at A/O= 1:1, whereby the organic phase was derived from stripped loaded organic phase from solvent extraction with 20% w/w D2EHPA in kerosene and 3% and 5% (v/v) TBP.

2.5.3.2 Effluent pretreatment by pH adjustment

The study of the effect of pH on the concentration of zinc and iron in the zinc-plating effluent was achieved by adjusting the pH of the sample to 3, 4, 5, 5.5, 6, 7, 8, 9, 10, 11 using 5 M NaOH and stirred at 400 rpm, after which the samples were left overnight to stabilize and ensure a complete precipitation. The samples were then centrifuged at 4000 rpm for 10 minutes and analyzed using the standard analytical method to determine the concentration of zinc and iron remaining in the pH-treated effluent samples.

2.5.3.3 Effect of pH pretreatment on the extraction efficiency of D2EHPA

Based on the result from the study of the effect of pH adjustment on the concentration of zinc and iron in the effluent, aqueous samples were adjusted at selected pH values 3, 4, 5,

5.5 and 6 before being subjected to liquid-liquid extraction (2 replicates) with the selected standard extraction condition (20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP).

2.5.4 Performance of D2EHPA

2.5.4.1 Contact time (kinetics)

The kinetics study to evaluate the effect of contact time on the efficiency of the solvent system was conducted using the standard condition of organic phase and zinc-plating effluent whose pH was adjusted to 5.5 as the aqueous phase. The two phases (A/O = 1:1) were stirred for 5, 15, 30, 45 and 60 minutes, each time interval was done in 2 replicates.

2.5.4.2 Reusability of organic phase

To study the reusability, solvent extraction was conducted using selected extraction conditions (extractant, diluent, modifier, etc.) to transfer zinc to the loaded organic phase followed by stripping with the stripping solution of choice. Then, the stripped loaded organic phase was reused as the organic phase of the next cycle of solvent extraction without iron scrubbing. The reusability of the extraction system was evaluated based on the extraction efficiency in successive extraction and stripping cycles.

The study of the reusability of the organic phase (20% (w/w) D2EHPA in kerosene with 3% (v/v) TBP) was tested in 3 replicates on two types of zinc-plating effluents, the raw and pH-adjusted (pH 5.5) samples, in three consecutive cycles. In the case of raw effluent samples, the contact times for both solvent extraction and stripping with 0.2 M H_2SO_4 were 1 hour. The contact times for solvent extraction and stripping (0.6 M H2SO4) of pH-adjusted effluent were 1 hour and 5 minutes, respectively.

2.5.4.3 Loading capacity of organic phase (equilibrium isotherms)

Two isotherms at equilibrium were tested on two types of aqueous phases, one with zinc-plating effluent pretreated with pH adjustment to 5.5 and another with raw effluent (no pretreatment) with the aim to determine the loading capacities at these conditions. Both were tested with 2 replicates. Solvent extraction with raw zinc-plating effluent were stirred for 1 hour, while the contact time for pretreated effluent was 5 minutes with the established standard

condition of the organic phase. Based on a study by Azizitorhabeh *et al.* (2016) which suggested that 3 molecules of D2EHPA are needed to extract 1 molecules of zinc, a theoretical calculation was done based on D2EHPA:zinc molar ratio of 3:1 and the calculation suggest an optimum A/O ratio of 30:1. Hence, the two conditions were tested with increasing aqueous-to-organic phase ratio from 1:1 to 35:1. The pretreated effluent was tested at A/O = 1:1, 5:1, 10:1, 15:1, 20:1, 25:1, 30:1 and 35:1, while the raw effluent was tested at A/O = 1:1, 2:1, 3:1, 4:1, 5:1, 10:1, 15:1, 20:1, 25:1, 30:1 and 35:1.

2.6 Liquid-liquid extraction with ionic liquids

2.6.1 Screening of ionic liquids

Three ionic liquids, diluted to 0.04M in toluene as organic solvent, were first tested as potential extractants for liquid-liquid extraction of zinc-plating effluent: Cyphos® 102 (Figure 2.6, Table 2.4), Cyphos® 103 (Fig. 2.7 and Table 2.5), and Cyphos® 104 (Fig. 2.8, Table 2.6). All ionic liquids were tested at molar concentrations of 0.04M.

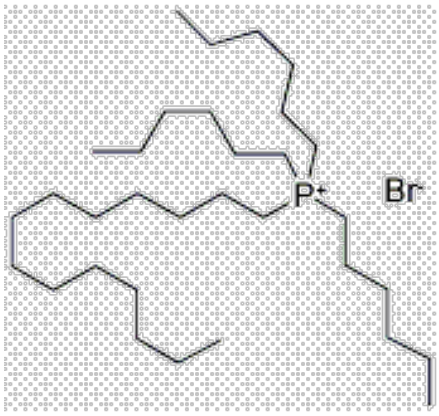


Figure 2.6. Chemical structure of Trihexyl(tetradecyl)phosphinium bromide (Cyphos® 102). *Note*. Retrieved from "Trihexyl(tetradecyl)phosphonium bromide" by ChemicalBook, 2019 (https://www.chemicalbook.com/ProductChemicalPropertiesCB2730576_EN…). Copyright 2019 by ChemicalBook.

Table 2.4. Chemical properties of Cyphos® 102. *Note*. Adapted from "Trihexyl(tetradecyl)phosphonium bromide" by ChemicalBook, 2019 (https://www.chemicalbook.com/ProductChemicalPropertiesCB2730*576_EN*...). Copyright 2019 by ChemicalBook.

Chemical formula	$C_{32}H_{68}BrP$
Molar mass	563.76 g/mol
Density	0.96 g/mL at 20^{o}C

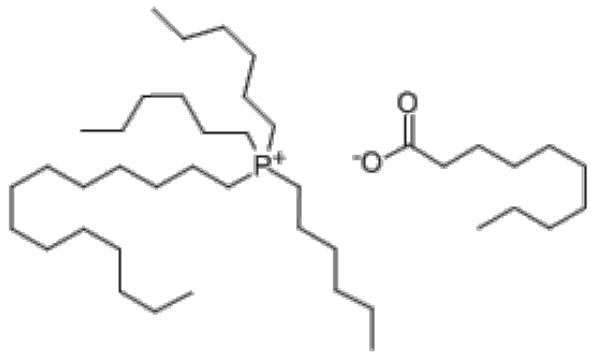


Figure 2.7. Chemical structure of Trihexyl(tetradecyl)phosphonium decanoate (Cyphos® 103). *Note.* Retrieved from "Trihexyl(tetradecyl)phosphonium decanoate" by Chemical Book, 2019 (https://www.chemicalbook.com/ProductChemicalProperties CB3408902_EN.htm). Copyright 2019 by ChemicalBook.

Table 2.5. Chemical properties of Cyphos® 103. *Note.* Retrieved from "Trihexyl(tetradecyl) phosphonium decanoate" by Chemical Book, 2019 (https://www.chemicalbook.com/ ProductChemicalPropertiesCB3408902_EN.htm). Copyright 2019 by ChemicalBook.

Chemical formula	$C_{42}H_{87}O_2P$
Molar mass	655.11 g/mol
Density	0.883 g/mL
Specific Gravity	0.883

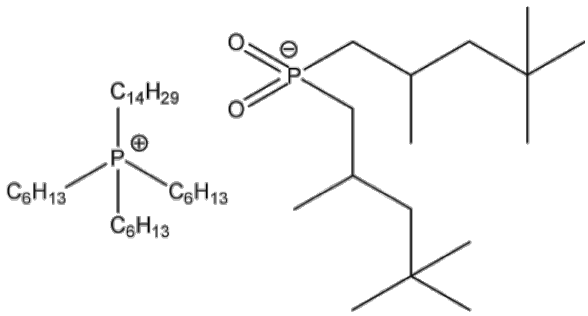


Figure 2.8. Chemical structure of Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® 104). *Note*. Retrieved from "Cyphos IL 104" by ChemicalBook, 2019 (https://www.chemicalbook.com/ChemicalProductProperty_EN_CB9319859.htm). Copyright 2019 by ChemicalBook.

Table 2.6. Chemical properties of Cyphos® 104. *Note*. Retrieved from "Cyphos IL 104" by ChemicalBook, 2019 (https://www.chemicalbook.com/ChemicalProductProperty_EN_*CB9319859.htm). Copyright 2019 by ChemicalBook.*

Chemical formula	$C_{48}H_{10}O_2P_2$
Molar mass	773.27 g/mol
Density	0.895 g/mL at 20^{o}C
Specific Gravity	0.887

2.6.2 Screening tests with Cyphos® 102

2.6.2.1 Diluents and modifiers for Cyphos® 102

Diluent screening for 0.08 M Cyphos® 102 was conducted using two diluents, toluene and kerosene. The extraction system was tested with and without modifiers. The three modifiers tested were 3% (v/v) octanol, decanol and TBP.

2.6.2.2 Stripping solutions for Cyphos® 102

Twelve stripping solutions were tested as stripping agents for loaded organic phase from liquid-liquid extraction of raw zinc-plating effluent with 0.08 M Cyphos®102 in

kerosene: 1.3 M oxalic acid, 1.3 M ammonium sulfate, 0.2 M H_2S0_4, 0.6 M H_2S0_4, 1 M H_2S0_4, 0.6 M HCl, 1 M HCl, 0.6 M HNO_3, 1 M HNO_3 and 2 M HNO_3.

2.6.3 Optimization with Cyphos®102

2.6.3.1 Extractant-to-zinc ratios

The effect of increased volume of organic phase (A/O ratio) on the extraction efficiency was tested with 0.08 M Cyphos® 102 in kerosene and 3% (v/v) decanol at A/O ratio of 1:1, 1:2, 1:3 and 1:4.

Moreover, two additional molar concentrations (0.16 M and 0.24 M) of the extractant were tested with kerosene as the selected diluent of choice and 3% (v/v) decanol as the modifier (A/O = 1:1). In this experiment, stripping of loaded organic phases from liquid-liquid extraction with both extractant molar concentrations was tested using 2 M HNO_3.

2.6.4 Screening tests with Cyphos® 104

2.6.4.1 Diluents for Cyphos® 104

Diluent screening for liquid-liquid extraction with 0.04 M Cyphos® 104 was conducted using toluene and kerosene. No modifier was added.

2.6.4.2 Stripping solutions for Cyphos® 104

The same stripping solutions tested in the experiments with 0.08 M Cyphos® 102 were tested with the loaded organic phase from liquid-liquid extraction with 0.04 M Cyphos® 104 in toluene: 1.3 M oxalic acid, 1.3 M ammonium sulfate, 0.6 M H_2S0_4, 1 M H_2S0_4, 0.6 M HCl, 1 M HCl, 0.6 M HNO_3, 1 M HNO_3, 2 M HNO_3, 3 M HNO_3 and 4 M HNO_3.

2.6.5 Optimization with Cyphos® 104

2.6.5.1 Effect of pH pretreatment on the extraction efficiency of Cyphos® 104

Liquid-liquid extraction was performed on zinc-plating effluent whose pH was adjusted to 5.5, with 0.04 M Cyphos® 104 in toluene (A/O = 1:1, 30 minutes, 3 replicates). Moreover, another set of stripping solution screening using the resulting loaded organic phase was conducted with 0.2 M H_2SO_4, 0.6 M H_2SO_4, 1 M H_2SO_4, 0.6 M HCl, 1 M HCl and 1.3 M ammonium sulfate.

2.6.6 Performance of Cyphos® 102

2.6.6.1 Contact time (kinetics)

The kinetics of the efficiency of the selected extractant with its optimized conditions (0.24 M Cyphos® 102 in kerosene and 3% (v/v) decanol) was studied by testing the contact times of 5, 10, 20, 30, and 40 minutes in 2 replicates.

2.6.6.2 Reusability of organic phase

The reusability of 0.24 M Cyphos® 102 in kerosene and 3% (v/v) decanol as the organic phase for the extraction of zinc from the zinc-plating effluent was tested in 2 cycles (2 replicates), whereby the loaded organic phase stripped with 2 M HNO_3 from the first cycle was reused as is in the second cycle of liquid-liquid extraction and stripping.

2.6.6.3 Loading capacity of organic phase (equilibrium isotherms)

The loading capacity of the selected extraction system (0.24 M Cyphos® 102 in kerosene and 3% (v/v) decanol) was tested with A/O ratio of 1:1, 2:1, 3:1, 5:1 and 10:1 in two replicates.

3. RESULTS & DISCUSSIONS

3.1 Liquid-liquid extraction with commercial extractants

D2EHPA was selected as one commercial extractant to be tested based on the extraction condition reported by Vahidi *et al.* (2009) and the preliminary results provided by another member of the team which showed a high extraction efficiency of 20% (w/w) D2EHP for zinc found in this type of zinc-plating effluent.

Cyanex® 272 was selected based on the result of a research conducted by Mansur *et al.* (2008) which reported that the extractant was effective in the extraction of zinc from spent hydrochloric acid pickling liquors from metal-plating process containing 33.9 g/L Zn, 203.9 g/L Fe and 2 M HCl. The concentration of Cyanex® 272 was calculated based on a 100:1 molar ratio of Cyanex® 272 to zinc found in the wastewater sample (a generic ratio which, based on the experience of the team, was a good starting concentration for many extractants) resulting in a molar concentration of 0.55 M (active compound), or approximately 20% (w/w).

3.1.1 Screening tests with D2EHPA

3.1.1.1 Diluents and modifiers for D2EHPA

Preliminary results (not mentioned here) showed the formation of third phase between the aqueous and the organic phases when D2EHPA was used as the extractant for the liquid-liquid extraction of zinc-plating effluent. Similar phenomenon was observed and mentioned in a U.S. patent No. US4235713A (1980) which reported that the extractant's high affinity towards iron, even in low concentrations, allowed the extractant to readily form complexes with the metal and polymerized in the organic phase. The polymerization can reach a molecular weight of order of 2000 (U.S. patent No. US4235713A, 1980). Therefore, the effect of several modifiers on the third phase formation and the overall extraction efficiency of the extraction system was studied and the results can be found in Figure 2.9. Of the three diluents tested, kerosene showed the most favorable extraction selectivity towards zinc and 3% (v/v) TBP was selected as the modifier of choice. The selected diluent-modifier system extracted up to 92% zinc with 65% co-extraction of iron.

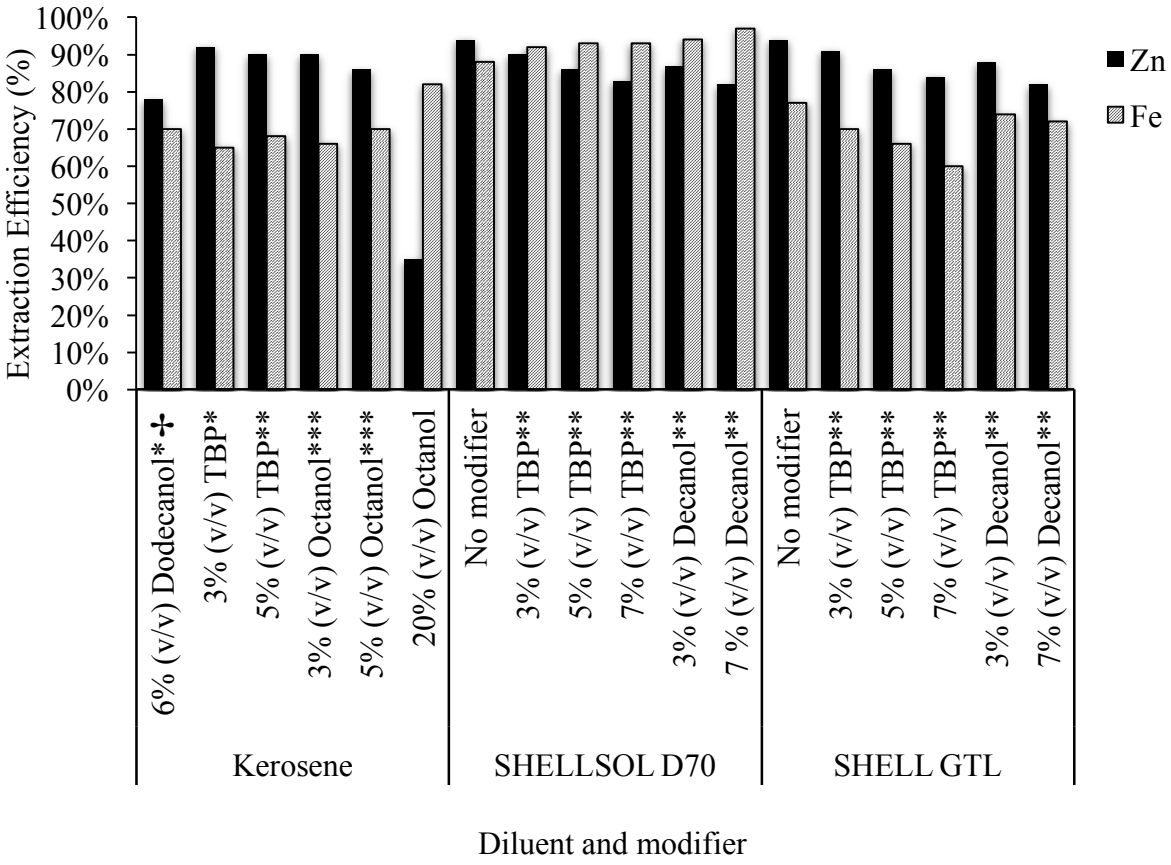


Figure 2.9. Effect of diluents and modifiers on solvent extraction efficiency of Zn and Fe from zinc-plating effluent with 20% (w/w) D2EHPA (A/O: 1:1, 21 ± 2℃, 1 h, no replicates)

*Thin layer of third phase observed.

**Moderate layer of third phase observed.

***Large layer of third phase observed.

✢Modifier solidified at 21 ± 2°C.

3.1.1.2 Stripping solutions for D2EHPA

Stripping solutions used in this experiment were selected based on a study by Ali *et al.* (2006) which investigated the stripping efficiencies of HNO_3, HCl and H_2SO_4 on loaded organic phase from liquid-liquid extraction of synthetic aqueous solution containing 1.53 x 10^{-2} M Zn(II). The molar concentration of 0.2 M used in this experiment were calculated in (with excess) based on the molar concentration of 0.01 M H_2SO_4 selected by Ali *et al.* (2006) to strip loaded organic phase derived from extracting industrial waste solution containing 186 mg/L of

Zn to align with the zinc concentration of approximately 360 mg/L found in the zinc-plating wastewater sample being tested in this experiment.

Figure 2.10 shows the results of stripping the loaded organic phase derived from the solvent extraction of zinc-plating effluent under aforementioned reaction conditions. The result was favorable to our objective with the target metal, zinc, being effectively stripped by all three acidic solutions at 0.2 M, while iron, the co-extracted metal, remained in the organic phase. The efficiency of each acid solution in the stripping of zinc increases in this following order: HCl (74%) <H_2SO_4 (85%) <HNO_3 (87%). Deionized water is not an effective stripping agent for any of both metals (Zn and Fe).

Despite the result indicating that HNO_3 display the highest stripping efficiency of all the stripping solutions, the small difference between the efficiencies between HNO_3 and H_2SO_4, along with the reason given by Ali *et al*. (2006) who suggested that the use of HNO_3 as a stripping solution was observed to negatively affect the subsequent electrowinning step, was the reason why H_2SO_4 was selected as the zinc stripping agent.

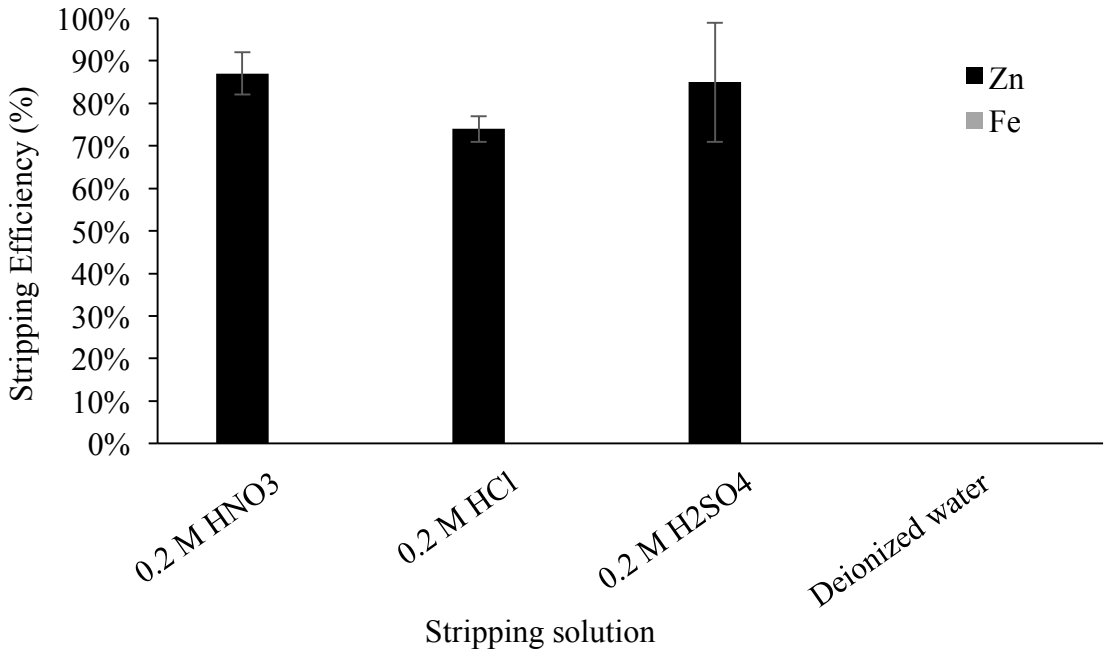


Figure 2.10. Screening of stripping solutions for the removal of Zn and Fe from loaded organic phase of zinc-plating effluent extracted by solvent extraction using 20% w/w D2EHPA in kerosene and 3% (v/v) TBP (A/O = 1:1, 21 ± 2℃, 1 h). Concentrations of stripped Fe < 0.25 mg/L. The error bars are mean absolute deviations (2 replicates).

3.1.2 Screening tests with Cyanex® 272

3.1.2.1 Diluents and modifiers for Cyanex® 272

The result of diluents and modifiers screening tests for liquid-liquid extraction of zinc-plating effluent using 0.55 M Cyanex® 272 can be found in Figure 2.11. Despite it being reported that Cyanex® 272 can selectively extract zinc over iron in HCl media (Regel-Rosocka & Wisniewski, 2011), the result with the zinc-plating effluent used in this work shows a higher selectivity towards iron instead of zinc with all diluents tested. The most likely explanation to this observation is that Cyanex® 272 was selective towards Fe(III), the main iron specie found in the zinc-plating effluent being tested while the effluent tested by Mansur *et al.* (2008) consist mainly of Fe(II) specie. Therefore, an additional step to reduce Fe(III) to Fe(II) prior to solvent extraction would be necessary to produce higher extraction efficiency for Zn. Due to the necessity of this additional step, along with the persistent formation of third phases in every diluent and modifier solutions, Cyanex® 272 was considered as an inferior candidate for Zn extraction for this effluent in comparison to D2EHPA.

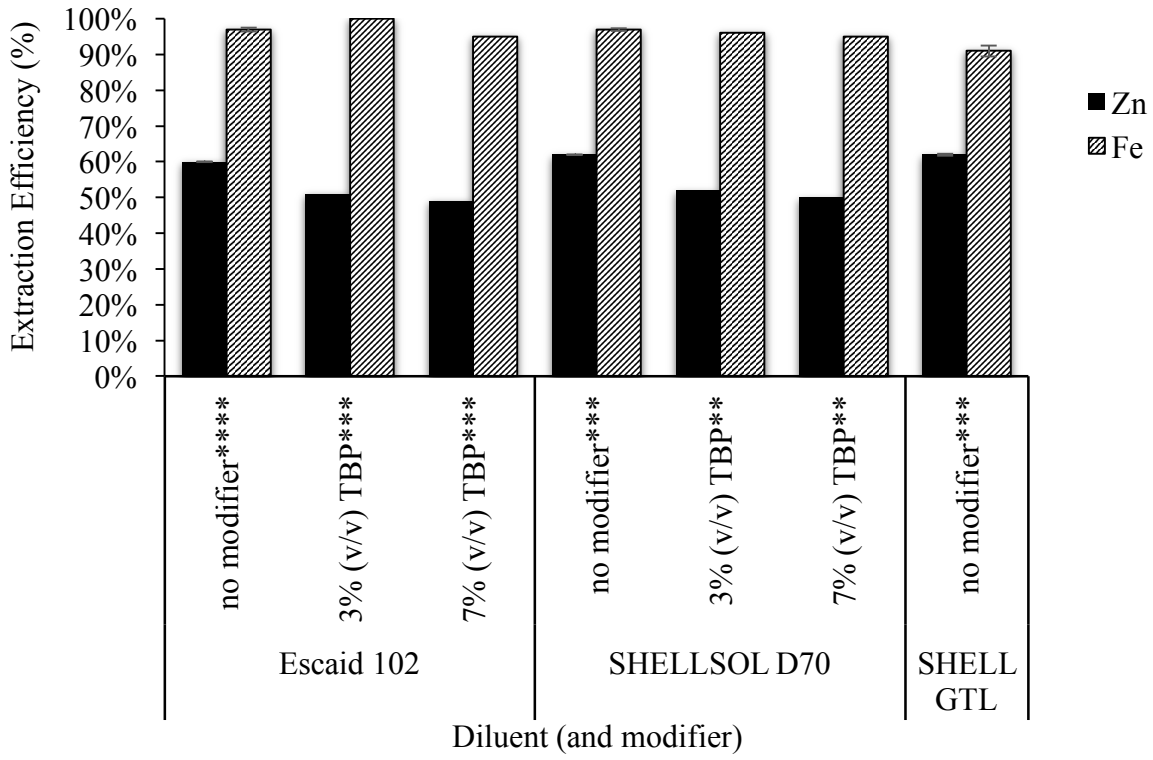


Figure 2.11. Effect of diluents and modifiers on solvent extraction efficiency of Zn and Fe from zinc-plating effluent with 0.55 M Cyanex® 272 (A/O: 1:1, 21 ± 2℃, 1 h). All liquid-

liquid extractions performed with no modifier were carried out in 2 replicates. In such cases, the error bars depicted mean absolute deviations.

*Thin layer of third phase observed.

**Moderate layer of third phase observed.

***Large layer of third phase observed.

****Extremely large layer of third phase observed.

3.1.2.2 Stripping solutions for Cyanex® 272

The result of Zn and Fe stripping from loaded organic phases resulting from the solvent extraction of zinc-plating effluent with 0.55 M Cyanex® 272 in different diluents (Escaid 102, Shellsol D70 and SHELL GTL) and with or without TBP as the modifier can be found in Figure 2.12. The presence of TBP seemed to enhance the stripping efficiency as well as the selectivity towards zinc. However, since Cyanex® 272 was more selective to iron, particularly Fe(III), the study of Cyanex® 272 was concluded after stripping of Zn from the loaded organic phase with 0.2 M H_2SO_4.

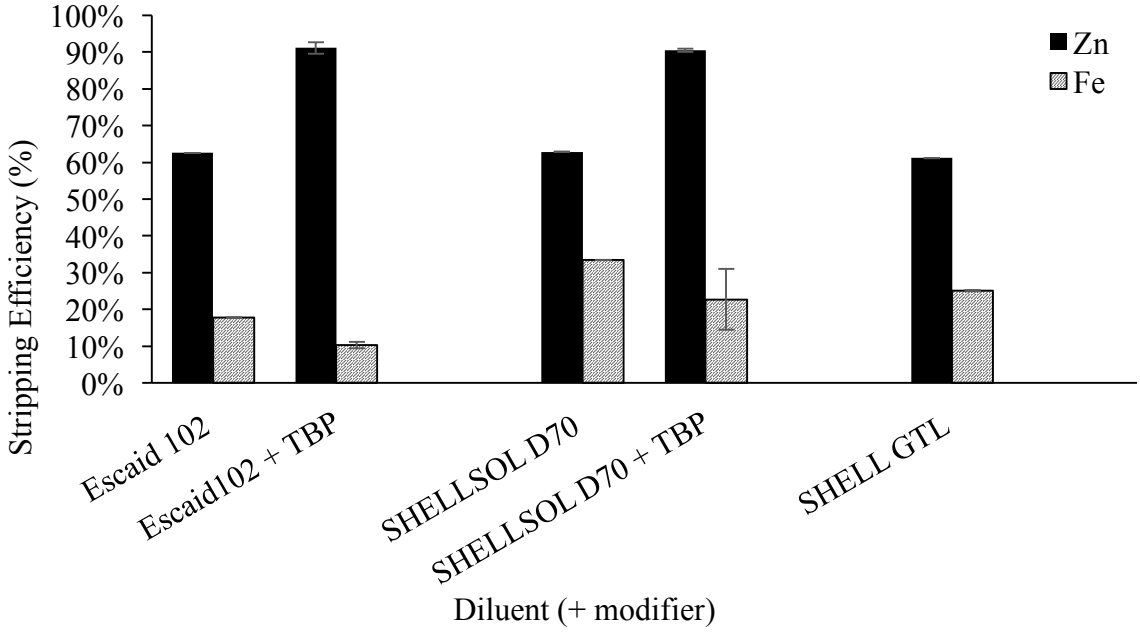


Figure 2.12. Stripping of Zn and Fe from several loaded organic phases (0.55 M Cyanex® 272) composed by different diluents with or without a modifier (TBP) using 0.2 M H_2SO_4 (A/O: 1:1, 21 ± 2℃, 1 h, 2 replicates). The error bars depicted mean absolute deviations and are not visible for values below 1%.

3.1.3 Optimization with D2EHPA –iron removal

The optimization of the extraction system comprising of 20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP was focused on the removal of iron using two techniques: scrubbing the co-extracted metal from the organic phase and pH adjustment of the effluent as a form of pretreatment to precipitate iron.

3.1.3.1 Iron scrubbing agents

Scrubbing is employed in metal extraction processes when removal of co-extracted metal(s) is necessary. The results of the study of the scrubbing efficiency of several aqueous solutions to remove iron from the zinc stripped loaded organic phase resulting from solvent extraction with 20% (w/w) D2EHPA with various scrubbing agents can be found in Figure 2.13. With a scrubbing efficiency of approximately 69%, 1.3 M oxalic acid (D. Singh, Mishra, & H. Singh, 2006) was the most logical choice of iron scrubbing solution. It is possible that complete scrubbing of iron can be achieved with higher concentrations of oxalic acid. However, due to the multiple steps required per one extraction cycle (solvent extraction, stripping, and scrubbing), this method of iron removal may not be the most economically viable option available. Therefore, the study proceeded to explore the potential of pH pretreatment as an alternative strategy for iron removal prior to the application of solvent extraction for zinc separation.

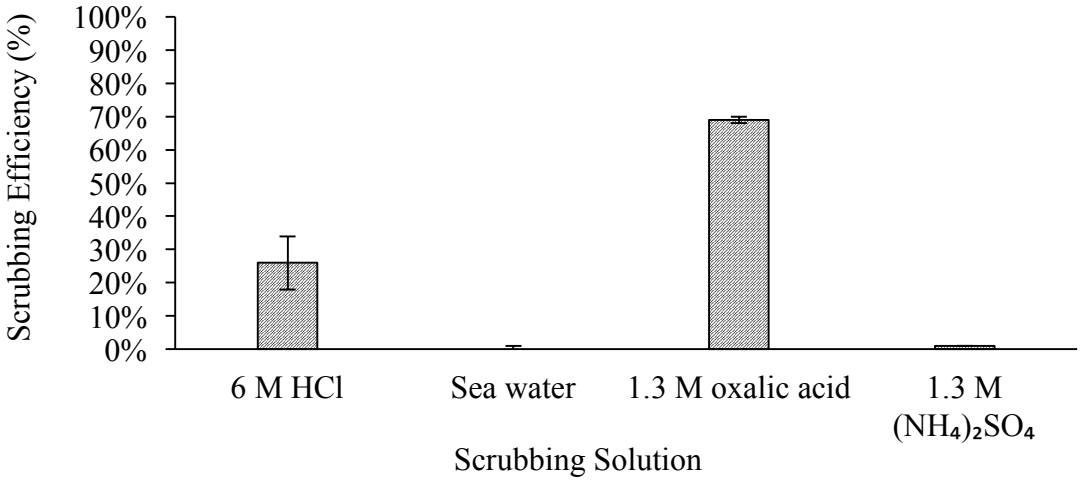


Figure 2.13. Screening of scrubbing solutions for the removal of Fe from zinc stripped loaded organic phase resulting from zinc-plating effluent extracted using 20% (w/w)

D2EHPA in kerosene and 3% (v/v) TBP (A/O = 1:1, 21 ± 2℃, 1 h, 2 replicates). The error bars depicted mean absolute deviations and are not visible for values below 1%.

3.1.3.2 Effluent pretreatment by pH adjustment

Figure 2.14 shows the average concentration of zinc and iron remaining in the aqueous samples at different pH levels as a result of pH adjustment with NaOH. While the presence of iron in the effluent decreased progressively from pH 2 to 6 before approaching a complete precipitation at pH 7, the concentration of zinc in the effluent remains relatively unchanged from pH 2 to 7. In fact, the concentration of zinc decreased from approximately 352 mg/L at pH 6 to 323 at pH 7 before drastically decreasing to 72 mg/L at pH 8. Therefore, the pH levels selected for the consequential study of the effect of pH on the solvent extraction of zinc-plating effluent are between pH 2 and 6.

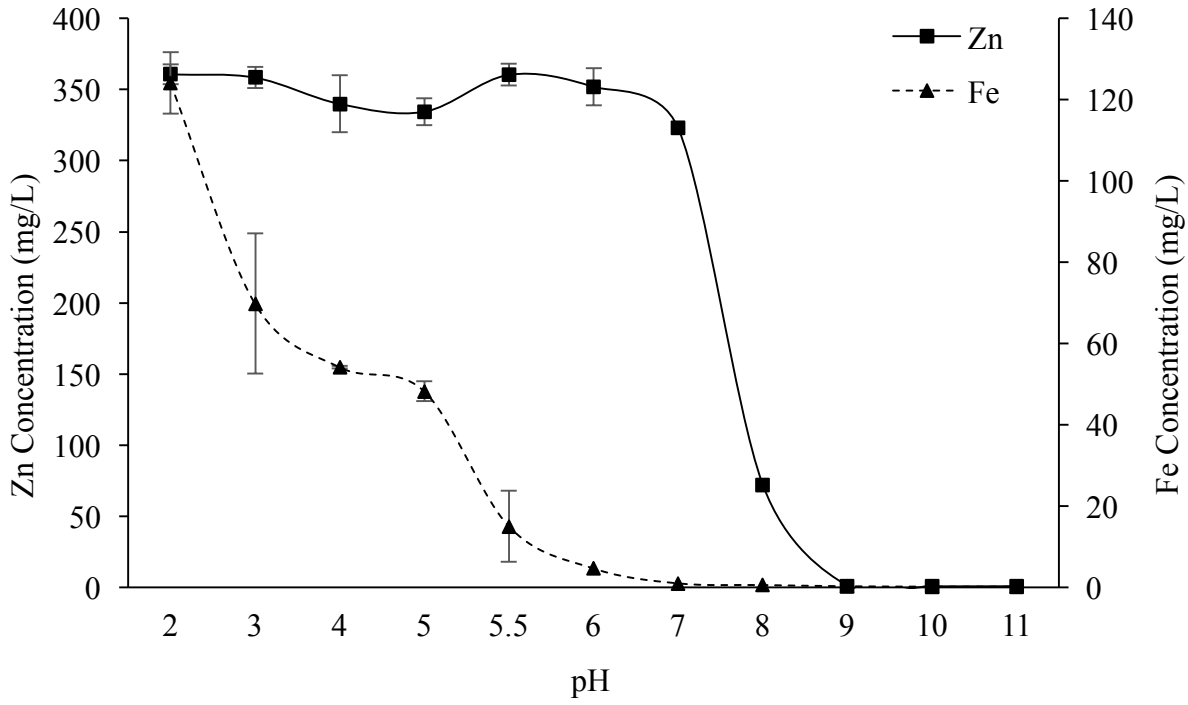


Figure 2.14. Effect of pH adjustment with 5 M NaOH on Zn and Fe concentrations in zinc-plating effluent. Error bars are standard deviations (3 replicates) and in some cases are smaller than the symbols, thus not visible.

3.1.3.3 Effect of pH pretreatment on the extraction efficiency of D2EHPA

The result of the effect of pH pretreatment (pH 3, 4, 5, 5.5, and 6) using 5M NaOH on the extraction efficiency of 20% (w/w) D2EHPA in kerosene with 3% (v/v) TBP is shown in Figure 2.15. The extraction efficiency for zinc increased from 87% in liquid-liquid extraction of raw effluent (pH 2) to 97% in effluent pretreated to pH 3 before reaching a constant of 98% with effluent pretreated to pH 5.5 and 6.

Based on the result of the experiment along with that of the study of the effect of pH on metal concentrations in zinc-plating effluent, pH 5.5 (Zn = 360 ± 8 mg/L, Fe = 15 ± 9 mg/L) was selected as the pH level for zinc-plating effluent pretreatment prior to liquid-liquid extraction with 20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP.

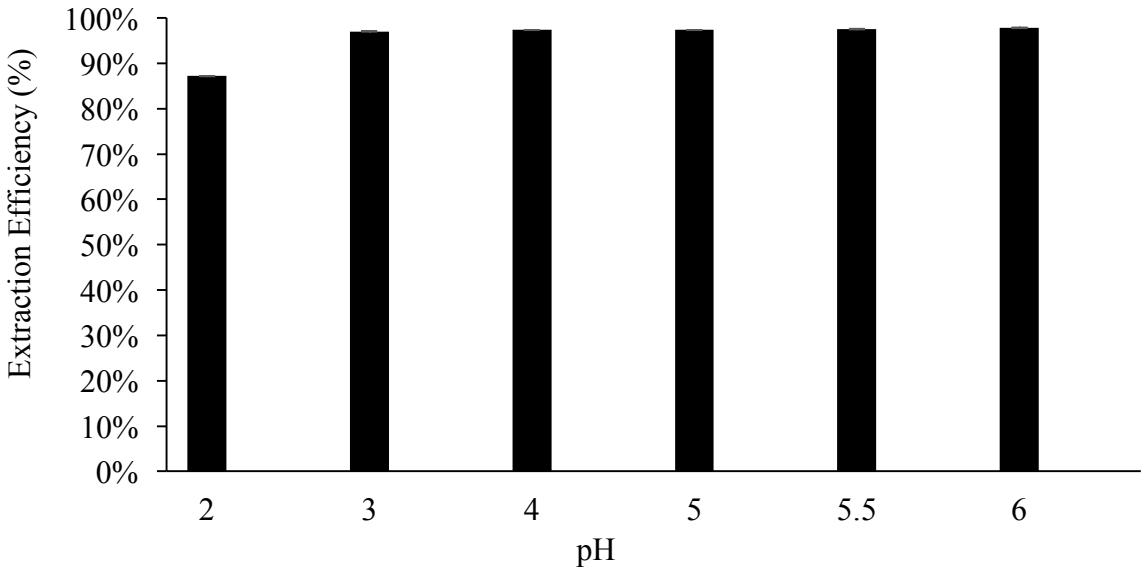


Figure 2.15. Effect of pH adjustment with 5 M NaOH on solvent extraction of Zn using 20% (w/w) D2EHPA in kerosene with 3% (v/v) TBP (21 ± 2℃, 1 h, 2 replicates). The error bars depict mean absolute deviations (with values below 0.2%; thus, might not be visible).

3.1.4 Performance of D2EHPA

3.1.4.1 Contact time (kinetics)

The effect of contact time between the aqueous and the organic phase on the extraction of zinc and iron is shown in Figure 2.16. The results suggested that 98% recovery

of zinc can be achieved with pretreated zinc-plating effluent (pH adjusted to pH 5.5) after five minutes of stirring, after which an increase in the contact time does not further increase the extraction efficiency for zinc. Contrarily, the co-extraction of iron continued to increase from approximately 71% after the contact time of five minutes to 89% at 15 minutes before being nearly completely co-extracted after 30 minutes. (However, it is important to keep in mind that after pH-pretreatment, only approximately 15.06 mg/L of Fe was left in the pretreated effluent.) Therefore, the ideal contact time for the solvent system with 20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP, in which the highest percentage of recovery of zinc can be achieved with the lowest co-extraction of iron, is within five minutes.

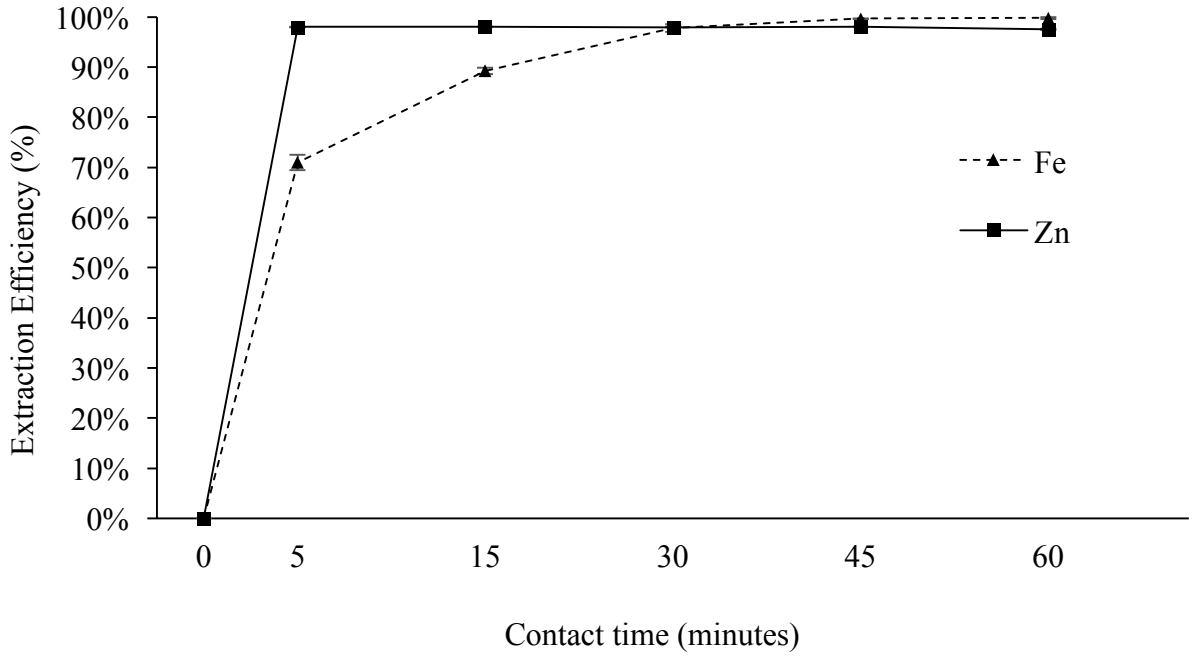


Figure 2.16. Effect of contact time on extraction efficiency of solvent extraction of Zn and Fe from pretreated zinc-plating effluent (pH adjusted to 5.5) using 20% (w/w) D2EHPA in kerosene and 3% TBP (A/O: 1:1, 21 ± 2℃, 1 h, 2 replicates). The error bars depict mean absolute deviations (with values below 0.2%; thus, might not be visible).

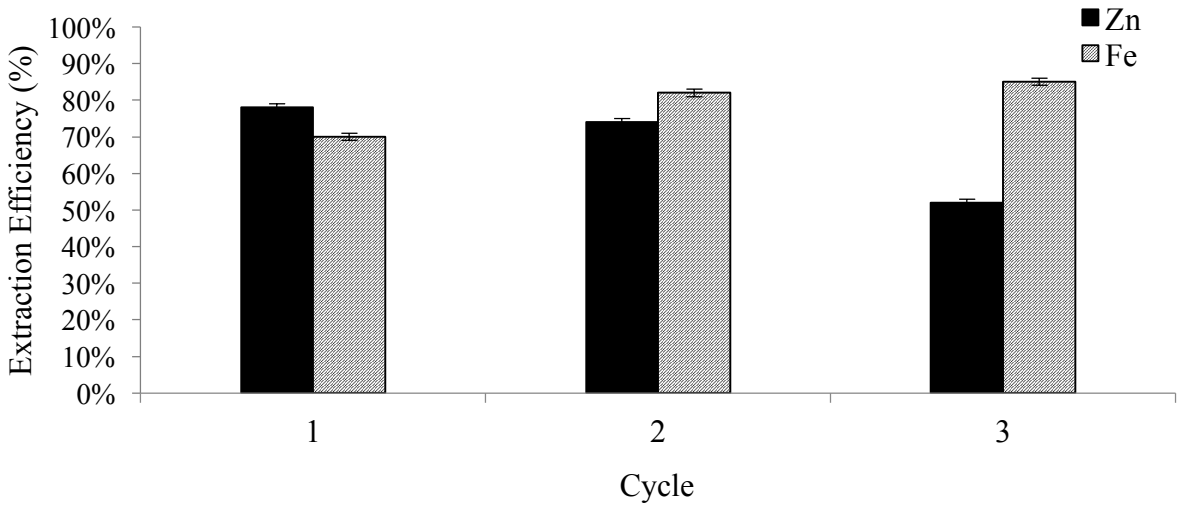
3.1.4.2 Reusability of organic phase

The objective of this experiment is to determine the reusability of the extraction system after 3 consecutive cycles of solvent extraction and stripping. Figures 2.17 and 2.18 show the results of the study of the reusability of 20% (w/w) D2EHPA in kerosene and 3%

(v/v) TBP on raw zinc-plating effluent without any pretreatment (Fig. 2.17-A for liquid-liquid extraction and Fig. 2.18-A for stripping with 0.2 M H_2SO_4) and on pretreated effluent using 5 M NaOH to pH 5.5 (Fig. 2.17-B for liquid-liquid extraction and Fig. 2.18-B for stripping with 0.2 M H_2SO_4).

The result of liquid-liquid extraction of raw zinc-plating effluent showed a slight decrease in the extraction efficiency of zinc from 78% to 74%. Simultaneously, co-extraction of iron increase from 70% in the first cycle to 82% in the second, influencing the extraction of zinc. In fact, the extraction efficiency of the extraction system for zinc drastically dropped to 52% after the third cycle, whereas co-extraction of iron increased to 85%. Meanwhile, stripping efficiency of the loaded organic phase with 0.2 M H_2SO_4 decreased from 95% in the first cycle to 74% in the following cycle, before decreasing to 62% in the final cycle. The most likely explanation for this behavior is that the accumulation of iron in every extraction cycle inhibits the interaction between D2EHPA and zinc; thereby progressively decreasing the extraction efficiency of the extractant in the second and third cycles. For example, the concentration of iron transferred to the organic phase from the first cycle, approximately 85.42 mg/L, was retained in the organic phase after stripping. Due to the stripping solution's high selectivity towards zinc, the stripping efficiency was affected to a lower degree. However, the incomplete stripping of zinc from the second cycle compounded with the small increase of zinc after the third extraction translates into a further decrease in the stripping efficiency of 62%.

A



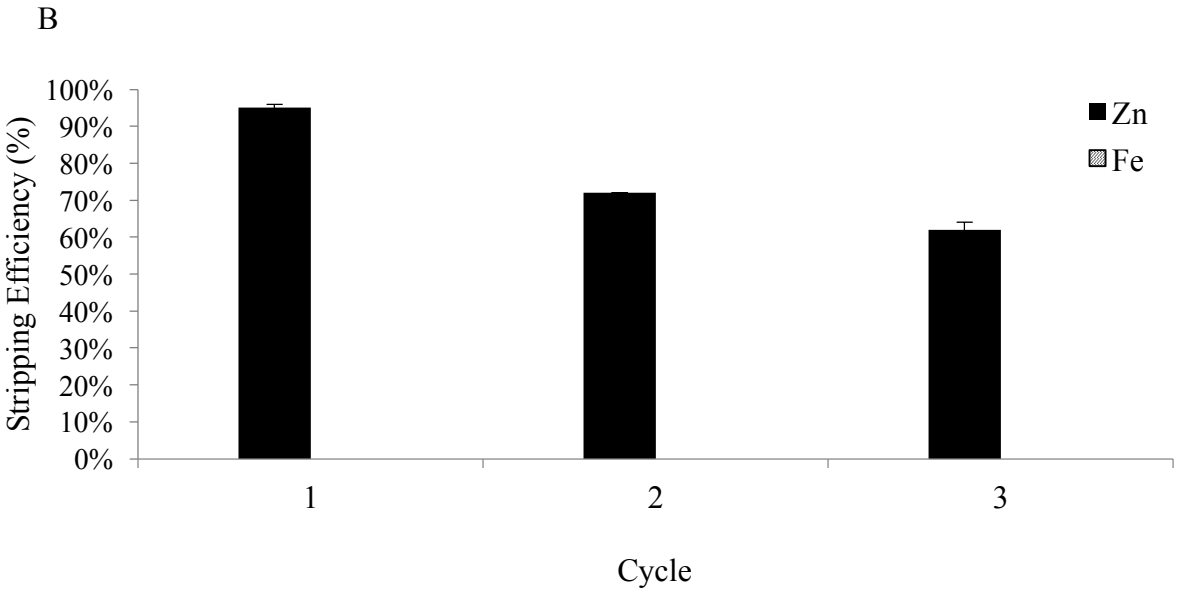


Figure 2.17. (A) Extraction efficiency of liquid-liquid extraction of raw zinc-plating effluent with 20% w/w D2EHPA in kerosene and 3% v/v TBP in 3 consecutive cycles (A/O: 1:1, 21 ± 2℃, 1 h, 3 replicates) and *(B)* stripping efficiency of zinc with 0.2 M H_2SO_4 in 3 consecutive cycles (A/O: 1:1, 21 ± 2℃, 1 h, 3 replicates). The error bars depict standard deviations.

After pH-pretreatment (pH 5.5), with the initial concentration of iron reduced to only 15 ± 9 mg/L, the results for extraction with 20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP were more straightforward and conform to the expected predictions with relatively constant extraction efficiency maintained at approximately 98% for zinc, and co-extraction of the small amount of iron still remaining in the pretreated effluent. The increase in the extraction efficiency of zinc meant the increase in the concentration of the metal in the loaded organic phase and it was observed that 0.2 M H_2SO_4 was no longer a sufficient concentration to achieve a similar stripping efficiency that was observed in the stripping of loaded organic phase from liquid-liquid extraction of raw zinc-plating effluent (results not shown). Therefore, the concentration of H_2SO_4 used in the stripping of loaded organic phase resulting from liquid-liquid extraction of pH-adjusted effluent was increased to 0.6 M. As a result, complete stripping of zinc from the reused loaded organic phases from the three cycles were observed, resulting in aqueous phases containing highly purified zinc. Therefore, although 1.3 M oxalic acid was able to remove up to 69% co-extracted iron from the stripped organic phase, pH-pretreatment seems the most attractive method to prevent co-extraction of iron with zinc.

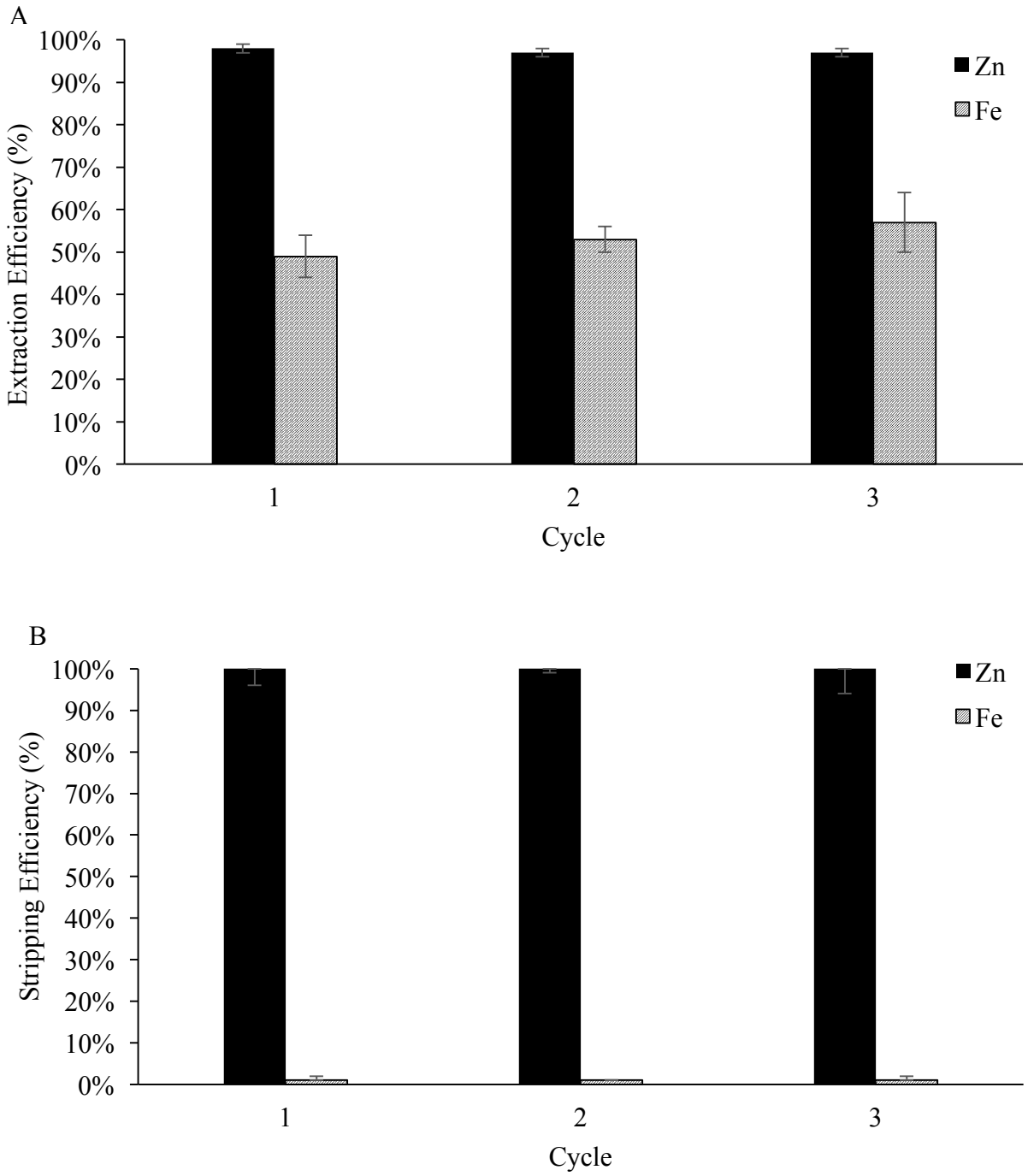


Figure 2.18. (A) Extraction efficiency of liquid-liquid extraction of pH-pretreated (pH 5.5) zinc-plating effluent with 20% w/w D2EHPA in kerosene and 3% v/v TBP (A/O = 1:1, 21 ± 2℃, 5 min., 3 replicates) and *(B)* stripping efficiency of zinc with 0.6 M H_2SO_4 (A/O = 1:1, 21 ± 2℃, 1 h, 3 replicates) in 3 consecutive cycles. The error bars depict standard deviations.

3.1.4.3 Loading Capacity of organic phase (equilibrium isotherms)

Equilibrium isotherms were built to determine the maximum loading capacity of selected extractants at selected conditions. The equilibrium isotherm of the extractant system consisting of 20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP with raw zinc-plating effluent and with pretreated zinc-plating effluent (pH 5.5) were shown in Figure 2.19 and Figure 2.20, respectively.

As seen in Figure 2.19, the maximum loading capacity of the extractant system for zinc in raw zinc-plating effluent was reached at 1664 mg/L at A/O ratio of 10:1, after which the extraction efficiency progressively decreased due to the increasing difference between the volume of the aqueous and the volume of the organic phase inhibiting a good contact between the extractant and zinc ions.

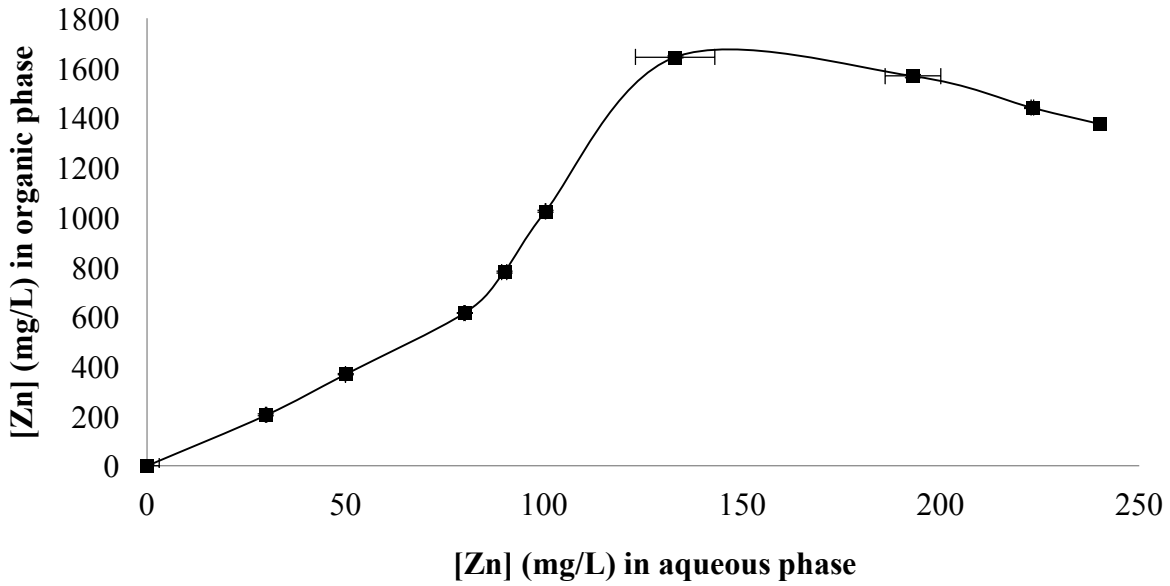


Figure 2.19. Equilibrium isotherm of Zn extraction from raw zinc-plating effluent at 21±2°C using 20% (w/w) D2EHPA in kerosene with 3% (v/v) TBP as modifier with extractions at different A/O ratios (1/1, 2/1, 3/1, 4/1, 5/1, 10/1, 15/1, 20/1 and 25/1 (21 ± 2℃, 1 h, 2 replicates). The error bars depict mean absolute deviations (smaller than the symbols in most cases).

On the other hand, the loading capacity of the same extractant and conditions with the pretreated zinc-plating effluent whose pH was adjusted to 5.5 continued to increase even beyond A/O ratio of 35:1 (see Fig. 2.20). Such phenomenon suggests that the removal of iron

prior to liquid-liquid extraction is highly advantageous, allowing the extractant to accumulate significantly more zinc. One possible cause contributing to this observation may be the significant decrease of iron in the effluent which could have competed for the extractant in the case of the raw effluent. However, as the difference between the volumes of aqueous and organic phases rises, the extraction efficiency of the extractant decreased from 97% with A/O=1:1 to 88% with A/O = 5:1 before decreasing to 62% from A/O = 20:1 onwards. Therefore, despite not reaching the maximum loading capacity, the study of the loading capacity of the liquid-liquid extraction of pH-adjusted zinc-plating effluent was concluded at A/O ratio 35:1, with zinc concentration in the organic phase of 6024 ± 7 mg/L. However, according to the result of the study on metal recovery from Zn-Mn-Co-Ni bearing solutions produced from hot filter-pressed cakes from zinc production (pH 1.5) with 0.6 M D2EHPA in kerosene, it is possible that the maximum loading capacity of D2EHPA can be as high as 13000 mg/L (Darvishi, Fatmehsari, Alamdari, & Sadrnezhaad, 2011). Therefore, it is possible that the maximum loading capacity of the extraction system with its optimized condition may be reached if applied on zinc-plating effluents containing higher concentrations of Zn.

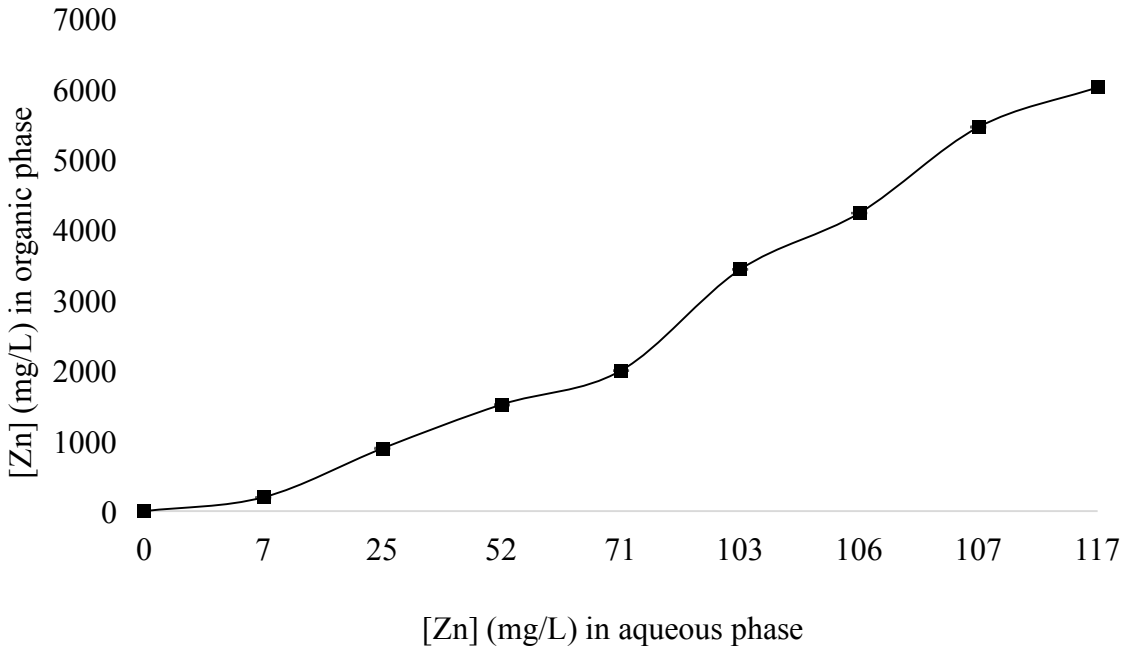


Figure 2.20. Equilibrium isotherm (loading capacity) of Zn extraction of pretreated zinc-plating effluent (pH 5.5) at 21±2°C using 20% (w/w) D2EHPA in kerosene with 3% (v/v) TBP as modifier (21 ± 2℃, 5 min., 2 replicates). The error bars depict mean absolute deviations (smaller than the symbols in most cases).

3.2 Liquid-liquid extraction with ionic liquids

To the best of our knowledge, while Cyphos® 102 was successfully tested to extract zinc from zinc-plating mud (Singh *et al*., 2017) and Cyphos® 104 was successfully tested to extract zinc from spent pickling solutions used in hot-dip galvanization (Marszałkowska, Regel-Rosocka, Nowak, & Wiśniewski, 2010), both ionic liquids, as well as Cyphos® 103 have never been tested on any zinc electroplating effluent. Since very limited information was available, the objective of this set of experiment was to explore the potential and limitations of each ionic liquid in the application of zinc extraction from the zinc-plating effluent in chloride media collected for this work by carrying out screening tests and optimize, as well as possible, the conditions for the selected ionic liquid.

3.2.1 Screening of ionic liquids

The standard concentration of 0.04 M used for all extractants were adjusted from the concentration reported by Regel-Rosocka et al. to be effective in the recovery of synthetic aqueous solution consisting of 5 g/L of zinc and 0.58 M HCl with Cyphos® 104 (Regel-Rosocka *et al.*, 2012).

The results from the preliminary tests for the selection of ionic liquids as extractant candidates for liquid-liquid extraction can be found in Figure 2.21. Based on the result, the ionic liquid exhibiting the highest extraction efficiency was 0.04 M Cyphos® 104 with 98% extraction of zinc, albeit with approximately 43% co-extraction of iron. At the concentration of 0.04 M, Cyphos® 102 suggested a high selectivity towards zinc despite a lower extraction efficiency of approximately 49%. Therefore, another liquid-liquid extraction test was carried out by increasing the concentration of Cyphos® 102 to 0.08 M. In this case, the results showed an increase in the extraction of the target metal to 61%, with significantly low iron co-extraction. On the other hand, solvent extraction with Cyphos® 103 display no selectivity with high iron co-extraction of approximately 88%. Therefore, the two ionic liquids selected for further studies were Cyphos® 102 and Cyphos® 104.

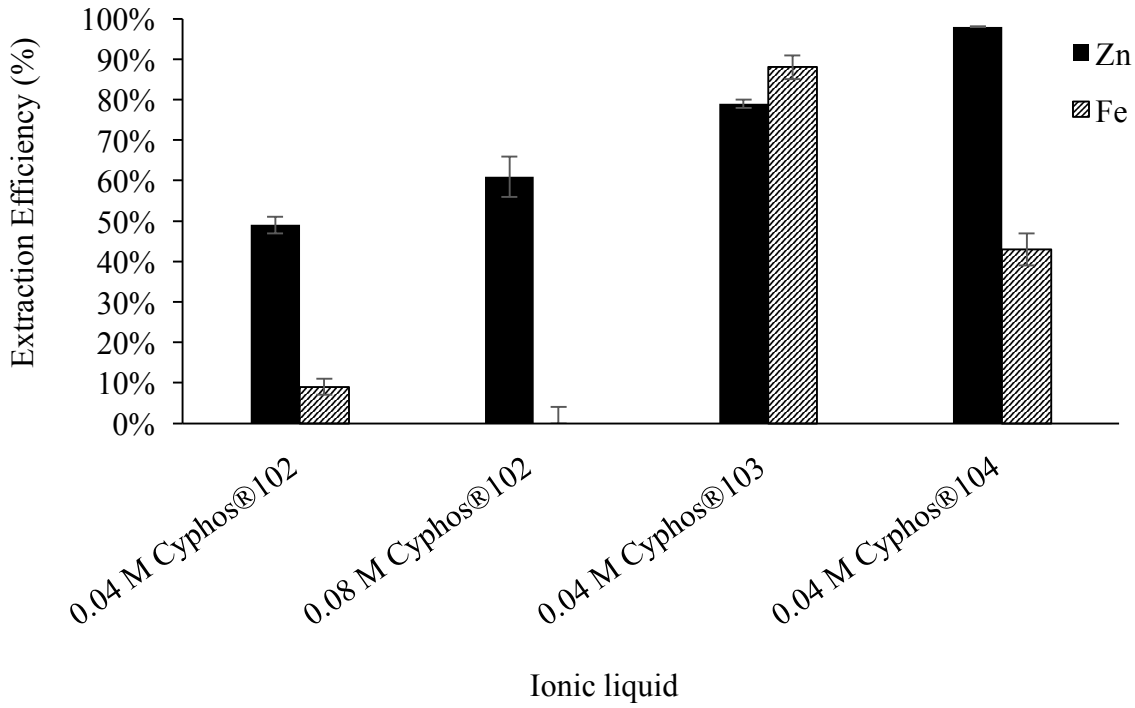


Figure 2.21. Liquid-liquid extraction of Zn and Fe from zinc-plating effluent with 0.04 M and 0.08 M Cyphos® 102, 0.04 M Cyphos® 103 and 0.04 M Cyphos® 104 liquids diluted in toluene (A/O: 1:1, 25 ± 2℃, 30 min. 2 replicates). Concentration of Fe in loaded organic phase from liquid-liquid extraction with 0.08 M Cyphos® 102 < 0.5 mg/L. The error bars depict mean absolute deviations.

3.2.2 Screening tests with CYPHOS® 102

3.2.2.1 Diluents and modifiers for Cyphos® 102

In the study of the effect of diluents on the extraction efficiency of Cyphos® 102, kerosene was tested since it is the diluent typically used in liquid-liquid extraction. On the other hand, toluene was tested since the co-solvent was used by Regel-Rosocka *et al.* (2012) for solvent extraction with Cyphos® 104. The results for the solvent extraction of zinc and iron from zinc-line effluent with 0.08 M Cyphos® 102 (see Fig. 2.22) show a difference in the effect of the diluents in the extraction efficiency of the system with 61% extraction of zinc with toluene as the diluent and 83% with kerosene. The extractant remained highly selective towards zinc with little to no co-extraction of iron in both cases. Furthermore, while liquid-liquid extraction with Cyphos® 102 did not cause a third-phase formation when diluted in kerosene,

the phenomenon occurred with toluene as the diluent. It is also important to note that the loaded organic phase from the solvent extraction of the extractant in toluene should not be stored in plastic tubes as it causes deformation of the tube.

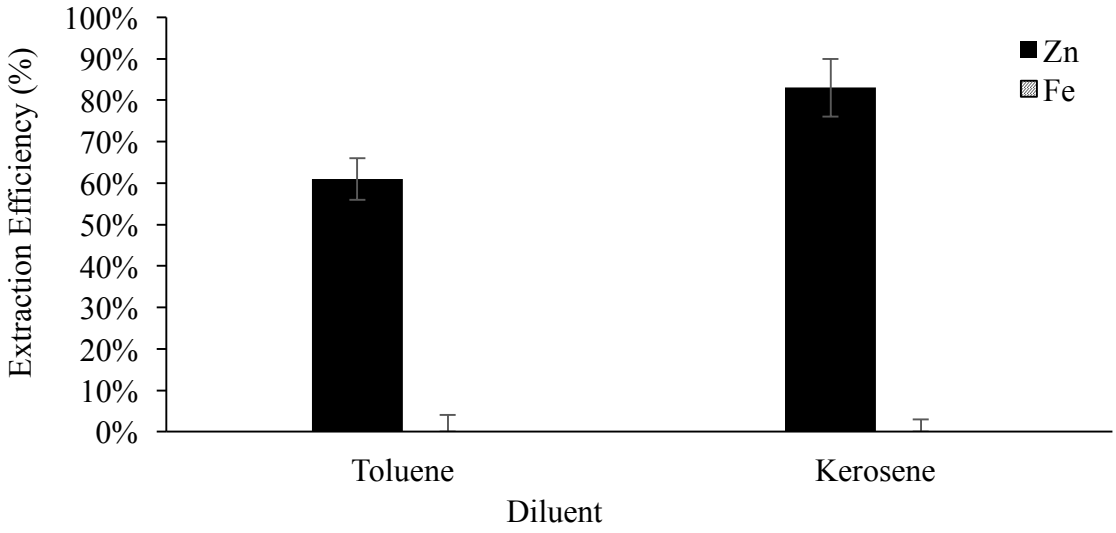


Figure 2.22. Effect of diluents on solvent extraction efficiency of Zn and Fe from zinc-plating effluent with 0.08 M Cyphos® 102 (A/O = 1:1, 25 ± 2 ℃, 30 min. 3 replicates). Concentrations of Fe in loaded organic phase < 0.5 mg/L. The error bars are standard deviations.

Despite the promising results, it was observed that Cyphos® 102 was not completely soluble in kerosene. Upon perturbation, the ionic liquid was observed to form an opaque mixture in kerosene which readily settles out to the bottom after being left to stand for several minutes, in which the resulting two layers became clear again. Due to this insolubility, the resulting loaded organic phase were separated into two layers. The thin layer on the bottom was suspected to be the insoluble Cyphos® 102 that settled and form its own layer. This phenomenon was unlike that of the typical third phase formation but can be assigned to the solubility issue of the ionic liquid in the selected co-solvent.

Because the insolubility of the ionic liquid in its co-solvent can lead to significant loss of ionic liquid and zinc during decantation, further tests were performed with the addition of modifiers. The result shows that several modifiers tested were effective in increasing the solubility of the organic phase (see Fig. 2.23). However, the presence of modifiers resulted in a marked decrease in the extraction efficiency of the system in the following order: no modifier > 3% (v/v) TBP > 3% (v/v) decanol > 3% (v/v) octanol. Furthermore, it is important to note that despite the high extraction efficiency with 3% (v/v) TBP, the addition of the modifier did not increase the solubility of the ionic liquid in this particular diluent. Therefore, kerosene and

3% (v/v) decanol were selected as the condition to be further optimized for liquid-liquid extraction with 0.08 M Cyphos® 102.

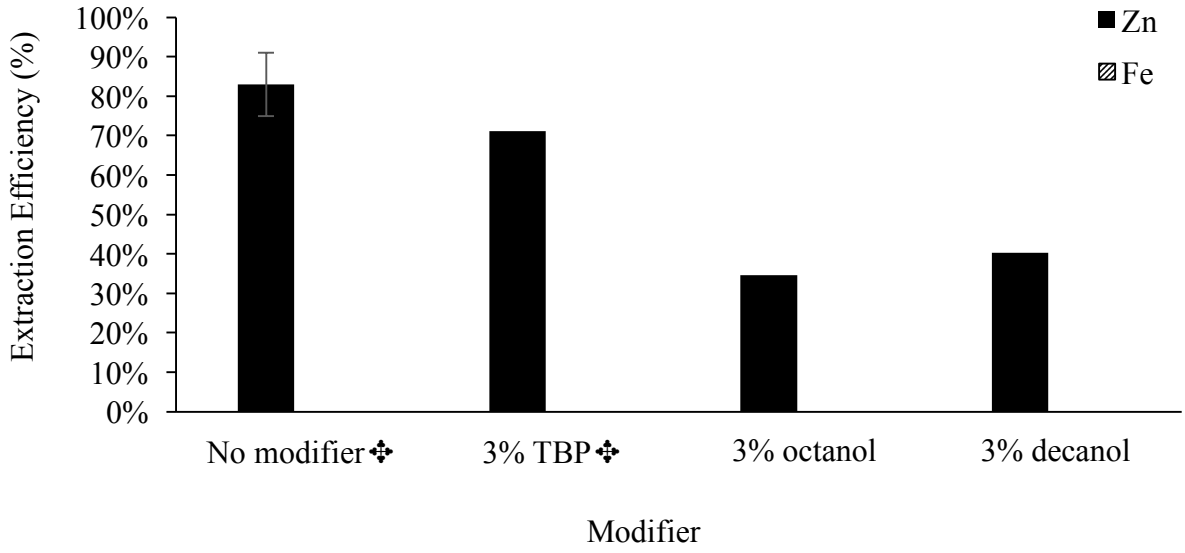


Figure 2.23. Effect of modifiers on solvent extraction efficiency of Zn and Fe from zinc-plating effluent with 0.08 M Cyphos® 102 diluted in kerosene (25 ± 2 ℃, Contact time = 30 min.). Concentrations of Fe in loaded organic phase < 0.5 mg/L. The error bars depict standard deviations for liquid-liquid extractions performed with no modifier carried out in 3 replicates. Liquid-liquid extractions performed with modifiers were carried out just with 1 replicate.
✣Ionic liquid not soluble in the tested diluent (and modifier).

3.2.2.2 Stripping solutions for Cyphos® 102

It has been suggested by Regel-Rosocka *et al.* (2012) that stripping of loaded organic phases comprising ionic liquids may be difficult due to the strong interaction between ions of the metal and the extractant. In fact, it is commonly known that ionic liquids are capable of stabilizing reactive compounds like catalysts (C. Trombini, personal communication, March 13, 2018). The stability of ionic liquids was confirmed in this work: the stripping solutions with higher efficiencies were HNO_3 solutions of higher concentrations (see Fig. 2.24). Oxalic acid and ammonium sulfate previously tested as scrubbing solutions of stripped loaded organic phases from solvent extraction with D2EHPA were also tested as stripping solutions in this experiment.

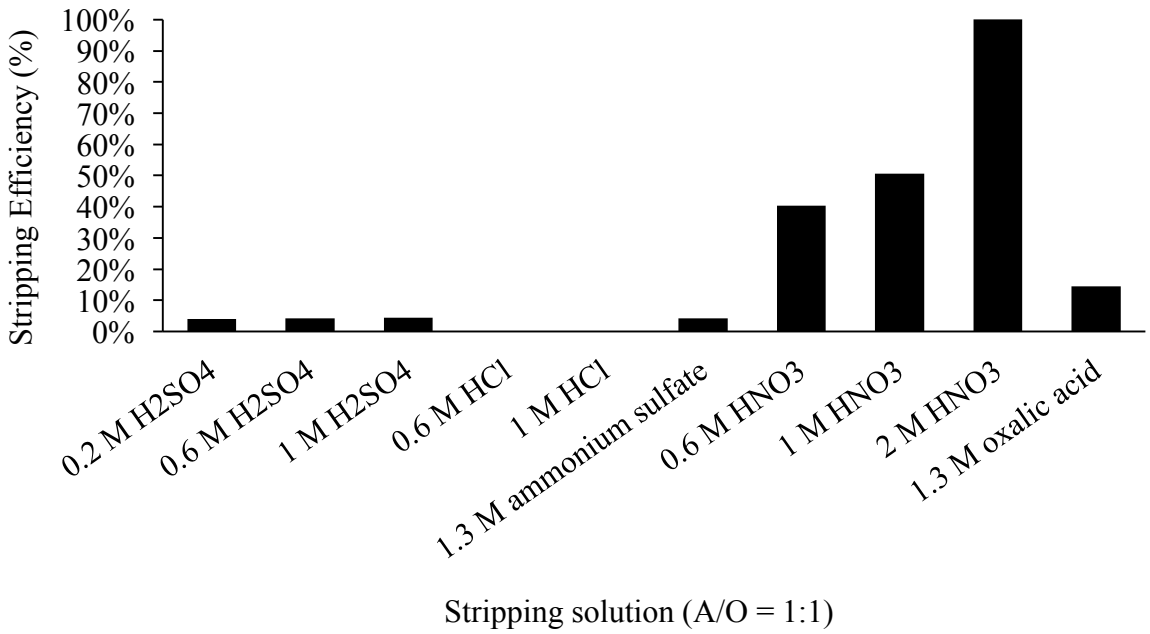


Figure 2.24. Screening of stripping solutions for the removal of Zn from loaded organic phase of raw zinc-plating effluent extracted by liquid-liquid extraction with 0.08 M Cyphos® 102 in kerosene with no modifier (A/O = 1:1, 25 ± 2℃, 30 min., 1 replicate).

Based on the result of the study of the effect of different acid solutions on the stripping efficiency of loaded organic phase from liquid-liquid extraction with Cyphos® 102, all concentrations of nitric acids exhibit high percentage of stripping, particularly at 2 M in which complete stripping of zinc was observed. This results agree with that observed by Singh *et al.* (2017) who reported that 1 M HNO_3 was capable of stripping approximately 99% Zn as well as Cd from loaded organic phase from liquid-liquid extraction of zinc-plating mud with the same ionic liquid. Therefore, 2 M HNO_3 was selected as the stripping solution for the optimization stages.

3.2.3 Optimization with Cyphos® 102

3.2.3.1 Extractant-to-zinc ratios

The focus of the optimization was to increase the extraction efficiency by raising the extractant-to-zinc ratios. To achieve this objective, two alternatives were employed: the increase of the volume of the organic phase to the aqueous phase (zinc-plating effluent) or the

increase of the molar concentration of the extractant. The results of the two alternatives are shown below.

Aqueous-to-organic phase ratios:

The result of the effect of the aqueous-to-organic phase ratio on the extraction efficiency of the extraction system can be found in Figure 2.25. The extraction efficiency increased as the volume of organic phase increased. However, only 74% extraction efficiency was achieved even when four times the volume of the organic phase was used. The increase can be considered slight, particularly when compared to the extraction efficiency observed in liquid-liquid extraction with the same concentration of ionic liquid but with no modifier. Therefore, increasing the molar concentration of Cyphos® 102 was explored as an alternative in increasing the extraction efficiency.

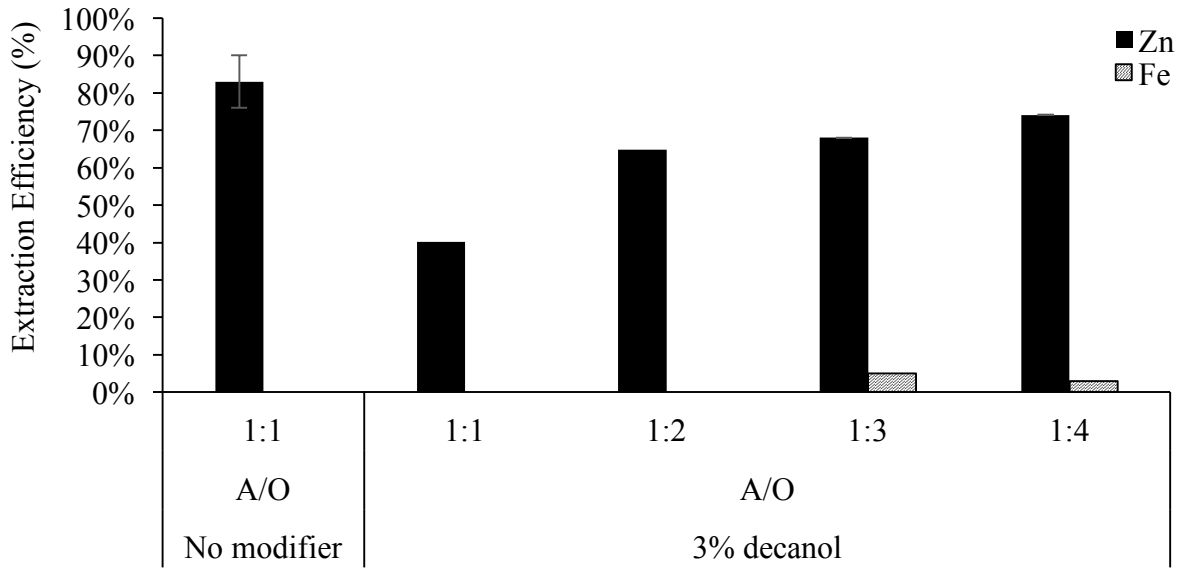
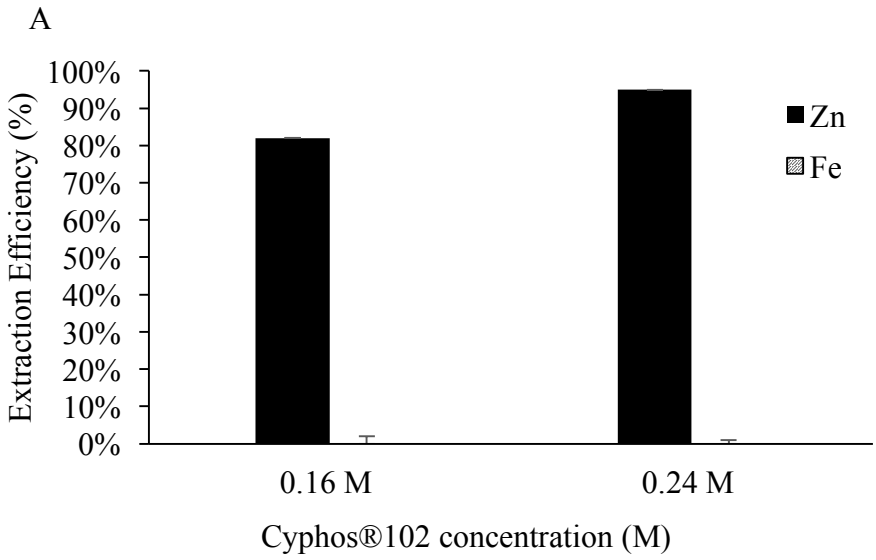


Figure 2.25. Effect of aqueous-to-organic (A/O) ratio on liquid-liquid extraction of Zn and Fe from raw zinc-plating effluent with 0.08 M Cyphos® 102 diluted in kerosene, with 3% decanol as modifier (25 ± 2℃, 30 min.) Concentrations of Fe in loaded organic phase that are not visible are lower than 0.5 mg/L. The error bar depicts liquid-liquid extraction performed with no modifier carried out in 3 replicates. All liquid-liquid extractions performed with modifiers were carried out in 1 replicate.

Effect of extractant concentration on extraction and stripping efficiency:

Due to the relatively low extraction efficiency of 0.08 M Cyphos® 102 even with the A/O ratio of 1:4, two additional molar concentrations (0.16 M and 0.24 M) of the extractant were tested at A/O = 1:1. The result (Figure 2.26-A) showed an increase in the extraction efficiency from 40% with 0.08 M Cyphos® 102 to 82% with 0.16 M Cyphos® 102 and 95% with 0.24 M Cyphos® 102. Despite the solubility of the extractant being resolved with the addition of 3% (v/v) of decanol, an additional phase was observed in the loaded organic phase after extraction with 0.24 M Cyphos® 102. The organic phase was divided into two uncolored layers of more-or-less similar volumes. This additional phase was unlike the usual third phase, which was also observed albeit as a fine, thin layer between the loaded organic and aqueous phase, nor could it likely be assigned to the insolubility of the ionic liquid in the diluent which was prior resolved by the addition of the selected modifier (refer to Section 3.2.2.1).

Therefore, the two loaded organic layers were stripped with 2 M HNO_3 to determine the distribution of zinc between them. The results indicate that approximately 25 ± 7% of Zn extracted was distributed in the top layer while 75% ± 7% Zn can be found in the bottom layer. Since complete stripping was achieved on loaded organic phases from both extractant concentrations (see Fig. 2.26-B), it was uncertain whether this observed behavior might negatively affect the overall extraction and stripping efficiency of the entire system. It is, however, expected that a more definite conclusion can be made from the reusability study.



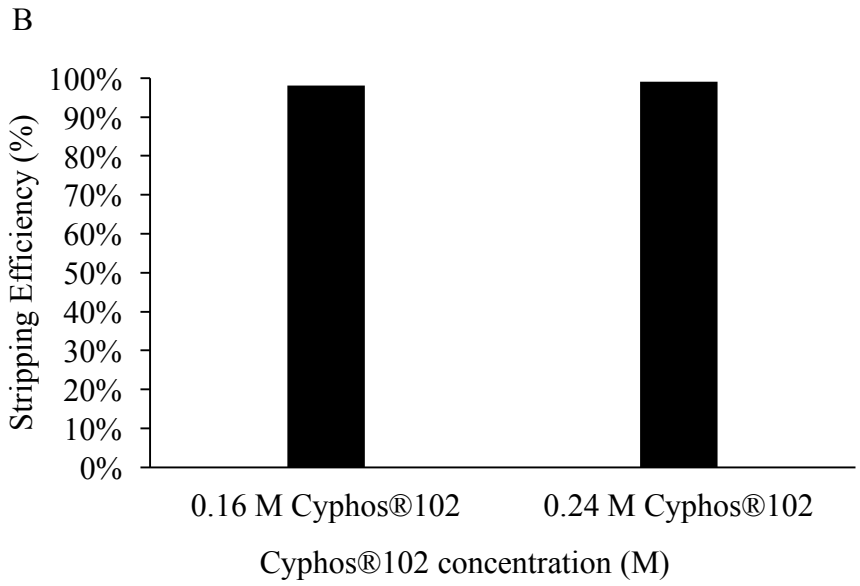


Figure 2.26. Effect of extractant concentration (0.16 M and 0.24 M) of Cyphos® 102 in kerosene and 3% decanol (A/O = 1:1, 25 ± 2℃, 30 min.) on *(A)* extraction efficiency of Zn and Fe from raw zinc-plating effluent and *(B)* stripping efficiency (2 M HNO_3, A/O = 1:1, 25 ± 2℃, 1 h) of Zn from resulting loaded organic phases. The error bars not visibly depicted were mean absolute deviations (2 replicates) with values of less than 1%. Stripping was carried out in 1 replicate.

3.2.4 Screening tests with Cyphos® 104

3.2.4.1 Diluents for Cyphos® 104

A similar experiment conducted using 0.04 M Cyphos® 104 in toluene *vs.* kerosene show equal efficiency in the extraction of zinc in both diluents (see Fig. 2.27). However, third phase was formed after solvent extraction with kerosene as the diluent while no third phase was observed with toluene. Therefore, since the difference in co-extraction of iron in both diluents were insignificant and with no third phase formation observed, toluene was selected as the diluent of choice for further studies and the addition of modifiers was unnecessary.

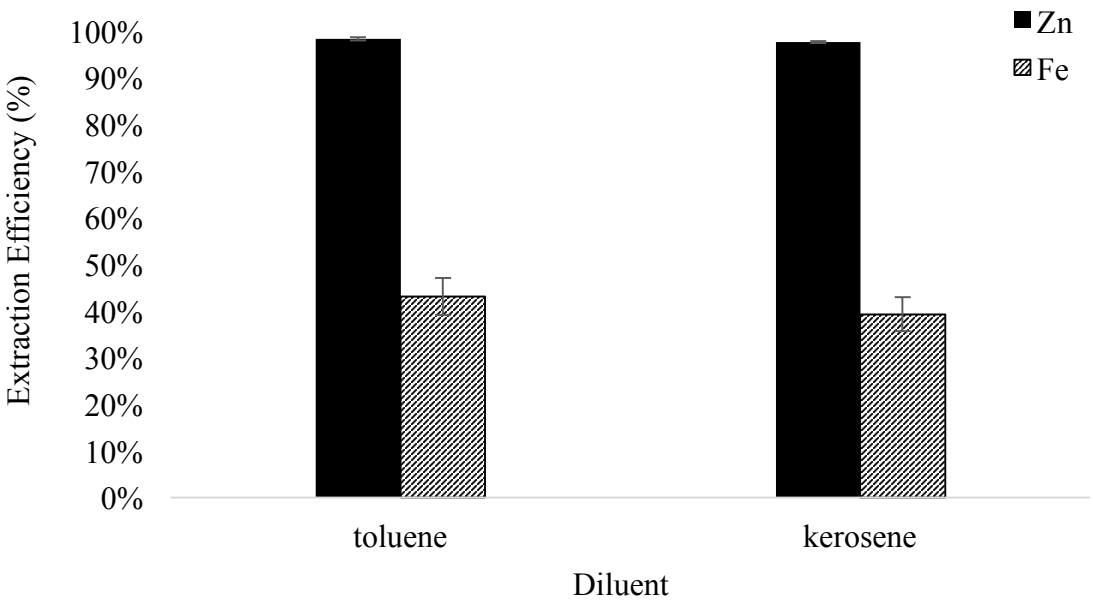


Figure 2.27. Effect of diluents on solvent extraction efficiency of Zn and Fe from zinc-plating effluent with 0.04 M Cyphos® 104 (A/O = 1:1, 25 ± 2 ℃, 30 min. 4 replicates). The error bars depict standard deviations.

3.2.4.2 Stripping solutions for Cyphos® 104

The result of the study of the effect of stripping solution on the stripping efficiency of the loaded organic phase from liquid-liquid extraction of raw zinc-plating effluent with 0.04 M Cyphos® 104 in toluene (see Fig. 2.28) showed low selectivity towards zinc in all tested stripping agents except ammonium sulfate. Moreover, none of the tested solutions revealed a combination of high efficiency and high specificity for iron scrubbing. Thus, two alternatives were available for the optimization of the extraction system with Cyphos® 104 as the extractant: increase the concentration of ammonium sulfate to improve zinc stripping efficiency and pretreat the effluent by adjusting the pH to 5.5 to precipitate iron prior to liquid-liquid extraction.

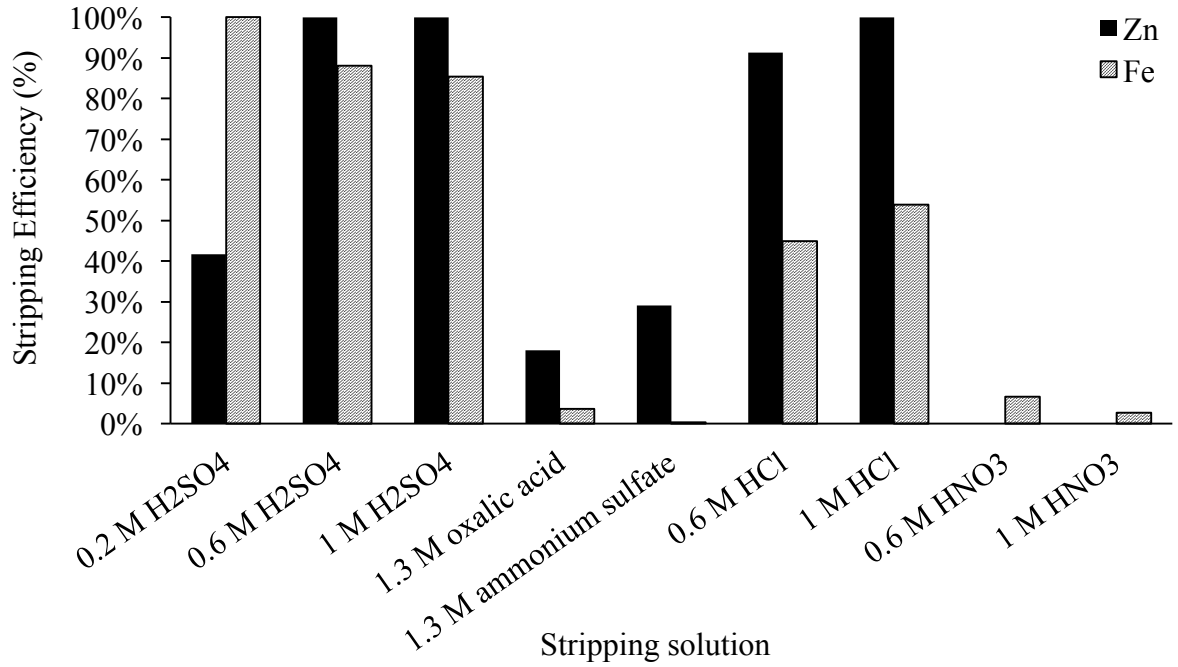


Figure 2.28. Screening of stripping solutions for the removal of Zn and Fe from loaded organic phase of raw zinc-plating effluent by liquid-liquid extraction with 0.08 M Cyphos® 104 in toluene (A/O = 1:1, 25 ± 2℃, 30 min., 1 replicate)

3.2.5 Optimization with Cyphos® 104

3.2.5.1 Effect of pH pretreatment on the extraction efficiency of Cyphos® 104

Since the previous experiments revealed that the pretreatment of raw zinc-plating effluent by pH adjustment (to 5.5) to remove iron prior to solvent extraction with 20% (w/w) D2EHPA in kerosene and 3% (v/v) TBP resulted in a marked improvement in extraction efficiency (in the case where the extractant was not entirely selective towards the target metal), a similar approach was tested for liquid-liquid extraction of zinc using 0.04 M Cyphos® 104 diluted in kerosene whereby iron was co-extracted in significant concentrations.

The results show that the extraction of zinc after effluent pretreatment (see Fig. 2.29-A) remains high (97%) while co-extraction of iron decreased from 43% to 18%. Moreover, the initial concentration of iron is higher in the raw zinc-plating effluent than in the case of pH adjusted to 5.5, therefore the co-extracted iron decreased significantly from 45 ± 4 mg/L to 3.8 ± 0.3 mg/L.

The stripping efficiency tests (see Fig. 2.29-B) of the resulting loaded organic phase confirmed the preference of 1.3 M ammonium sulfate. In addition, prior removal of iron by pH adjustment markedly increased zinc stripping efficiency from 29% in the raw effluent to 98% when the organic phase was obtained after pH-pretreatment. Simultaneously, the selectivity of the stripping solution remained high, with only 8% stripping of iron (0.32 mg/L).

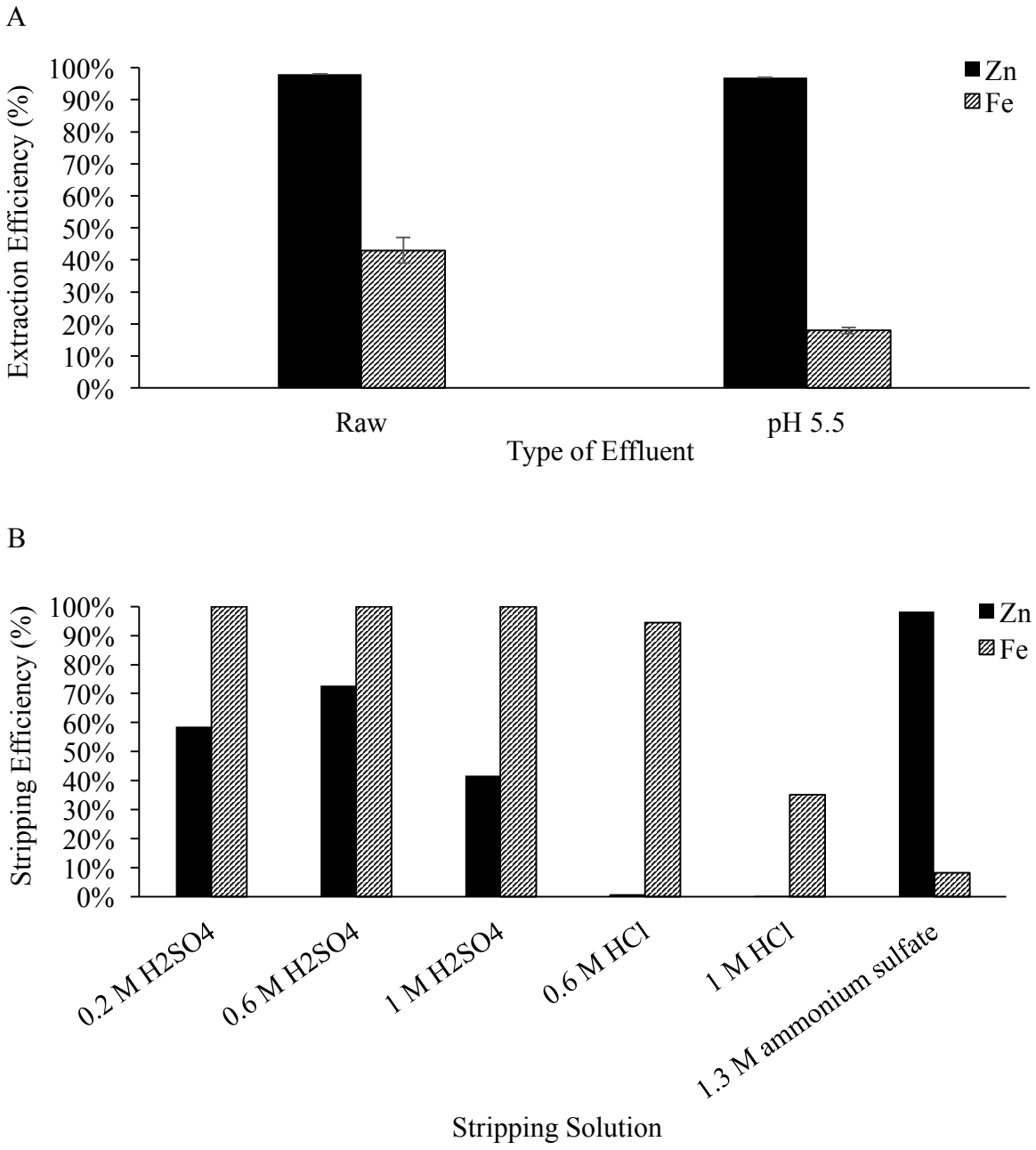


Figure 2.29. (A) Liquid-liquid extraction efficiency of zinc and iron from the raw zinc plating effluent and from zinc electroplating effluent after pH adjustment to 5.5 with 5 M NaOH using 0.04 M Cyphos® 104 diluted in toluene (A/O = 1:1, 25 ± 2℃, 30 min. 3 replicates).

(B) Screening of stripping solutions for the removal of Zn and Fe from loaded organic phase of pretreated (pH 5.5) zinc-plating effluent by liquid-liquid extraction with 0.08 M Cyphos® 104 in toluene (A/O = 1:1, 25 ± 2℃, 30 min., 1 replicate). The error bars depict standard deviations which may be lower than 1% and thus may not be visible.

3.2.6 Performance of Cyphos® 102

Due to the high selectivity of Cyphos® 102 towards Zn over Fe, the extractant was selected for further characterization of its liquid-liquid extraction performance.

3.2.6.1 Contact time (kinetics)

The result of the study of the effect of contact time on the extraction efficiency of the selected extractant and its optimized condition (see Fig. 2.30) revealed that an extraction efficiency of 95 % can be achieved after a contact time of five minutes.

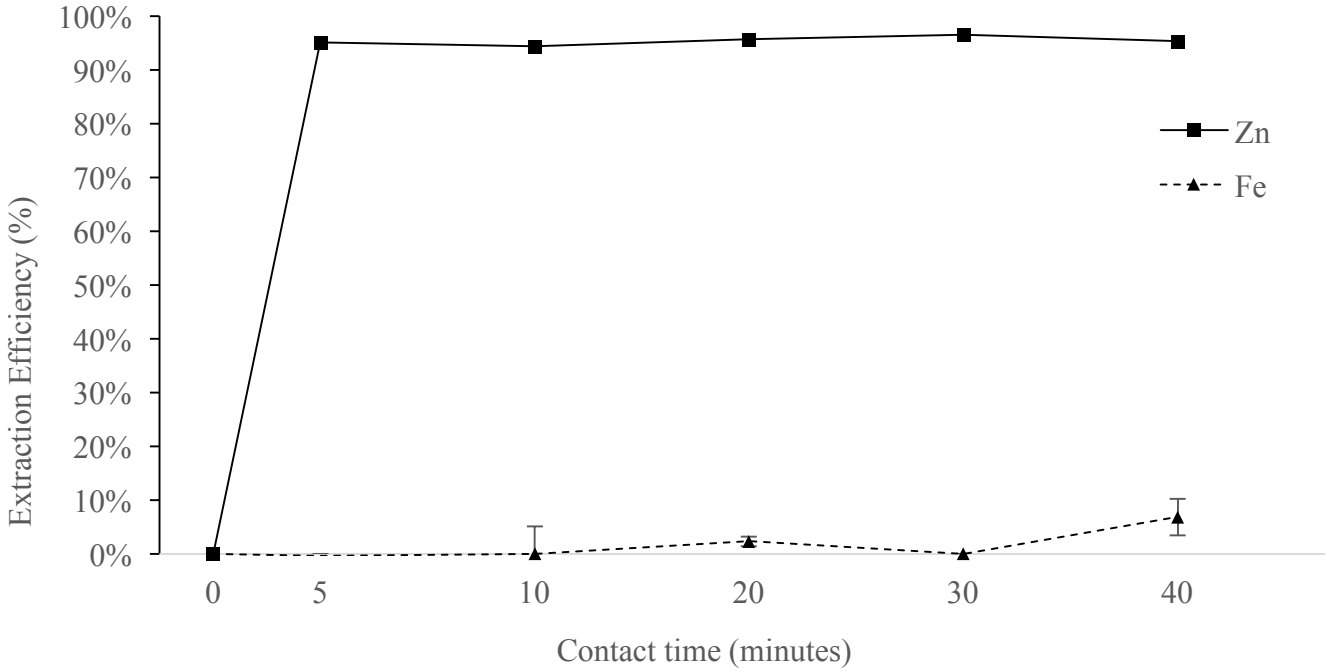


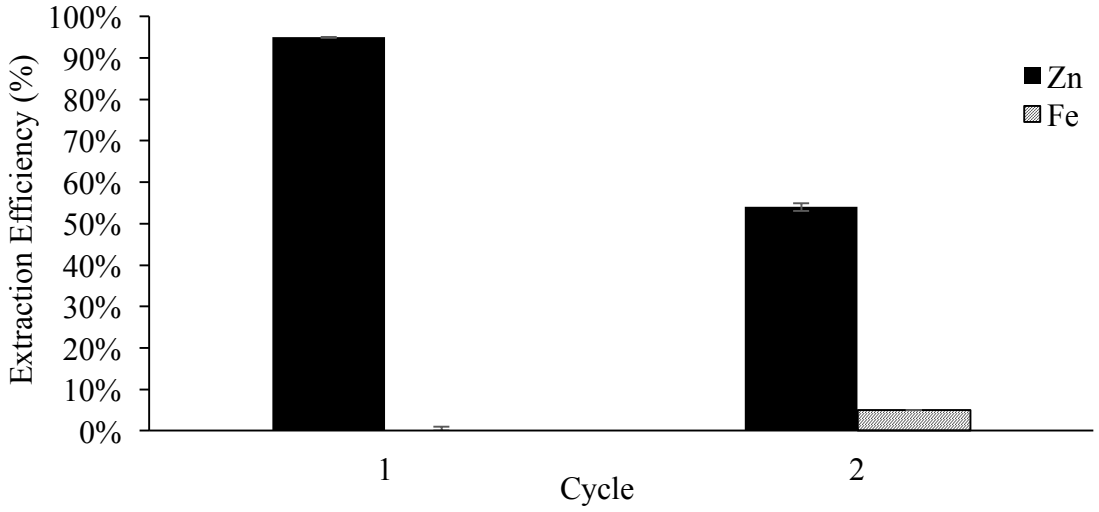
Figure 2.30. Effect of contact time on extraction efficiency of solvent extraction of Zn and Fe from raw zinc electroplating effluent using 0.24 M Cyphos® 102 in kerosene (A/O = 1:1, 25 ± 2℃,30 min). The error bars for Zn not visibly depicted were mean absolute deviation (2

replicates) with values lower than 1%. The error bars for Fe not visibly depicted were mean absolute deviation (2 replicates) with values lower than 1%.

3.2.6.2 Reusability of organic phase

The study of the reusability of the optimized extraction conditions (0.24 M Cypho®102 in kerosene and 3% (v/v) decanol, A/O = 1:1, 25 ± 2℃, 30 minutes) showed that the extraction efficiency decreased drastically from approximately 95% in the first cycle to 54% in the second cycle (see Fig. 2.31-A). At the same time, stripping efficiency of the extraction system drastically decreased from approximately 99% in the first cycle to only 5% in the second cycle (see Fig. 2.31-B). This may be due to the separation of the loaded organic phase into two layers of equal volumes observed after the stripping step. It might be the case that the separation of the organic phase signified that Cyphos® 102 extracts Zn via two different mechanisms, resulting in different densities. One might extrapolate, then, that one interaction may be more stable than the other and that the ionic liquid may be transferred along with zinc upon stripping due to said stable interaction between the extractant and the target metal.

A



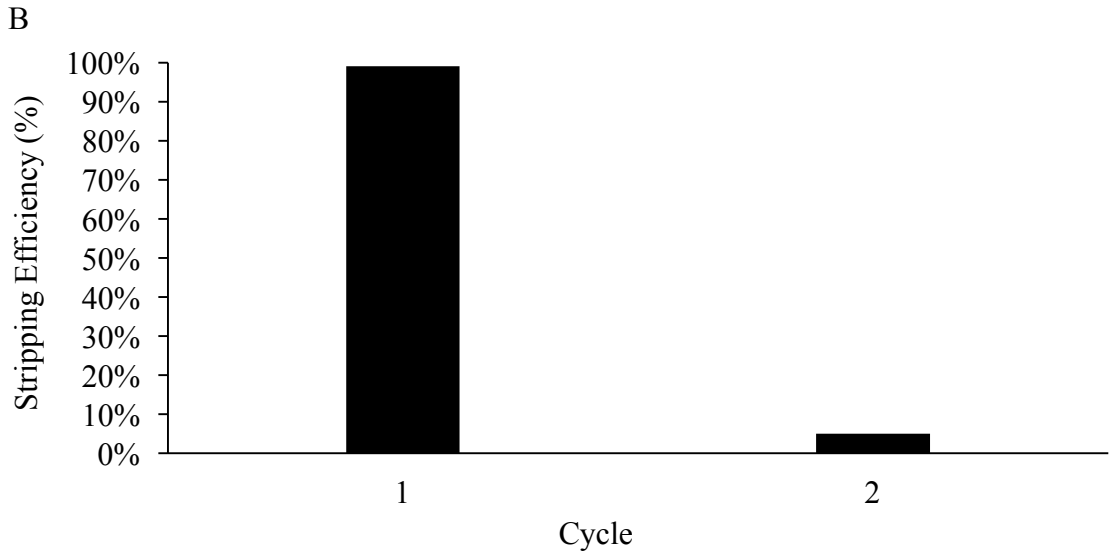


Figure 2.31. (A) Extraction efficiency of liquid-liquid extraction of Zn and Fe from raw zinc-plating effluent with 0.24 M Cyphos® 102 diluted in kerosene in 2 consecutive cycles (A/O = 1:1, 25 ± 2℃, 30 min.) and *(B)* stripping efficiency of Zn from raw zinc-plating effluent with 2 M HNO_3 in 2 consecutive cycles (A/O = 1:1, 25 ± 2℃,1 h). Concentrations of Fe not visible < 0.9 mg/L. The error bars not visibly depicted were mean absolute deviations (2 replicates) with values lower than 1%.

3.2.6.2 Loading capacity of organic phase (equilibrium isotherm)

Despite the extraction efficiency decreasing immediately from 95% at A/O = 1:1 to 84% at A/O = 2:1 and 51% at A/O = 10:1, the results (see Fig. 2.32) showed that the loading capacity of 0.24 Cyphos® 102 continuously increased as the A/O ratios increased from 1:1 until 10:1. Thus the maximum loading capacity was not reached and it is only possible to conclude that the value would be higher 1616.5 mg/L. However, as was mentioned in the same test with D2EHPA, the main drawback of constructing the equilibrium isotherm by raising the A/O ratio is the decrease in the contact between the extractant and the metal. Hence, maximum loading capacity should eventually be tested with zinc-plating effluent containing higher concentration of zinc than has been tested in this research project.

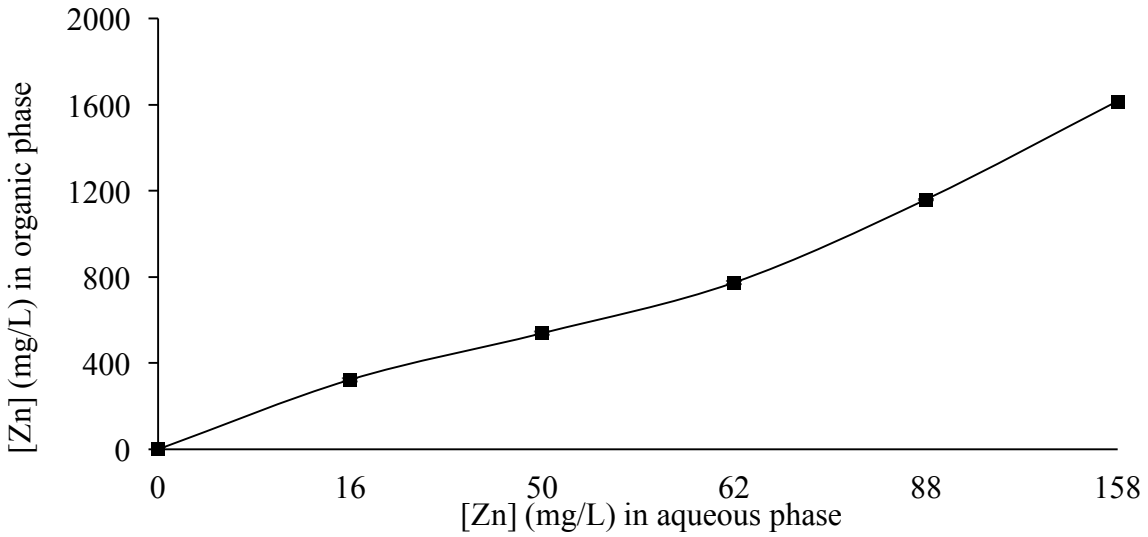


Figure 2.32. Equilibrium isotherm of Zn extraction of raw zinc-plating effluent at 25±2°C using 0.24 M Cyphos® 102 in kerosene with 3% (v/v) decanol as modifier (25 ± 2℃, 130 min.). The error bars not visibly depicted were mean absolute deviation (2 replicates) of less than 8 mg/L.

4. CONCLUSIONS

Among the two commercial extractants tested D2EHPA and Cyanex® 272, the first exhibited higher selectivity and efficiency for zinc extraction from a zinc electroplating industrial wastewater and was selected for further performance evaluation. At optimized conditions, with 20% w/w D2EHPA in kerosene and 3% v/v TBP being used with pH-pretreated zinc-plating effluent (to pH 5.5) for at least five minutes at A/O = 1:1 and room temperature (21 ± 2°C), the organic phase can be reused at least three cycles without compromising the extraction efficiency, and its loading capacity for zinc was proved to be above 6,024 ± 7 mg/L.

Among the three ionic liquids tested, Cyphos® 102 exhibited impressive selectivity towards zinc with little to no co-extraction of iron in liquid-liquid extraction of raw zinc electroplating effluent. At a concentration of 0.24 M in kerosene, zinc was extracted with 95% efficiency. Additionally, complete stripping was achieved using 2 M HNO_3. Despite the success in solving the issue of solubility of the ionic liquid by the addition of 3% (v/v) decanol as the modifier, the resulting loaded organic phase was separated into to layers of equal volumes. This unprecedented behavior might be the cause of the decrease in the reusability of

the extraction system, with the extraction efficiency decreasing from 95% to 54% and stripping efficiency decreasing from 99% to 5%, respectively. In order for the use of Cyphos® 102 to be viable in the industrial scale, it is of great importance that a condition be discovered that result in high reusability, and/or requiring the least amount of the extractant, such that its advantages outweighs the cost of the ionic liquid itself.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Shikotra, P. (2005). Selective Extraction of Metals from Mixed Oxide Matrixes Using Choline-Based Ionic Liquids. *Inorganic Chemistry, 44*(19), 6497-6499. doi:10.1021/ic0505450

Ali, A., Ahmad, I., & Daoud, J. (2006). CYANEX 272 for the extraction and recovery of zinc from aqueous waste solution using a mixer-settler unit. *Separation and Purification Technology,47*(3), 135-140. doi:10.1016/j.seppur.2005.06.015

Azizitorghabeh, A., Rashchi, F., & Babakhani, A. (2016). Stoichiometry and structural studies of Fe(III) and Zn(II) solvent extraction using D2EHPA/TBP. *Separation and Purification Technology,171*, 197-205. doi:10.1016/j.seppur.2016.07.037

Chelate. (2007). In Encyclopedia Britannica. Retrieved from https://www.britannica.com/science/chelate

ChemicalBook. (2019a). Cyphos IL 104. Retrieved July 11, 2019, from https://www.chemicalbook.com/ChemicalProductProperty_EN_CB9319859.htm

ChemicalBook. (2019b). Trihexyl(tetradecyl)phosphonium bromide. Retrieved July 11, 2019, from https://www.chemicalbook.com/ProductChemicalPropertiesCB2730576_EN…

ChemicalBook. (2019c). Trihexyl(tetradecyl)phosphonium decanoate. Retrieved July 11, 2019, from https://www.chemicalbook.com/ProductChemicalProperties CB3408902_EN.htm.

Darvishi, D., Fatmehsari, D. H., Alamdari, E., & Sadrnezhaad, S. K. (2011). Extraction of ZN, MN and CO from ZN-MN-CO-CD-NI containing solution using D2EHPA, Cyanex® 272 and Cyanex® 302. *International Journal of Engineering, 24(2),* 183-192.

Dreisinger, D. (2009). Keynote address: Hydrometallurgical process development for complex ores and concentrates. *Journal of the Southern African Institute of Mining and Metallurgy, 109*(5), 253-271.

Egorov, V. M., Djigailo, D. I., Momotenko, D. S., Chernyshov, D. V., Torocheshnikova, I. I., Smirnova, S. V., & Pletnev, I. V. (2010). Task-specific ionic liquid trioctylmethylammonium salicylate as extraction solvent for transition metal ions. *Talanta, 80*(3), 1177-1182. doi:10.1016/j.talanta.2009.09.003

Gallacher, L. V. (1981). Liquid Ion Exchange in Metal Recovery and Recycling. In *Third Conference on Advanced Pollution Control for the Metal Finishing Industry: Presented at Orlando Hyatt House, Kissimmee, FL, April 14-16, 1980*. Cincinnati, OH: U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory.

Hagiwara, R., & Ito, Y. (2000). Room temperature ionic liquids of alkylimidazolium cations and fluoroanions. *Journal of Fluorine Chemistry, 105*(2), 221-227. doi:10.1016/s0022-1139(99)00267-5

International Zinc Association. (2019). "ZINC." *ZINC. International Zinc Association*. Accessed January 24. http://www.zinc.org/.

Kobya, M., Demirbas, E., Ozyonar, F., Sirtbas, G., & Gengec, E. (2017). Treatments of alkaline non-cyanide, alkaline cyanide and acidic zinc electroplating wastewaters by electrocoagulation. *Process Safety and Environmental Protection, 105*, 373-385. doi:10.1016/j.psep.2016.11.020

Le, H. L., Jeong, J., Lee, J., Pandey, B. D., Yoo, J., & Huyunh, T. H. (2011). Hydrometallurgical Process for Copper Recovery from Waste Printed Circuit Boards (PCBs). *Mineral Processing and Extractive Metallurgy Review, 32*(2), 90-104. doi:10.1080/08827508.2010.530720

Mansur, M. B., Rocha, S. D., Magalhães, F. S., & Benedetto, J. D. (2008). Selective extraction of zinc(II) over iron(II) from spent hydrochloric acid pickling effluent by liquid-liquid extraction. *Journal of Hazardous Materials, 150*(3), 669-678. doi:10.1016/j.jhazmat.2007.05.019

Marszałkowska, B., Regel-Rosocka, M., Nowak, Ł, & Wiśniewski, M. (2010). Quaternary phosphonium salts as effective extractants of zinc(II) and iron(III) ions from acidic pickling solutions. *Polish Journal of Chemical Technology,12*(4), 1-5. doi:10.2478/v10026-010-0039-5

Midwest Metal Products. (2019). Zinc Coatings. Retrieved June 3, 2019, from http://anglerings.com/Value-Added/Zinc-Coatings

Nguyen, T. H., Wang, L., & Lee, M. S. (2017). Separation and Recovery of Precious Metals from Leach Liquors of Spent Electronic Wastes by Solvent Extraction. *Korean Journal of Metals and Materials,55*(4), 247-255. doi:10.3365/kjmm.2017.55.4.247

Nogueira, E. D., Abad, A. L. R., & Vega, J. M. R. (1980). *U.S. Patent No. US4235713A*. Washington, DC: U.S. Patent and Trademark Office. Process for the elimination of accumulated iron in organic phases of fluid-fluid extraction that contain di-2-ethyl-hexyl phosphoric acid

Pilli, S. R., Banerjee, T., & Mohanty, K. (2014). Performance of different ionic liquids to remove phenol from aqueous solutions using supported liquid membrane. *Desalination and Water Treatment,54*(11), 3062-3072. doi:10.1080/19443994.2014.907750

Regel-Rosocka, M. & Alguacil, F. J. (2013). Recent trends in metals extraction. *Revista De Metalurgia, 49*(4), 292-316. doi:10.3989/revmetalm.1344

Regel-Rosocka, M., Nowak, Ł, & Wiśniewski, M. (2012). Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids. *Separation and Purification Technology, 97*, 158-163. doi:10.1016/j.seppur.2012.01.035

Regel-Rosocka, M. & Wisniewski, M. (2011). Selective removal of zinc(II) from spent pickling solutions in the presence of iron ions with phosphonium ionic liquid Cyphos IL 101. *Hydrometallurgy, 110*(1-4), 85-90. doi:10.1016/j.hydromet.2011.08.012

Ríos, A. P., Hernández-Fernández, F. J., Lozano, L. J., Sánchez, S., Moreno, J. I., & Godínez, C. (2010). Removal of Metal Ions from Aqueous Solutions by Extraction with Ionic Liquids†. *Journal of Chemical & Engineering Data, 55*(2), 605-608. doi:10.1021/je9005008

Rusynyk, G. (2012, June 27). Hot-Dip Galvanizing vs Zinc Plating. Retrieved from https://www.portlandbolt.com/technical/faqs/hot-dip-galvanizing-vs-electrogalvanizing-zinc-plating/

Sigma Aldrich. (2019). Bis(2-ethylhexyl) phosphate 237825. Retrieved July 11, 2019, from https://www.sigmaaldrich.com/catalog/product/aldrich/237825?lang=pt®ion=PT&gclid=CjwKCAjwvJvpBRAtEiwAjLuRPZR0jc96u9zt8n-jIRgapCNoMA1CYn12WIL_jfNwxSYnIUdgCaZfyRoCwd4QAvD_BwE

Solvay. (2019). CYANEX® 272. Retrieved July 11, 2019, from https://www.solvay.com/en/product/cyanex-272

Singh, D., Mishra, S., & Singh, H. (2006). Stripping of iron (III) from the D2EHPA+TBP extract produced during uranium recovery from phosphoric acid by oxalic acid. *Hydrometallurgy, 81*(3-4), 214-218. doi:10.1016/j.hydromet.2005.12.006

Singh, R., Mahandra, H., & Gupta, B. (2017). Solvent extraction studies on cadmium and zinc using Cyphos IL 102 and recovery of zinc from zinc-plating mud. *Hydrometallurgy,172*, 11-18. doi:10.1016/j.hydromet.2017.06.017

Vahidi, E., Rashchi, F., & Moradkhani, D. (2009). Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA. *Minerals Engineering,22*(2), 204-206. doi:10.1016/j.mineng.2008.05.002

Yang, J., Wu, Y., & Li, J. (2012). Recovery of ultrafine copper particles from metal components of waste printed circuit boards. *Hydrometallurgy, 121-124*, 1-6. doi:10.1016/j.hydromet.2012.04.015