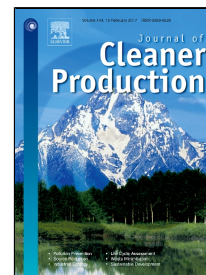# Accepted Manuscript

Recovery of Zn (II), Mn (II), Cd (II) and Ni (II) from the unsorted spent batteries using solvent extraction, electrodeposition and precipitation methods

Kulchaya Tanong, Lan-Huong Tran, Guy Mercier, Jean-François Blais

Highlights

- A sulfuric acid leaching process is applied on unsorted spent batteries.

- The pregnant leach solution (PLS) contains Zn, Mn, Cd, Ni and Co.

- Zn and Cd are separated from PLS using solvent extraction and electrodeposition.

- Mn and Ni are recovered using chemical precipitation as metal carbonates.

Recovery of Zn (II), Mn (II), Cd (II) and Ni (II) from the unsorted spent batteries using solvent extraction, electrodeposition and precipitation methods

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Abstract

This investigation presents the development of a waste batteries recycling technology, that could lead to the minimization of waste discharged and contamination problems and to the depletion of natural resources. This study mainly focused on the recovery of metals from a pregnant leach solution (PLS) obtained from a sulphuric leaching process applied to unsorted spent batteries. The PLS mainly contains Zn, Mn, Cd, Ni and Co. Cyanex 272 (di-2,4,4-trimethylpentyl phosphinic acid) was used to selectively recover Zn from the mixed solution. The Zn-Cyanex 272 was stripped and electrodeposited in metallic form and approximately 134 kg of Zn were recovered. Cd and Mn were co-extracted in the organic solvent D2EHPA (2-ethylhexylphosphonic acid) from the Zn-depleted solution and they were stripped using H_2SO_4. Consequently, Cd was selectively electrodeposited from a sulphate-stripped solution where the amount of Cd recovered was equal to 21.6 kg Cd per ton of waste battery powder. Residual Mn was recovered in the carbonate form by the addition of Na_2CO_3 (238 kg of Mn t^{-1} of waste battery powder). In the following step, Cyanex 272 was used to remove Co and other impurities from the Zn-Cd-Mn depleted solution, while Ni was not extracted. Finally, Ni was precipitated from the pure $NiSO_4$ solution with Na_2CO_3 and 23.8 kg of Ni were recovered per ton of waste battery powder. The costs of the process develop to recover metals (including only chemical costs and energy consumption) are estimated at \$814 t^{-1} of battery powder, while the metal revenues obtained are estimated at \$2,132 t^{-1} of battery powder. The chemical cost /metal revenue ratio is lower than 50%, which indicates that the process is feasible.

Keywords

1   Introduction

The number of spent batteries produced is increasing each year in several countries due to the high consumption in various electronic devices, such as mobile phones, laptops, lamps, remote controls and cameras (Barrett et al., 2016). In the province of Quebec, approximately 173 M units of primary cells and 5.2 M units of secondary cells were predicted to be sold in 2015 (Roberge, 2010). There is a possibility that these huge quantities of waste could be discharged into landfill sites due to the ease and low cost of this disposal method. Alkaline batteries are the main batteries commercialized across the world compared to the other type of batteries (Roberge, 2010). Once they reach their end-of-life, most of spent batteries are discharged into landfill sites with municipal wastes (Al-Thyabat et al., 2013) in some countries across the world including Canada due to the ease and low costs of this disposal option. Landfilling could pose a serious threat to the environment due to the potential release of metals into the groundwater (Granata et al., 2012). Indeed, some metals contained in spent batteries are harmful to aquatic life and humans. To avoid this problem, these metals should be recycled and reused. In Quebec, strict regulations regarding the potential discharge of hazardous metals in the environment and the application of the concept of regeneration/recycling/reuse of waste have encouraged the establishment of a non-profit organization, Recyc-Quebec, responsible of the collect and the recycling of spent batteries. In addition to the protection of the environment, the recycling strategy could also be an interesting alternative to alleviate the scarcity of metal resources and to increase the job opportunity for the community. Metal recycling not only benefits to the investors but also increases public incomes through recycling projects (Granata et al., 2012). Nowadays, the costs related to spent batteries sorting was estimated at 730$ t^{-1} of waste

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batteries in the province of Quebec, which could prevent the economic feasibility of various battery recycling projects (personal contact with Call2Recycle). Therefore, it is of great interest to develop a new process to treat unsorted waste batteries to decrease the operating costs.

1.1 Toxicity of the metals contained in spent batteries

Cadmium is the main metal contained in nickel-cadmium batteries. In the future, this kind of battery would be replaced by lithium ion battery due to the toxicity of cadmium. This metal could interfere with the physiological balance of other divalent metals by binding with hydrosulfo, carboxy and imidazolyl groups in enzymes (Ghosh et al., 2015).

Zn was mainly found in alkaline batteries. Even if zinc is not considered as hazardous waste in the province of Quebec (Règlement sur les matières résiduelles dangereuses), its uptake in high concentration could pose a serious problem for microorganisms or humans. For example, high uptake of Zn disrupts the absorption of calcium resulting in hypocalcaemia and finally causes fish death (Macrae et al., 2016). The toxicity of Zn for human has also been studied. The exposure to zinc oxide by inhalation causes acute symptoms such as fever, muscle soreness, nausea, fatigue and respiratory effects. A long exposure to this metal causes bronchiolar leukocytes (Plum et al., 2010).

Manganese, which is mainly present in alkaline batteries, is considered as an essential trace metal for some biochemical functions of animals and humans. However, an exposure to high concentration of Mn can lead to severe health effects such as malfunction of reproduction or central nervous systems, ataxia, etc. (WHO, 2001).

Nickel is mainly present in nickel-metal hydride and nickel-cadmium batteries. It may be considered as an essential trace element at low concentration. However, an exposure to high concentration of nickel can have significant health effects. The most common symptom for human is an allergic skin reaction. The inhalation of nickel causes acute toxic effects such as headache, vertigo, nausea, insomnia, etc. (Das et al., 2008). The well-known chronic symptom when exposed to nickel dusts is respiratory disorders such as asthma, bronchitis, rhinitis, sinusitis, pneumoconiosis, etc. (Das et al., 2008).

Cobalt and lithium are found in lithium battery. Lithium is considered as an essential element for human but could be toxic at high concentration. Exposure to cobalt could lead to cardiomyopathy, skin allergy, respiratory illness, etc. (Kim and Gibb, 2006). Lithium was widely used to treat bipolar patients. The exposure to lithium at certain concentration causes nausea, vomiting, leukocytosis, drowsiness, myopathy neuropathy, etc. (Timmer et al., 1999).

Even if some metals are considered as trace elements, most of them can cause problems to human and animal health at high concentrations. So, the recovery of those metals is necessary to prevent environmental impacts and at the same time to decrease the exploitation of natural resources.

1.2   Current processes for battery recycling

Among numerous methods, hydrometallurgical and pyrometallurgical processes have been widely applied to recover valuable metals contained in spent batteries. Pyrometallurgical method usually requires high-energy, expensive investment costs and produces a lot of dust. Hydrometallurgical processes represent a better option compared to pyrometallurgical ones.

Hydrometallurgical processes have several advantages over pyrometallurgical processes, such as higher selectivity toward metal, lower greenhouse gaseous emission and lower energy consumption (Freitas et al., 2007). However in this method, the need of an effective leaching is necessary to recover the greatest possible amounts of metals while pyrometallurgical processes do not (Sobianowska-Turek et al., 2016). There are several efforts made to treat spent batteries at laboratory scale by applying hydrometallurgical processes (Ku et al., 2016). Some commercialized processes such as modified Zincex MZP allows the recycling of alkaline and zinc-carbon waste batteries. For example, the company Recytec combines hydrometallurgical, pyrometallurgical and physical treatments to treat all the types of waste batteries. The company Snam-Savam applies a pyrometallurgical process to treat Ni-Cd batteries (Espinosa et al., 2004). Inmetco and Raw Material Company were the main recycling companies in the North of America able to recycle alkaline batteries and to divert most of these wastes from landfill sites (Bonhomme et al., 2013). Inmetco applies a pyrometallurgical process to treat alkaline batteries while Raw Material Company uses mechanical method. In Canada, the "polluter pays principle" policy was applied to manage waste batteries. Some waste batteries were recycled and managed by the non-profit organization Call2recycle. The alkaline battery directive in Canada reinforces battery collection points with 45% recovery goal varying in different province (Bonhomme et al., 2013).

1.3 Chemical organic solvent for metals recycles

In the present study, solvent extraction method was the main process use to recover the metals from a pregnant leach solution (PLS). Cyanex 272 and D2EHPA were classified in the group of phosphorus extractants that are normally effective in acidic solutions. They were widely used in

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the field of hydrometallurgy to recover metals at both laboratory and commercial scales. Cyanex 272 was used to separate Co from Ni in laterite ore at Bulong Nickel, Western Australia, due to the high Co/Ni separation factor obtained with this solvent (Hutton-Ashkenny et al., 2015). This organic solvent was also applied by the Sumitomo Metal Mining Company to obtain pure cobalt in a mini-plant (Tsakiridis and Agatzini-Leonardou, 2004). Provazi et al. (2011) recovered individual metals from a leaching solution obtained from unsorted batteries and applied Cyanex 272 to extract the metals at different pH values. Over 99% of Ti^{4+} could be extracted at pH = 1.0; 99% of Zn^{2+} were extracted at pH = 2.5; 85% of Ni^{2+} were extracted at pH = 3.0; and 80% of Cd^{2+} and La^{3+} were co-extracted at pH = 3.5. Mishra et al. (2015) applied TOPS-99 (Talcher Organo phosphorus solvent) and Cyanex 272 to selectively recover Zn, Mn, Co and Ni from nickel laterite leach liquor. The results showed that 96% of Mn and 98% of Zn were selectively extracted by TOPS-99 at pH 2.5 and 6.7, respectively. In this study, Co was also removed by Cyanex 272 at pH 3.4 and 99.8% of Ni were recovered by TOPS-99 at pH 2.5.

1.4 Benefits and environmental impacts of an organic solvent extraction, electrodeposition and precipitation methods

In this study, three methods include solvent extraction, electrodeposition and precipitation were applied. The limitations and advantages of each process were presented as follows.

Solvent extraction has been proven to be an efficient method due to the specific group function, which is highly selective for metal recovery. The high purity of the metal could be achieved by this method, fulfilling the need for high-grade metals in industrial processes (Avilaa et al., 2011). Laki et al. (2016) state that, solvent extraction method was considered simplicity, flexibility, economical benefits, rapidity, high enrichment factors, low costs and being

environmentally friendly, etc. for metals recoveries. However, some type of organic solvents were considered as highly flammable, toxic and detrimental to the environment (Li et al., 2016). From the previous reasons, the disposal and handling cost for the waste organic solvent could be expensive (Li et al., 2016) and it could prevent their application at the commercial scale. Normally the solvent extraction was carried out in close system to prevent the volatilization of the organic compounds so it could mitigate their leakage to the atmosphere. Cyanex272 and D2EHPA could be reused so it could offer the advantage in the term of disposal cost comparing to the metals revenues obtained. Green solvent was one of alternative technology that could be used to replace the conventional solvents. However, they were not yet commercialised. In the future study, the green solvent could be used to replace the current solvent so it could mitigate the environmental impact and improve the social acceptance.

Wei et al. (2003) studied the performance of a green solvent [C4mim][PF6] (1-butyl-3-methylimidazolium hexafluorophosphate) to selectively extract metals aqueous solutions at different pH values. According to their experiment results, the selectivity of metals was defined as follows: Ag (II) > Cu (II) > Pb (II) > Cd (II) > Zn (II). Wellens et al. (2014) investigated the selective extraction of metals using Cyphos® IL101 (trihexyl tetradecyl phosphonium chloride (P_{66614}Cl)) and 1,4-dioxine (50 mL with 10% HCl) as green solvent. This solvent was used to selectively recover the metals from a solution containing dissolved NiO, CuO, Fe_2O_3, ZnO, CaO, MnO and CoO. Their results showed that it is possible to separate calcium and nickel from manganese and cobalt and further from zinc, iron and copper. The authors also stated that nickel could be removed from the other transition metals in one step. Indeed, cadmium could be removed from the solution containing zinc and iron by using a green solvent, BMIN PF6 (1-

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butyl-3-methylimidazolium hexafluorophosphate), in a solution of 1 M HCl (De los Rios et al., 2010). According to Prado et al. (2016), the use of green solvents such as omin BF4- (1-octyl-3-metyllimidazolium tetrafloroborate) and omim PF6- (1-octyl-3-metyllimidazolium-hexafluorophosphate) seems to be interesting to separate Zn (II) and Fe (III) and to separate Cd (II) and Fe (II). From these studies, it could be seen that ionic liquid solvents (green solvent) can be used to replace volatile organic solvent due to their non-volatile, non-flammable, low vapour pressure, high thermal and chemical stability properties (Prado et al., 2016). These green solvents will be used in the future at industrial scale, if their application is economically feasible.

The electrodeposition method has many advantages in the terms of having a low environmental impact, a low energy consumption and a high metals recovery rate (Diaz et al., 2016). However it was considered as non-viable process for the diluted solution, as high electrical resistances and the development of the concentration polarization phenomena could limit the economic feasibility (Lu et al., 2015).

The precipitation method was widely used in the industrial scale because of its simplicity and inexpensive process. However there are some limitations including high sludge volume production, dewatering and disposal sludge problem (Lu et al., 2015) and low metal selectivity (Sobianowska-Turek at al., 2016). These three methods were chosen in this study because there are more advantages comparing to their limitations. However the further study at pilot scale and industrial scale should be conducted to evaluate the feasibility of the process in the term of economic and environment.

1.5 Objective of the present study

Generally, existing processes for metal recycling from waste batteries have been only applied to a specific type of waste battery at laboratory scale (Bertuol et al., 2009;) and at commercial scale (Espinosa et al., 2004) as mentioned previously. The main objective of this study is to treat all batteries together without a sorting step, which is considered as the main drawback step in the battery recycling process. Manual sorting as well as automatic sorting has a high labour cost in developed countries, such as those in Europe or North America (Granata et al., 2012).

The present process differs from methods in other studies by combining the solvent extraction and electrodeposition methods for the recovery of metals. A PLS was used instead of a synthetic solution, demonstrating that the process can be applied in reality. This study aims to do the following:

- Apply the experimental conditions (Tanong, 2016) for solvent extraction, electrodeposition and precipitation, obtained from previous studies, to selectively recover metals (Zn, Mn, Cd and Ni) from the PLS obtained from unsorted battery wastes.

- Reuse the organic solvents and acid solutions emerging from the electrodeposition process to observe the potential loss of efficiency of the process when recycling used organic solvents and therefore to limit the production of waste and to reduce the costs related to the consumption of chemical products.

- Investigate the feasibility of the whole process and use PLS on a larger scale (400 mL) compared with the volumes applied in previous studies (50 mL) (Tanong, 2016).

- Evaluate the chemical cost and energy consumption relative to metal revenues.

2   Materials and methods

The conditions for metal recovery by solvent extraction, electrodeposition and precipitation methods were previously determined with synthetic solutions (Tanong, 2016). In the present study, the experiment conditions determined in the previous studies were applied to the leach liquor obtained from the mixture of spent batteries. Fig. 1 presents the metal recovery process developed in this study. The PLS was obtained from the leaching process developed in previous studies and applied to the mixture of waste batteries. This mixture was mixed in the presence of a solution containing H_2SO_4 and a reducing agent under optimum conditions. Firstly, Zn was selectively extracted from the leach liquor by Cyanex 272 solvent extraction and electrodeposited as Zn metal. Secondly, Cd and Mn were extracted from Zn-depleted leach liquor by D2EHPA solvent extraction and Cd was selectively separated from Mn by electrodeposition. Then, Mn was recovered as carbonate by precipitation. In the final extraction step, the impurities were removed from the Zn-Cd-Mn depleted solution by Cyanex 272 solvent extraction and Ni was finally recovered as $NiCO_3$ by precipitation. All the experiments, including solvent extraction, precipitation and electrodeposition were conducted in triplicate to ensure the reliability of the process.
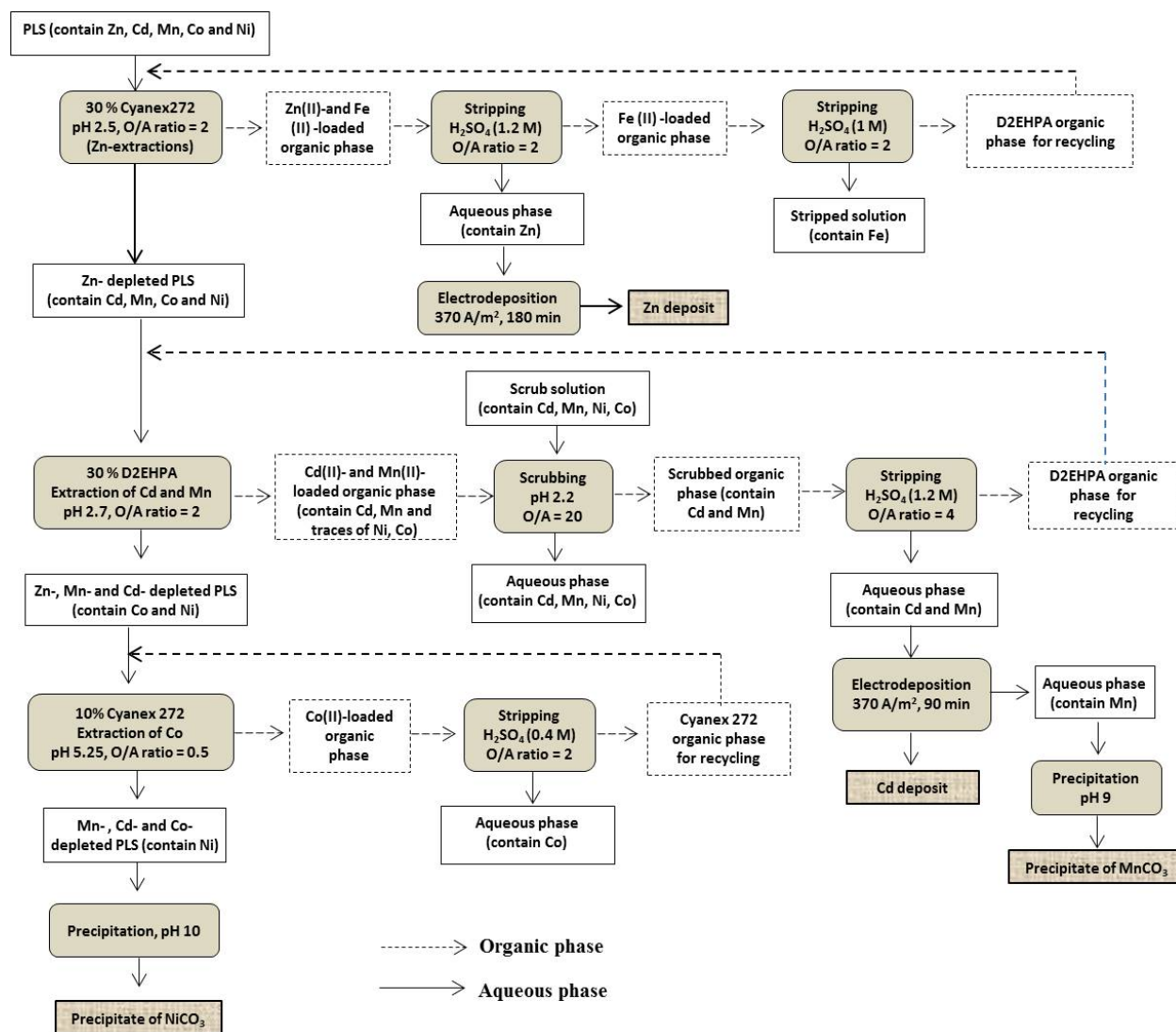
Stripping: Process where acid solution was applied to remove the metals from the organic phase

Stripped solution: Acid solution rich in metals obtained after the stripping process

PLS: Pregnant leach solution rich in metals emerging from the leaching process

Metal-depleted PLS: Aqueous solution obtained after metal removal by solvent extraction (ex. Zn-depleted PLS: pregnant leach solution obtained after Zn removal by extraction)

Metal-loaded organic phase: Organic solvent rich in target metal obtained by solvent extraction (ex. Zn-loaded organic phase: organic solvent rich in Zn)

Scrubbing: Process in solvent extraction which was applied to remove the impurities from the organic solvent

Scrub solution: Solution rich in target metal which was introduced in the scrubbing process

Scrubbed solution: Effluent emerging from the scrubbing process rich in impurities.

Fig. 1. Detailed flowsheet of the hydrometallurgical route to treat the mixture of waste batteries.

2.1 Preparation of spent batteries powder

The amounts of alkaline, nickel-metal hydride (Ni-MH), nickel-cadmium (Ni-Cd), lithium ion (Li-ion), lithium metallic (Li-M) were estimated according to the information from Recyc-Quebec. All batteries were crushed to obtain metal powders. These metal particles were leached in sulphuric acid in the presence of a reducing agent, in the optimal conditions found in previous studies (Tanong, 2016). Alkaline, Zn-C, Ni-Cd, Ni-MH, Li-ion and Li-M batteries were mechanically pre-treated by dismantling, crushing and grinding. Li-M and Ni-MH batteries were frozen in liquid nitrogen before dismantling, as they could react violently when exposed to air. The procedure for preparing the battery powder was slightly different for each type of battery. However, in reality, all batteries could be crushed together under a free-oxygen atmosphere. A fine power was obtained from alkaline, Ni-MH and Ni-Cd batteries by manual crushing and grinding with a mortar. Li-ion, Li-M and Ni-Cd cathode materials were uncurled and cut into small pieces, followed by manual grinding to obtain a fine powder. The undesirable coarse particles, including paper and plastic particles, were eliminated through the apertures of 1-mm and 2-mm sieves. The proportions of each type of spent battery in the mixture were fixed according to the battery consumption in the Canadian market (66.5% $Zn-MnO_2$, 15.4% Zn-C, 15.4% Ni-Cd, 1.7% Ni-MH, 0.3% Li-ion and 0.7% Li-primary batteries) (Roberge, 2010). The mixture of battery powders was dried at 25°C over 24 h and ground by a pulverizer (Fritsh pulverisette, Serial no. 06 2000/01908, Germany) to obtain an average particle size of 333 μm.

2.2 Preparation of the pregnant leach solution

In a previous study (Tanong, 2016), the following optimal leaching conditions were defined: 10.9% solid/liquid (S/L) ratio, 1.34 M H_2SO_4 combined with $Na_2S_2O_5$ (0.45 g $Na_2S_2O_5$ g^{-1} of waste battery powder) at ambient temperature (T = 25°C) and a leaching period of 45 min. The chemical products in this step were purchased from Sigma Aldrich, Canada. The leaching solution was obtained after solid/liquid separation on a G6 filter (Fisher Science) and it mainly contained 3.58 g Cd L^{-1}, 0.289 g Co L^{-1}, 0.691 g Fe L^{-1}, 28.6 g Mn L^{-1}, 4.41 g Ni L^{-1} and 20.8 g Zn L^{-1} (0.1 g Li L^{-1}). It also contained Na (12.8 g L^{-1}), S (54.7 g L^{-1}) and K (5.3 g L^{-1}).

2.3 Preparation of the scrub solution

Scrubbing is the additional step in the solvent extraction method to remove the unwanted metals from an organic phase. The concentrated metal solution (preference metal) was used as a scrubbed solution. This solution was mixed intensively with the organic solvent containing the preferred metals and the impurities. The preferred metals in the scrubbing solution can replace the unwanted metals in the organic phase. To prepare the scrubbing solution, chemical grade $MnSO_4$ and $CdSO_4$ (Labouratoire MAT, Canada) were dissolved in distilled water and the pH of the solution was adjusted to 2.0 by a concentrated H_2SO_4 solution.

2.4 Laboratory-scale method for solvent extraction assays

The solvent extraction assays, including extraction, scrubbing and stripping, were carried out in a 2,000 mL capacity beaker installed on a hot plate (with the temperature set at 50°C). A laboratory overhead paddle stirrer with a velocity of 400 rotations per minute (rpm) was used

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during the extraction. The volumes of the leaching solution and organic solvent were fixed at 400 mL and 800 mL, respectively. The duration of extraction was set at 20 min.

After extraction, a separator funnel was used to separate the organic phase from the aqueous phase. The metals were stripped from the organic phase by mixing with H_2SO_4 over 20 min at 50°C. A 10 M NaOH solution was used to control the pH in all solvent extraction experiments. The organic and aqueous phases were separated after the stripping step by a separator funnel. The samples were taken from the aqueous phase and preserved in 5% HNO_3 before analysis.

2.5   Cyanex 272-Zn extraction

Cyanex 272 was used to selectively recover Zn from the PLS obtained from the leaching process. To prepare the organic solvent, 20% of Cyanex 272 (Cytec Canada Inc.) and 2% of TBP tributylphosphate (TBP) (97%, Sigma Aldrich, Canada) were dissolved in kerosene (Recochem. Inc., Canada). The percentage of Cyanex 272 was obtained from the stoichiometric calculation. The extraction assays were carried out at pH of 2.2 - 2.5, O/A ratio of 2 and in two extraction stages. Zn was transferred from the organic phase to the aqueous phase by vigorously mixing the organic solvent with 0.4 M H_2SO_4 (O/A = 2). Finally, Zn was recovered from $ZnSO_4$ solution by an electrodeposition method.

2.6   D2EHPA-Cd, D2EHPA-Mn extraction

D2EHPA was applied to simultaneously recover Cd and Mn into the organic phase. To prepare the organic solution, 30% D2EHPA (Sigma Aldrich Company) and 5% TBP were diluted in kerosene to decrease its viscosity. The amounts of D2EHPA as well as Cyanex 272 were obtained by stoichiometric calculations. The equilibrium pH was fixed as approximately 2.5-2.9,

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with an O/A ratio of 2. Two extraction stages were required to recover the maximum quantities of the metals.

The impurities in the organic phase were scrubbed out with concentrated Mn and Cd solutions under an O/A ratio of 20 and mixing at 400 rpm. The scrubbed solution (concentrated in Mn and Cd) was mixed intensively with the D2EHPA organic solvent (containing Cd, Mn, Ni and Co) over 20 min, then the separator funnel was used to separate the aqueous phase from the organic phase. The organic solvent was regenerated by 1.2 M H_2SO_4 with an O/A ratio of 4. After stripping with the acid, a high-purity stripped solution containing mainly $CdSO_4$ and $MnSO_4$ was obtained.

2.7   Electrochemical experiment

A reactor made of acrylic with dimensions of 3.5 cm (width), 13.5 cm (length) and 17 cm (depth) was used in the electrodeposition experiments. The rectangular sheets of the cathode and anode were made of stainless steel and Ti/IrO_2, respectively. The geometric area was calculated and estimated to be 110 cm^2. The distance between the two electrodes was equal to 1 cm and the electrodeposition volume was fixed to 500 mL for all electrodeposition experiments. The experiments were carried out at ambient temperature. $ZnSO_4$ (pH = 2) from section 2.5 was used in the electrodeposition experiment, in which Zn was deposited on the cathode surface with a current density of 370 A m^{-2} and electrodeposition time of 180 min. The samples were taken at 5, 10, 20, 30, 60, 120 and 180 min. At the end of the electrodeposition experiment, the cathode was rinsed with 5% HNO_3 to determine the impurities present in the deposited Zn.

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The stripped solution from section 2.6 mainly consisted of Cd and Mn. Cd was separated from Mn by the electrodeposition method, where the initial pH of the solution was fixed to 2.0. A current density of 370 $A\,m^{-2}$ was also applied for the Zn-electrodeposition assays. The electrodeposition was extended to 240 min, which was different from the previous study (Tanong, 2016). In this experiment, the samples were taken at 10, 30, 60, 120, 180, 240, 300 and 360 min and preserved in 5% HNO_3 before analysis. The purity of the Cd deposited in the electrodeposition experiment was determined by the digestion method (3050B) (APHA, 1999).

2.8 Cyanex 272-Ni

Co and the other impurities were removed from a Zn-Cd-Mn free solution at a pH approximately between 5.7-5.9 by Cyanex 272 with an O/A of 0.5. The organic solvent was prepared by dissolving 10% Cyanex 272 and 2% TBP in kerosene. The stoichiometry value of Cyanex 272 was lower than 10%. This concentration was chosen due to the loss of organic solvent during processing, which was not feasible if the percentage of organic solvent was too low. The unwanted metals were transferred to the organic phase, which was later regenerated by 0.4 M H_2SO_4 with an O/A ratio of 2. Pure $NiSO_4$ solution was obtained in this experimental step.

2.9 Precipitation

Sodium carbonate was used to precipitate Ni and Mn from the solutions obtained in section 2.7 and section 2.8, respectively. Distilled water was used to eliminate dissolved sulfur and sodium from the metallic powder after precipitation. The metal sludge was mixed vigorously (200 rpm)

with distilled water by applying a S/L ratio of 10% for 10 min. All precipitation experiments were carried out at ambient temperature.

2.10 Analytical techniques

Inductively coupled plasma - atomic emission spectroscopy (ICP – AES) (Varian 725 – ES) was used to determine the metals composition in the samples obtained from 3050B (APHA, 1999) digestion method, leaching, solvent extraction, electrodeposition and precipitation assays. The samples from digestion, leaching and precipitation assays were filtered with G6 glass fiber paper (G6, Fisher brand, Fisher Scientific, Canada, pore size = 1.5 µm) to remove solid particles before analysis. All samples were preserved in 5% HNO_3 before analysis.

2.11 Economic aspect

The economic evaluation including chemical and energy consumption was roughly studied in this process. Table 1 shows the unit prices of the different chemical products expressed in USD per ton of chemicals or USD per liter of chemicals for the inputs and the unit price of the products obtained (Zn metallic, Cd metallic, etc.) expressed in USD per ton of product used for the determination of the operating costs of the process. The costs related to the energy consumed, which was not presented in Table 1, were estimated based on the amount of energy required in the process and the unit price of electricity in the Province of Quebec (0.05 USD kWh^{-1}), Canada. The total costs and the revenues were then evaluated in terms of U.S. dollars per ton of battery powder (USD t^{-1}) based on the amounts of chemicals used and of products obtained and the unit price defined in Table 1.

Table 1   **Unit price of the chemicals used in the process and products obtained at the end of the process**

Chemical products	Price (USD t^{-1})	References
Inorganic products		
• H_2SO_4	100	ICIS, 2015
• $Na_2S_2O_5$	250	Alibaba, 2015
• NaOH	250	Personal contact with Cytec company, 2014
• Na_2CO_3	159	Alibaba, 2015
Metals		
• Zn metal	6,500	Alibaba, 2015
• Cd metal	1,000	Alibaba, 2015
• $MnCO_3$	1,300	Alibaba, 2015
• $NiCO_3$	13,500	Alibaba, 2015
Organic products	**Price (USD L^{-1})**	
• Cyanex 272	71.2	Barnard and Shiers
• D2EHPA	37.8	Sigmaaldrich, 2015
• TBP	2.15	Barnard and Shiers
• Kerosene	1.00	Bunnings, 2015

3   Results and discussion

3.1   Cyanex 272-Zn extraction and stripping

Cyanex 272 has been proven to be an effective agent to selectively recover Zn from PLS consisting mainly of Zn, Mn, Cd, Co and Ni. This PLS solution was obtained from a leaching process using the optimal conditions established in a previous study. The best conditions obtained in the previous study for Zn-Cyanex272 extraction include the following: O/A = 2, 30% Cyanex 272 + 2% TBP in kerosene, pH~2.5, reaction time of 20 min at 50°C and two direct extraction stages (Tanong, 2016). TBP was used as a phase modifier and aided the phase

separation (Fatmehsari et al., 2009). After the extraction stage, the raffinate (aqueous phase) was transferred to the next stage (section 3.2). The Zn-Cyanex 272 organic solution was stripped by sulphuric acid to recover Zn and to recycle the Cyanex 272. The results are shown in Table 2. A decrease in Zn content from 20.8 g L^{-1} to 0.07 g L^{-1} was observed, with a removal yield of 99.7% at an equilibrium pH ~ 2.2, while the other metals, including Mn, Cd, Co and Ni remained in the solution. The high Zn extraction efficiencies were similar to our previous results for synthetic solutions (Tanong, 2016). Similar results were also observed in the study of Salgado et al. (2013), where Zn was easily separated from Mn at pH~2 by 20% Cyanex 272, O/A ratio = 1 and T = 50°C (Salgado et al., 2013). However, the initial metal concentrations in their study, i.e., [Zn] = 5.24 g L^{-1} and [Mn] = 6.69 g L^{-1}, were different from this study. Consequently, a higher concentration of Cyanex 272 was necessary in the present study because of the higher Zn concentration in the PLS.

Table 2   Selective extraction performances of Zn from PLS using Cyanex 272 after two stages of extraction (30% (v v^{-1}) Cyanex 272 and 2% (v v^{-1}) TBP in kerosene, O/A = 2/1) at pH = 2.5.

	Residual concentration measured in the aqueous phase (g L^{-1})					
	Cd	Co	Fe	Mn	Ni	Zn
PLS solution (1 L)	3.57	0.29	0.69	28.6	4.49	20.8
EXTRACTION STAGE						
1st extraction	3.57 ± 0.08	0.29 ± 0.01	0.01 ± 0.00	28.6 ± 0.77	4.49 ± 0.13	6.27 ± 0.19
2nd extraction	3.53 ± 0.25	0.30 ± 0.02	0.00 ± 0.00	27.7 ± 1.77	4.36 ± 0.32	0.07 ± 0.04
STRIPPING STAGE						
1st stripping (2 L)	0.05 ± 0.01	0.01 ± 0.00	0.03 ± 0.01	0.82 ± 0.02	0.05 ± 0.02	9.55 ± 0.35
2nd stripping (2 L)	0.00 ± 0.00	0.00 ± 0.00	0.20 ± 0.01	0.03 ± 0.01	0.00 ± 0.00	0.47 ± 0.04

The co-extraction of Fe is inevitable, as it is extracted at a lower pH value compared with the equilibrium pH for Zn extraction (Cytec, 2008). The mixture of both organic phases was transferred to the stripping stage. From Table 2, at the first stripping, the average concentration of iron was decreased from 0.69 g L^{-1} to 0.01 g L^{-1}. This quantity of Fe was co-extracted with Zn and was not washed out with Zn when 0.4 M H_2SO_4 was applied as the strip solution. H_2SO_4 solution is widely used as a strip solution because it is cheap and less corrosive compared to other inorganic acids, such as HCl or HNO_3 (Kul and Oskay, 2015). 97% Zn was removed from the Cyanex 272 organic phase, with an O/A ratio of 2 and 0.4 M H_2SO_4 (at the first stripping stage). The average stripping efficiency was estimated at 97%, which was higher compared with the result obtained in a previous study (Tanong, 2016). The high stripping efficiency might be due to the longer reaction time and high agitation rate applied in the present experiments.

To regenerate the solvent, 1 M H_2SO_4 was used to remove Fe from the organic solvent. From Table 2, the average efficiency of iron removal was not as high as in the previous result (Tanong, 2016). Fe was removed from the organic phase with an efficiency of 58% in the second stripping stage. This solution was suitable to use for another stripping of Fe in the organic phase.

3.2 D2EHPA-Cd, Mn extraction and stripping of Cd and Mn from D2EHPA

The raffinate (Zn-depleted solution) obtained from section 3.1 was used in the experimental assays for the recovery of Cd and Mn. The Zn-depleted PLS used for this series of experiments contained 0.30 g Co L^{-1}, 4.36 g Ni L^{-1}, 3.53 g Cd L^{-1} and 27.7 g Mn L^{-1} (the raffinate concentration after the second extraction stage using Cyanex 272). After separation of the organic and

aqueous phases, the raffinate (aqueous phase) was transferred to the next stage (section 3.3). The organic phase was transferred to the scrubbing stage to remove impurities, followed by the stripping stage to recover Cd and Mn and to recycle the D2EHPA. The results are shown in Table 3.

Using the best conditions obtained in the previous study (Tanong, 2016), approximately 95% Cd and 99% Mn were extracted into the organic phase, while only 77.4% Cd (from 3.53 g L^{-1} to 0.80 g L^{-1}) and 93.1% Mn (from 27.7 g L^{-1} to 1.9 g L^{-1}) were extracted in the present study. The low extraction efficiencies in this experiment were due to the difference in the equilibrium pH obtained in the assays. In the present study, the average equilibrium pH after extraction was 2.2, while in the previous study, it was 2.7 with the addition of the same amount of NaOH. The low equilibrium pH obtained in the present study could not be controlled. This might be due to the presence of other basic consumer substances in the PLS solution, which were not present in the synthetic solution. With a single extraction (Table 3), efficiencies of 69.4% for Mn and 46.1% for Cd were recorded at pH = 2.2, which is more efficient compared with the study of Hosseini et al. (2010), in which approximately 30% of Mn was extracted at pH = 2.2 using 20% D2EHPA and an O/A ratio of 1 (Hosseini et al., 2010). In the study by Parhi et al. (2009), only 22% of Cd was extracted by 0.2 M D2EHPA at pH = 2.2 (O/A = 1 for 5 min) (Parhi et al., 2009). The lower efficiency in their results compared with the present study might be due to the shorter reaction times applied in their study.

Table 3   Simultaneously extraction performances of Cd and Mn from Zn-depleted PLS using D2EHPA after two stages of extraction (30% (v v^{-1}) D2EHPA and 5% (v v^{-1}) TBP in kerosene, O/A = 2/1) at pH = 2.2 following the scrubbing stage (O/A = 20) and stripping stage (O/A = 4, 1.2 M H$_2$SO$_4$).

	Concentration measured in the aqueous phase (g L^{-1})				
	Cd	Co	Mn	Ni	Zn
EXTRACTION STAGE					
Zn-depleted PLS (1 L) (raffinate of extraction using Cyanex 272)	3.53 ± 0.25	0.29 ± 0.02	27.7 ± 1.8	4.36 ± 0.32	0.07 ± 0.04
1st extraction	1.90 ± 0.10	0.22 ± 0.01	8.47 ± 0.77	3.52 ± 0.16	n.d
2nd extraction	0.80 ± 0.11	0.21 ± 0.00	1.89 ± 0.48	3.45 ± 0.02	n.d
Amount in organic phase after extraction (g) (before scrubbing)	*2.73*	*0.093*	*25.8*	*0.906*	*0.07*
SCRUBBING STAGE (O/A = 20)					
Scrub solution - before scrubbing	7.40	0	32.0	0	0
Direction of metal to organic phase	*in*	*out*	*in*	*out*	
Scrubbed solution - after scrubbing	4.50 ± 0.46	0.13 ± 0.04	19.1 ± 2.6	0.62 ± 0.25	
Amount in organic phase after scrubbing (g)	*3.31*	*0.068*	*28.4*	*0.783*	
STRIPPING STAGE (O/A = 4)					
Stripped solution (1 L)	2.32 ± 0.03	0.01 ± 0.00	23.8 ± 0.5	0.02 ± 0.01	0.13 ± 0.01

n.d = non detection.

At these conditions (pH~2.2), approximately 30.9% Co and 20.8% Ni were co-extracted with Cd and Mn (77.4% for Cd and 93.1% for Mn). This is consistent with the observation by Babakhani et al. (2014), where 36% Ni was co-extracted with 88% Cd at pH = 3.0 (Babakhania et al., 2014). To obtain the high Cd/Ni separation factor in their study, a mixture of Cyanex 302 and the organic solvent D2EHPA was used (for a synergistic effect). At pH = 3 and with this organic mixture, only 3% Ni was extracted with Cd and approximately 100% Cd was recovered (0.15 M D2EHPA + 0.45 M Cyanex 302, O/A = 1) (Babakhania et al., 2014). The experiment conducted with Cyanex 302 also resulted in the improvement of Cd/Ni separation, but it was not used in this study due to its high product cost. Instead of adding Cyanex 302 to the organic solvent D2EHPA, a scrubbing stage was applied to remove impurities from the organic solvent. Pagnanelli et al. (2016) obtained the similar results where 20% of Ni was co-extracted with 90% of Mn when D2EHPA was applied. In their study, D2EHPA was used to remove the impurities from leach liquor solution obtaining from li-ion battery leaching. In their experiment results, the high purity of Ni and Co solution was obtained after the removal of the impurities by precipitation and D2EHPA solvent extraction. Cobalt was finally recovered selectively by Cyanex 272 and precipitated as the carbonate form.

Contradictory results were obtained in the study of Rodrigues et al. (2010), in which Cd was almost completely separated from Co at pH = 3.0, with the sole application of 0.5 M D2EHPA (O/A = 1 at 25°C) (Rodrigues and Mansur, 2010). From our experimental results, the sequence of metal extraction using D2EHPA and when increasing the pH of the solution was: $Cd^{2+} > Co^{2+} > Ni^{2+}$, which is in agreement with the studies of Fatmehsari et al. (2009) and Noguerira and Delmas (1999).

The scrubbing method has been used to eliminate the impurities from the organic phase in various studies (Haghighi et al., 2015). The organic solvents from the two extraction stages were mixed before scrubbing. In Table 3, a total quantity of 123 mg Ni (from 906 mg to 783 mg) and 25 mg Co (from 93 mg to 68 mg) were eliminated from the organic phase by the scrubbing method. The removal yields were similar to previous results (Tanong, 2016). The contaminated scrubbed solution was supposed to be recycled in the extraction process, according to Owusu (1998).

To recover Cd and Mn from the organic solvent, the scrubbed organic solvent was intensively mixed with 1.2 M H_2SO_4 at O/A = 4. The average stripping efficacies were equal to 70% for Cd (2.32 g in stripped solution, compared to 3.31 g extracted in the organic phase) and 84% for Mn (23.8 g in stripped solution, compared to 28.4 g extracted in the organic phase), which are also less than those obtained in the previous study (Tanong, 2016).

It is noteworthy that a small decrease in the extraction and stripping performance was observed when the real solution was applied. Globally, the results for the Cd and Mn extractions were satisfactory but could be improved.

3.3 Cyanex 272-Co, Cd and Mn removal (purification of nickel sulfate solution)

The raffinate from section 3.2 was used in the experimental assays. The solution contained mainly Ni (3.45 g L^{-1}) and impurities included Co (0.21 g L^{-1}), Cd (0.79 g L^{-1}) and Mn (1.89 g L^{-1}). A single extraction stage with Cyanex 272 (10% Cyanex 272 and O/A = 1/2) was applied. Cyanex 272 was used in this experiment due to its high success in Co/Ni separation, as per previous reports (Cholico-Gonzalez et al., 2015). After purification using solvent extraction, the

aqueous phase was transferred for the precipitation of Ni (section 3.5). The organic phase was submitted to the stripping stage using 0.4 M H_2SO_4 and O/A = 0.5. From these experimental results (Table 4), the removal efficiencies of Cd (99.6%), Co (98.7%) and Mn (98.6%) were similar to the results obtained in the experiment with the synthetic solution. An equilibrium pH of 5.9 was necessary in this experiment, which is higher compared to the assays with the synthetic solution (pH = 5.5). Similar results were also found in the study of Guimaraes et al. (2014), where approximately 90% Co and Mn were removed from $NiSO_4$ solution at pH~5.9 (10% Cyanex 272, O/A = 1, T = 50°C and 10 min stirring rate) (Guimaraes et al., 2014). A temperature of 50°C was directly applied for easier separation of the two metals because the extraction of Co is more endothermic than that of Ni (Darvishi et al., 2005). It is noted that solvent extraction could be used to concentrate the metals from the PLS. In this case, after the single extraction step (O/A = 1/2) followed by the single stripping step (O/A = 2), the metal concentrations were four times higher compared with the metal concentrations in the aqueous feed. In this study, the stripped solution contained 2.83 g Cd L^{-1}, 7.28 g Mn L^{-1}, 0.803 g Co L^{-1} and 3.67 g Ni L^{-1}, and it was suitable for use in other stripping experiments, to accumulate metals before Ni recovery and/or to return to the initial PLS.

Table 4 **Removal of the impurities from Cd-, Mn- depleted PLS using Cyanex 272 after single stage of extraction (10% (v v^{-1}) Cyanex 272 and 5% (v v^{-1}) TBP in kerosene, O/A = 1/2) at pH = 5.9 to recover Ni.**

	Concentration measured in the aqueous phase (g L^{-1})			
	Cd	Co	Mn	Ni
Cd-, Mn-depleted PLS (raffinate of extraction using D2EHPA)-1 L	0.79 ± 0.11	0.21 ± 0.00	1.89 ± 0.48	3.45 ± 0.02
After EXTRACTION (O/A = 2) Raffinate – 1 L	0.003 ± 0.001	0.003 ± 0.001	0.026 ± 0.002	2.43 ± 0.11
Extraction efficiency (%)	99.6	98.7	98.6	29.6
After STRIPPING (O/A=2) Stripped solution – 0.25 L	2.83 ± 0.06	0.80 ± 0.04	7.28 ± 0.07	3.67 ± 0.09
Stripping efficiency (%)	88.9	98.2	97.4	89.6

n.d = non detection.

3.4 Electrochemical experiments

3.4.1 Zn electrowinning

The Zn electrodeposition experiments were carried out in the aqueous solution emerging from the Cyanex 272 stripping step (section 3.1). Fig. 2 presents the residual Zn concentration measured in the aqueous solution during the electrodeposition step performed at a current density of 370 A m^{-2}, pH = 2 and two successive electrodeposition stages. The energy consumption (kWh L^{-1}) was also observed as a function of time.
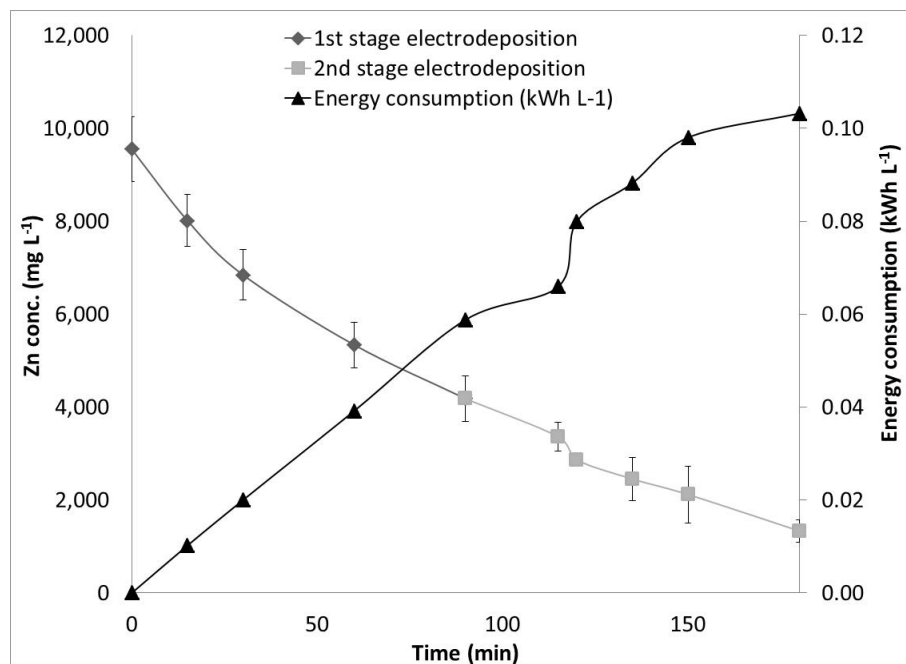
Fig. 2. **Variation of residual Zn concentration and energy consumption in two stages of Zn electrodeposition in function of the deposition time applying a current density of 370 A m^{-2}.**

Fig. 2 shows the decrease of the Zn concentration during the electrodeposition process. The Zn-rich stripped solution from section 3.1 was used. The chemical reactions of Zn electrodeposition in the solution could be revealed as follows.

The reactions at the cathode (Majuste et al., 2015) are shown in Equation 1a, 1b:

$$Zn^{2+} + 2e^- = Zn_{(s)}, E_0 = -0.76 \tag{1a}$$

$$2H^+ + 2e^- = H_{2(g)}, E_0 = 0.00V \tag{1b}$$

The reaction at the anode (Majuste et al., 2015) is shown in Equation 2:

$4 H^+ + 4 e^- + O_2 = 2 H_2O$, E_0 = -1.229V, $\mathbf{E_0}$ =- 1.229V   (2)
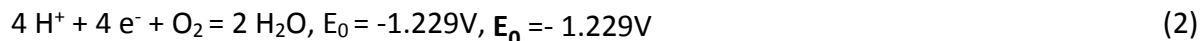
The cathode current efficiency (CE) could be defined as Equation 3 (Majuste et al., 2015):

CE (%) = (n.F.m/I.t).100   (3)

where F = 96,485 C mol^{-1} is the Faraday constant, "m" corresponds to the mass deposited (g), "I" represents the total current (C s^{-1}) and "t" is the deposition time (s).

The cathode current efficiency of Zn from the above equation was estimated to be 58% in the present result, which is similar to our previous study (Tanong , 2016).

A high concentration of Cd (55 mg L^{-1}) was present in the stripped Cyanex 272 solution (contained mainly of 9,550 mg Zn L^{-1}), while in our previous study, only 5 mg Cd L^{-1} was present. To attain a potential in Zn electrowinning, the Cd concentration should not be greater than 1 mg L^{-1} (Haghighi et al., 2015). From this previous statement, a scrubbing step is recommended to remove Cd impurities from the Zn–loaded Cyanex 272. Addition of the scrubbing stage should be considered in further work, to improve the purity of metallic Zn.

3.4.2 *Selective recovery of Cd from the aqueous phase containing Cd (II) and Mn (II)*

Cd was selectively recovered from the stripped solution from section 3.2, which mainly contained Cd and Mn. Cd could be deposited on the cathode surface according to the following equations:

Cathodic reaction (Equation 4) (Moradkhani et al., 2012),

$$Cd^{2+} + 2e^- = Cd_{(s)}, E = -0.40 \text{ V} \tag{4}$$

At the anode, in addition to the reaction of H^+ (Equation 2), the reaction of Mn occurred as follows (Equation 5) (Mahon and Alfantazi, 2014):

$$Mn^{2+} + 2 H_2O = MnO_2 + 4 H^+ + 2 e^-, E = +1.23 \text{ V} \tag{5}$$

The synthetic aqueous solution initially contained 4.29 g Cd L^{-1} and 27.3 g Mn L^{-1}.

According to Equation 5, Mn^{2+} is oxidized to MnO_2 at the anode, while only Cd^{2+} is reduced to metallic Cd and deposited on the cathode. From our experimental results, shown in Fig. 3, the Cd concentration was decreased from 2,207 mg L^{-1} to 900 mg L^{-1}, 5.6 mg L^{-1} and 4.6 mg L^{-1} after 90, 300 and 360 min, respectively. In the previous study, the Cd concentration was decreased from 4,200 mg L^{-1} to 10 and 8 mg L^{-1} after 90 and 360 min, respectively, under the same experimental conditions. The CE in the present study was only 10% while in the previous study, it was estimated as 32%. The decrease in the CE was due to the low initial concentration of Cd, which deteriorated the deposition efficiency (Safarzadeh and Moradkhani, 2010). The use of

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additives in the solution could likely improve the CE (Biswal et al., 2012), or Cd could be concentrated by a solvent extraction method. The Cd concentration could be increased by changing O/A ratio in the extraction or stripping steps. After 360 min, the concentration of Cd was found to be 4.6 mg L^{-1}, while Mn remained almost constant (19.97 g L^{-1} to 19.2 g L^{-1}) (results not shown). The Cd powder was easily peeled off and washed with distilled water to remove the dissolved Mn (Moradkhani et al., 2012). 2.36 g of Cd was obtained and washed with distilled water, to obtain ~98% purity.
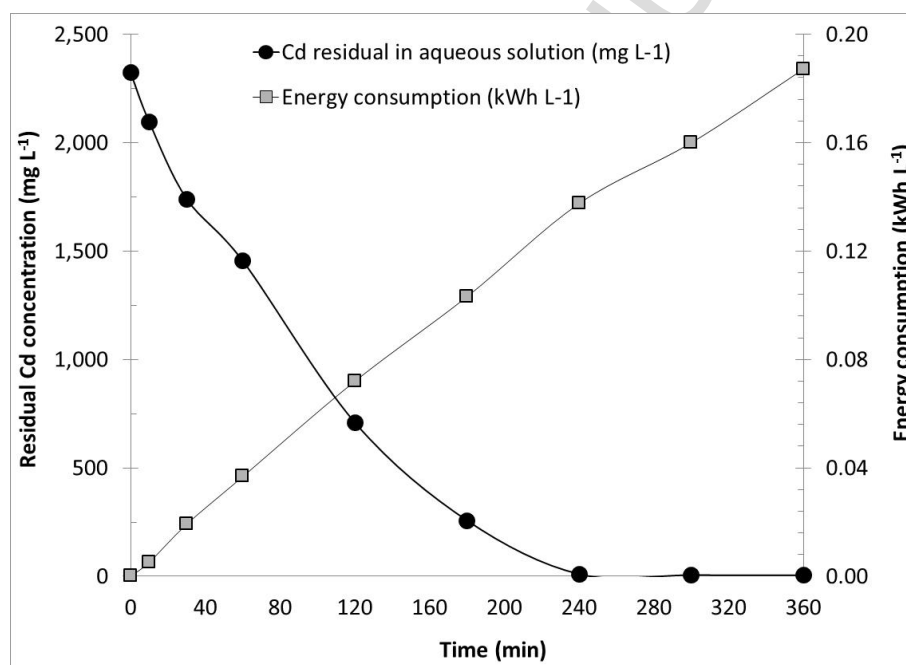

Fig. 3. **Variation of residual Cd concentration and energy consumption during electrodeposition in function of the deposition time applying a current density of 3.7 mA cm^{-2}.**

3.5 Precipitation

Ni and Mn were completely precipitated at pH = 9 by adding Na_2CO_3. 1 L of $MnSO_4$ (effluent from section 3.4.2) and 1 L of $NiSO_4$ (effluent from section 3.3) needed 65 g and 13 g of Na_2CO_3, respectively, to form the precipitated solids.

However, the $MnCO_3$ and $NiCO_3$ had a low purity due to the co-precipitation of sodium and sulfur. To eliminate Na, K and S, distilled water was intensively mixed with the precipitated solids, and two successive washing steps were necessary. From the experimental results, the average removal efficiencies were determined to be 91 ± 5% for Na, 99 ± 10% for K and 96 ± 2% for S, and $MnCO_3$ of average 7 for Na and 90 ± 1% for S, 0 after two successive washing steps. The average purity of $NiCO_3$ was 97 ± 1%, which is acceptable.

3.6 Mass balance

Fig. 4 presents the chemical products for the input and the metal recovery for the outputs. From this figure, it can be noticed that 109 g of black mass were mixed with 1 L of leaching solution containing sulphuric acid and a reducing agent as mentioned in the previous section. The leach liquor contains 20.8 g of Zn, 28.6 g of Mn, 4.49 g of Ni, 3.57 g of Cd, 0.69 g of Fe and 3.57 g of Co. Firstly, Zn was extracted using Cyanex 272 and stripped using sulphuric acid. Consequently, 16.4 g of Zn were recovered in metallic form by electrodeposition. It could be seen that, the electrodeposition efficiency was determined to be around 85.9% and needed to optimize to maximize Zn-electrodeposition rate. Secondly, Cd and Mn were extracted using D2EHPA and stripped using sulphuric acid. Then, 2.36 g of Cd were selectively electrodeposited and 23.8 g of Mn were recovered as carbonate. The impurities (Co, Mn and Cd) were eliminated

from the Zn-Cd-Mn-depleted solution using Cyanex 272 (extraction at pH = 5.9) to obtain a pure

NiSO$_4$ solution. Approximately 2.38 g of Ni were then recovered as carbonates. The cobalt was

not recovered and remained in the scrubbed solution emerging from the D2EHPA extraction

step and in the stripped solutions emerging from the Cyanex 272 extraction process (extraction

at pH = 5.9). From these results, around 70% of the metals including Zn, Mn, Cd and Ni were

recovered from the solution leach liquor. Further improvements in the performances of metals
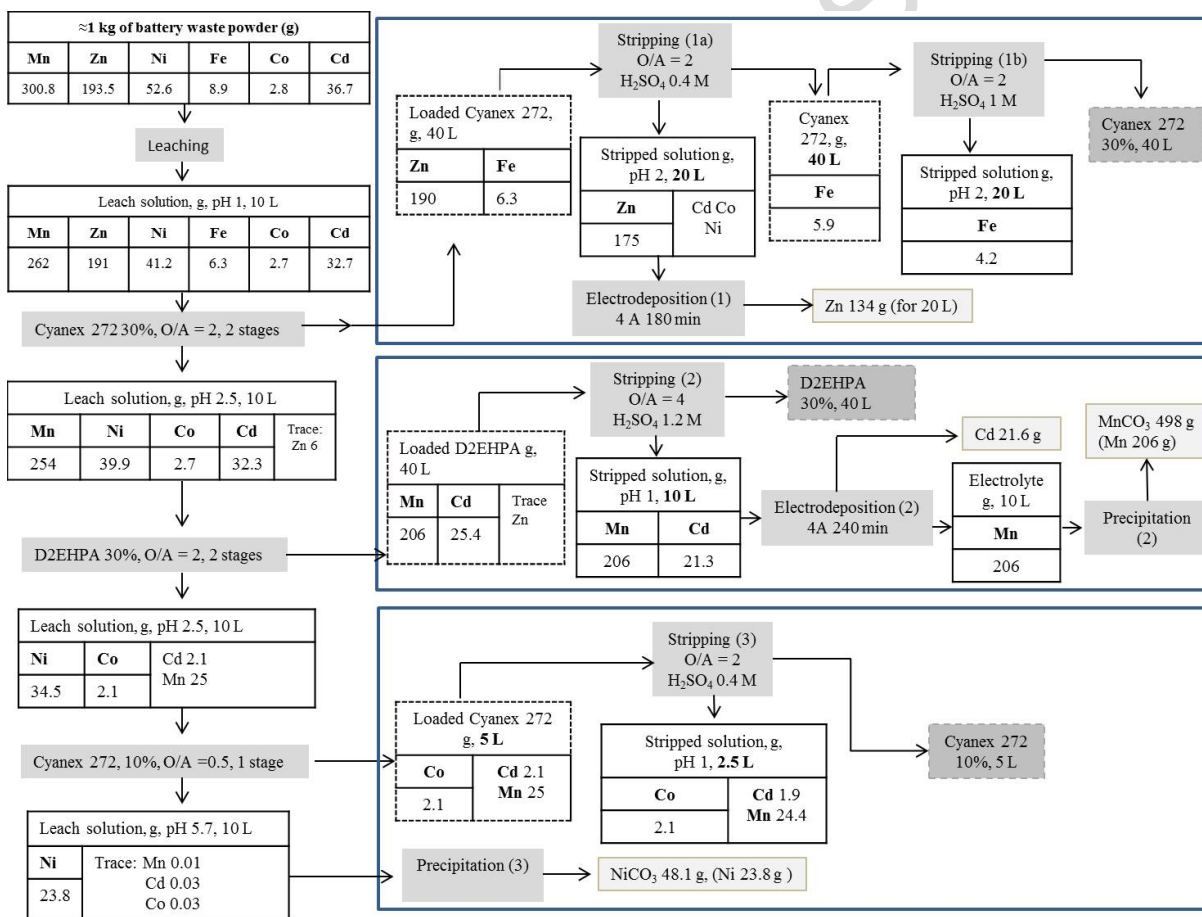
recoveries should be done.

Fig. 4. Metal compounds and chemical products at the different steps of the hydrometallurgical process for the treatment of spent batteries.

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Table 5 shows the volume of water recycled in the process. Ideally, the input and output should be equal. In this present study, the balance errors of water varied between 0.8 and 1.0, which was similar to the study carried out by Janin et al. (2012). A deviation of 20% was found for the $NiCO_3$ precipitation step, which could be due to a water loss during the filtration of the precipitate of $NiCO_3$.

Table 5   Water balance of the metal recycling process from spent batteries.

Inputs		Outputs (Recycle)		Output/Input ratio
Process	Volume (L)	Process effluent	Volume (L)	
Leaching	10	Precipitation (3) ($NiCO_3$)	0.9	0.90
Stripping (1a) - (Zn^{2+} solution)	20	Electrodeposition (1) (Zn)	20	1.00
Stripping (1b) - (Fe^{2+} solution)	20	Water recycling	20	1.00
Stripping (2) - (Cd^{2+} Mn^{2+}solution)	10	Precipitation (2) ($MnCO_3$)	9.5	0.95
Stripping (3)	2.5	Water recycling	2.5	1.00
Washing electrodeposition (1) Zn	5.0	Water recycling	5.0	1.00
Washing electrodeposition (2) Cd	0.3	Water recycling	0.3	1.00
Washing precipitation (2) $MnCO_3$	4.8	Water recycling	4.5	0.94
Washing precipitation (3) $NiCO_3$	1.0	Water recycling	0.8	0.80
Total	68.6	Total	66.6	0.97

Table 6 reveals the metal mass balance for the whole process defined for the treatment of 1 ton of waste battery powder. The sum of outputs (recovered metals) including the leaching residue and the accumulation of metals in the process are equal to the inputs (initial metals in battery powder). In Table 6, from the 193.5 kg of Zn initially present in one ton of battery

powder, approximately 33.9 kg of Zn remained in the solution after the electrodeposition process, 5.8 kg in the Zn-loaded Cyanex 272 and 2.8 kg in the final residue (residue of battery powder). The high accumulation of Zn in the aqueous phase was mainly due to the low electrodeposition efficiencies obtained in the study. A high amount of Mn was found in the aqueous phase (67.0 kg) as well as in the organic phase (44.5 kg) due to the non-effective leaching efficiencies and its accumulation during solvent extraction.

After D2EHPA extraction step, the residual amounts of Mn and Cd present in the aqueous phase were transferred to the Cyanex 272 (10%) organic solvent at pH = 5.7 (See figure 4). Considering the stripping stage, the Cd and Mn stripping efficiencies were not as high as expected.

Non-effective dissolution of Ni (78%) led to the high quantity of Ni in the final residues (11.5 kg) (Tanong, 2016). A high amount of Ni (14.5 kg) was co-extracted with Cd and Co during the D2EHPA and Cyanex 272 extractions. The Co was not recovered and remained in the stripped solution from Cyanex 272 extraction at pH = 5.7

Table 6 **Mass balance of metals defined for the treatment of one ton of battery powder (unity = kg).**

Metals	A	B		C		Metal recovery (%)	Output/ Input (B+C)/A
		Aqueous phase	Organic phase	Solid residual	Recovered metal		
Zn	194± 7	33.9 ± 4.4	5.8 ± 0.7	2.8 ± 0.3	150 ± 2	64	0.99
Cd	50.3 ± 1.9	10.4 ± 0.7	10.2 ± 0.5	3.9 ± 0.2	21.3 ± 0.1	59	0.90
Mn	360 ± 9	67.0 ± 4.5	44.5 ±3.1	38.5 ± 2.7	218 ± 3	73	1.02
Co	2.8 ± 0.2	2.1 ± 0.2	0.5 ± 0.0	0.2 ± 0.0	0.0	-	0.96
Ni	52.7 ± 2.0	3.1 ± 0.4	14.5 ± 1.1	11.5 ± 0.8	21.8 ± 1.1	41	0.97
Fe	8.9 ± 1.4	3.9 ± 0.7	2.6 ± 0.3	2.6 ± 0.3	0.0	-	1.02

A = Input (metals present in battery powder and in scrub solution)

B = Residual of metals in the process

C = Output (metals present in the residue after leaching and recovered metals)

3.7 Chemical agent costs and metal revenue

Table 7 reveals the quantity of each chemical product and their total cost for each assay. The highest quantity of chemical products was used in the leaching experiment, while the lowest chemical quantity was used in the electrodeposition assay. In this study, the organic solvent lost during the process was considered as the quantity of chemical used. In the case of Cyanex 272, D2EHPA, TBP and kerosene, the percentages of organic solvent lost were determined as approximately 50 ppm for each operation. These data were obtained from personal contact with the company. A very high quantity of NaOH was required for neutralization during the organic extraction, and this was the main drawback of the solvent extraction at an industrial scale.

Table 7   **The summary chemical cost in each step of metal extraction and the metal revenues.**

Inputs		Outputs	
Experiment step	Cost (USD t^{-1})	Metals	Revenue (USD t^{-1})
Chemical leaching	219	Zinc	799
Solvent extraction	335	$MnCO_3$	716
Electrodeposition	205	Cd	21.2
Precipitation ($MnCO_3$)	45.9	$NiCO_3$	596
Precipitation ($NiCO_3$)	9.18		
Total	**814**	**Total**	**2132**

In the present study, Zn, Mn, Ni and Cd were recovered in different forms. The final products can be used in many industrial applications. Metallic Zn is widely used in the field of corrosion-resistant coatings and energy storage (Samir et al., 2016). Metallic Cd can be used in many applications, including photovoltaic applications (Rudnik and Nikiel, 2007), coatings for corrosion protection, control rods in nuclear power plants, etc. (Safarzadeh and Moradkhani, 2010). $MnCO_3$ can be used to fabricate anodes in Li-ion products (Aragon et al., 2011). Nickel can be used to produce catalysis, coins, jewellery, batteries, industrial plumbing, nickel alloys, spark plugs, electroplating, machinery parts, stainless-steel, nickel-chrome and resistance wires (Salcedo et al., 2016).

From Table 7, the metal revenue in this study was equal to $2,132 t^{-1} of battery power treated. The total chemical cost was evaluated to be $814 t^{-1} of battery powder treated. It can be seen that the chemical cost is approximately 50% of the metal revenue. It can be concluded that the process is economically feasible.

Solvent extraction, electrodeposition and precipitation were used to selectively recover metals from a PLS to obtain high-purity products (more than 90%). The effluent from the process (recycled water) should be treated with care so as to limit the metals discharged into sewers (Cd = 0.5 mg L^{-1}, Co = 5 mg L^{-1}, Mn = 5 mg L^{-1}, Ni = 2 mg L^{-1}, Zn = 2 mg L^{-1}) (MDDELCC, 2015).

4   Future works and limitations

The pre-treatment method should be further conducted at pilot scale by applying the cryogenics system. The leaching performance should be further improved at pilot scale to obtain the maximum metals yields in leach liquor.

The drawbacks of this study are limited to the use of volatile organic solvents to selectively recover the metals from PLS. At laboratory scale, the problems related to the use of organic solvents were avoided by working in closed systems. Even if the disposal of volatile organic solvent can be problematic and expensive, the long life duration and high recirculation rates in the process of these solvents could compensate the costs related to their disposal. In the future, green solvent such as ionic liquids such as 1-(n-alkyl)-3-methylimidazolium and tetraalkylammonium cations and several anions (hexafluorophosphate, bis[(tri-fluoromethyl)sulfonyl]imide, tetrafluoroborate could be used to replace the volatile organic solvent actually commercialized. Another limitation is due to the low concentration of metals (Zn, Cd) in PLS for the electrodeposition steps. This limitation could be improved by concentrating the metals using solvent extraction.

The possibility to apply this process at pilot or industrial scale depends on many factors including public acceptable related to the use of organic solvent. When green solvents will be

available, the application of this process would be more environmentally friendly. Green solvent could be used to replace volatile organic solvent used in this study to mitigate the environmental and disposal problems due to the expensive costs related to the management of waste emerging from the current solvent extraction process. In conclusion, the experiments were only conducted at laboratory scale, so further researches are necessary at pilot scale to validate the process performances. In addition, the reuse of effluents emerging from precipitation and electrodeposition steps in the process treatment will be studied, so the minimization of wastewater discharged could be achieved.

5   Conclusions

High purities of metal were obtained in this study owing to the solvent extraction process developed. Cyanex 272 and D2EHPA were proved as effective agents for the selective recovery of individual metals. However, there is still needs to improve some processing steps, especially in the electrodeposition stage due to its low current efficiency and the presence of impurities in the deposited metals. When the PLS was used, similar process efficiencies were found for the solvent extraction step as those obtained for the assays carried out with the synthetic solution, where the metals recovering efficiencies were superior to 80% (from PLS synthetic and PLS obtained from the leaching process). However, lower electrodeposition efficiencies were found when the PLS was used instead of the synthetic solution because of the lower initial concentrations of metals. In the present study, only 77% of Zn were recovered by electrodeposition while almost 100% of Zn were electrodeposited from the synthetic solution (same electrodeposition times). For Cd, it was necessary to remove the maximum of Cd from Mn. In the present study, the electrodeposition time required to remove Cd from Mn

(approximately of 99.5% of Cd electrodeposition efficiency) was longer in PLS solution compared to the synthetic solution. In conclusion, 73% of Mn (218.3 kg), 78% of Zn (134 kg), 41% of Ni (23.8 kg) and 59% of Cd (21.6 kg) were recovered per ton of mixture of battery powder.

Acknowledgments

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Figure Caption List

Fig. 1.   Detailed flowsheet of the hydrometallurgical route to treat the mixture of waste

batteries.

Fig. 2.   Variation of residual Zn concentration and energy consumption in two stages of

Zn electrodeposition in function of the deposition time applying a current density

of 370 A m^{-2}.

Fig. 3.   Variation of residual Cd concentration and energy consumption during

electrodeposition in function of the deposition time applying a current density of

370 A m^{-2}.

Fig. 4.   Metal compounds and chemical products at the different steps of the

hydrometallurgical process developed for the treatment of spent batteries.

Table Caption List

Table 1   Unit price of the chemicals used in the process and products obtained at the end of the process

Table 2   Selective extraction performances of Zn from PLS using Cyanex 272 after two stages of extraction (30% (v v^{-1}) Cyanex 272 and 2% (v v^{-1}) TBP in kerosene, O/A = 2/1) at pH = 2.5.

Table 3   Simultaneously extraction performances of Cd and Mn from Zn-depleted PLS using D2EHPA after two stages of extraction (30% (v v^{-1}) D2EHPA and 5% (v v^{-1}) TBP in kerosene, O/A = 2/1) at pH = 2.2 following the scrubbing stage (O/A = 20) and stripping stage (O/A = 4, 1.2 M H$_2$SO$_4$).

Table 4   Removal of the impurities from Cd-, Mn- depleted PLS using Cyanex 272 after one stage of extraction (10% (v v^{-1}) Cyanex 272 and 5% (v v^{-1}) TBP in kerosene, O/A = 1/2) at pH = 5.9 to recover Ni.

Table 5   Water balance of the metal recycling process from spent batteries.

Table 6   Mass balance of metals defined for the treatment of one ton of battery powder (unity = kg).

Table 7   The summary chemical cost in each step of metal extraction and the metal revenue.