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RECOVERY OF METALS FROM HIGHLY CONCENTRATED ACID MINE DRAINAGE BY LIQUID-LIQUID EXTRACTION

UNIVERSIDADE DO ALGARVE
FACULDADE DE CIÊNCIAS E
TECNOLOGIA 2019

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Erasmus Mundus MSc in Chemical Innovation and Regulation

Mestrado Erasmus Mundus em Inovação Química Regulamentação

Trabalho efetuado sob a orientação de:

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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.

ALEMU BEJIGA MELKA

Acknowledgement

I dedicate this thesis
to my wife, and to my children.

Abstract

The growing consciousness and anxiety about the environment have motivated in the recent years extensive research aiming to develop new efficient technologies for the acid mine drainage (AMD) remediation. Such type of pollution is considered of serious concern because of its acidic nature (pH ranges around 2–4), and high concentrations of metals and sulfate. The AMD collected from the inactive São Domingos mine, Portugal for this work has the following concentrations of: 55.2 ± 0.4g/L Fe, 2.60 ± 0.03g/L Zn, 6.2 ± 0.1g/L Al, 4.60 ± 0.07g/L Cu and 123.9 ± 0.2mg/L Mn and 157.2 ± 3g/L of SO_4^{2-}. The recovery of largely used metals such as, copper, zinc and iron, from this type of highly concentrated AMDs is still eco-unfriendly and expensive, thus new recovery strategies should be investigated. In this study, liquid-liquid extraction (LLE) process, involving commercial industrially known extractants and new extractants were tested for the recovery of copper, iron and zinc from the AMD collected at São Domingos mine. Accordingly, the extraction of copper by ACORGA M5640 and the subsequent stripping of the metal with H_2SO_4 solution were optimized. The results revealed that copper can be extracted from such AMD by 30% (v/v) ACORGA M5640 diluted in Shell GTL, making an 8/1 ratio of its active compound (5-nonyl-2-hydroxy-benzaldoxime) to copper ions, with an efficiency of $96 \pm 3\%$. Copper was then efficiently stripped ($95 \pm 2\%$) from the metal loaded organic phase with a 2M H_2SO_4 solution. This organic phase has excellent reuse performance and can be recycled at least 5 times, according to this work and potentially much more times. Its maximum loading capacity of copper from AMD was determined to be 16.15 g/L and the accumulation of copper in the stripping solution in successive cycles reached 46 ± 3 g/L. After copper extraction, iron was successfully extracted from AMD $94 \pm 2\%$) by an ionic liquid diluted in kerosene containing ions from Aliquat 336 and from Cyanex 272 (ALiCY) both in a 3/1 ratio to iron ions to prevent further iron co-extracted with zinc. Complete stripping of Fe ($96 \pm 2\%$) was achieved using also a 2M H_2SO_4 solution. As an alternative, it was confirmed that iron can be simply removed from AMD by adjusting the pH to values between 5 and 6. Concerning the subsequent recovery of zinc, $52 \pm 2\%$ was extracted using a synergistic mixture of 80% D2EHPA and 20% Cyanex 272 (with 18/1 and 4.5/1 ratios to zinc ions, respectively) diluted in kerosene with 3% Tributyl phosphate (TBP), and $99 \pm 2\%$ of this metal was then stripped from such organic phase once again with 2M H_2SO_4.

Key words: Acid mine drainage, metals recovery, liquid-liquid extraction, extractants, ionic liquids.

Resumo

A crescente consciencialização e preocupação acerca da poluição ambiental tem motivado um extenso esforço de investigação procurando o desenvolvimento de novas tecnologias de remediação de drenagem ácida de mina (DAM). Este tipo de poluição é considerado de grande preocupação devido à sua acidez (valores de pH entre 2 e 4) e elevadas concentrações de metais e sulfato. A DAM colhida para este trabalho na mina inativa de São Domingos, Portugal, tem as seguintes concentrações: 55.2 ± 0.4 g/L Fe, 2.60 ± 0.03 g/L Zn, 6.2 ± 0.1 g/L Al, 4.60 ± 0.07 g/L Cu and 123.9 ± 0.2 mg/L Mn and 157.2 g/L of SO_4^{2-}. A recuperação de metais amplamente usados, como o cobre, o zinco e o ferro, deste tipo de DAMs altamente concentradas ainda é ecologicamente hostil e cara, sendo importante investigar novas estratégias de recuperação. Neste estudo foram testados processos de Extração Líquido-Líquido (ELL) com extratantes comerciais industrialmente conhecidos e com novos extratantes para a recuperação destes três metais da DAM colhida na mina de São Domingos. Assim, a extração de cobre com ACORGA M5640 e a subsequente reextração do metal com solução de H_2SO_4 foram otimizadas. Os resultados revelaram que o cobre pode ser extraído desta DAM com 30% (v/v) ACORGA M5640 diluído em Shell GTL, numa razão de 8/1 do seu composto ativo (5-nonyl-2-hydroxy-benzaldoxime) para iões de cobre, com uma eficiência de 96 ± 3%. O cobre foi depois eficientemente reextraído (95 ± 2%) da fase orgânica com uma solução de 2M H_2SO_4. De acordo com este trabalho, esta fase orgânica tem uma excelente capacidade de reutilização, podendo ser reciclada pelo menos 5 vezes e potencialmente muito mais vezes. A sua capacidade máxima de carregamento de cobre foi estimada em 16.15 g/L e a acumulação de cobre na solução de reextração em ciclos sucessivos chegou a 46 ± 3 g/L. Depois da extração de cobre, o ferro foi extraído da DAM com sucesso (94 ± 2%) com um líquido iónico diluído em querosene contendo iões provenientes de Aliquat 336 e Cyanex 272 (AliCy), ambos numa razão de 3/1 para os iões de ferro, para evitar posterior co-extração de ferro com o zinco. A reextração do ferro foi conseguida (96 ± 2%) também com uma solução de 2M H_2SO_4. Como alternativa confirmou-se que uma simples remoção do ferro da DAM é possível com um ajuste do pH para valores entre 5 a 6. No que respeita à subsequente recuperação do zinco, 52 ± 2% foram extraídos utilizando uma mistura sinérgica de 80% de D2EHPA e 20% de Cyanex 272 (com proporções de 18/1 e 4,5/1 para iões de zinco, respetivamente) diluídos em querosene com 3% de Fosfato de Tributilo (TBP), e em seguida 99 ± 2% deste metal foi reextraído desta fase orgânica mais uma vez com 2M H_2SO_4.

Palavras chave: drenagem ácida de mina, recuperação de metais, extração líquido-líquido, extratantes, líquidos iónicos.

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List of Abbreviations

AMD	Acid mine drainage
ANOVA	Analysis of variance
C	Concentration
D	Distribution ratio
D2EPHA	Di-(2-ethylhexyl) phosphoric acid
E_h	Redox potential
FAAS	Flame atomic absorption spectroscopy
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
IL	Ionic liquids
IX	Ion exchange
LLE	Liquid-liquid extraction
MP-AES	Microwave plasma-atomic emission spectroscopy
MSDS	Material safety data
MW	Molecular weight
RO	Reverse osmosis
SHG	Special high grade
SP	Sulfide precipitation
SX	Solvent extraction
TBP	Tributyl phosphate
UV-Vis	Ultraviolet – visible spectroscopy

1. INTRODUCTION

1.1 Environmental impacts of AMD

The growing consciousness and anxiety about the environment have motivated in the recent years extensive research into developing new efficient technologies for the acid mine drainage (AMD) remediation (Johnson and Hallberg 2005) AMD is characterized by high contents of acidity, heavy metals, and sulphates, and its potentially damaging impact when it incorporates into the surface water and groundwater system (Hallberg 2010).

It has been considered as a pollutant of serious concern because of its acidic nature, high content of toxic metal ions (Fe, Zn, Al, Cu, Mn), dissolved anions (sulfates, nitrates, chlorides, arsenates, etc.), hardness, and suspended solids (Tsukamoto and Miller 1999). The pH of AMD ranges around 2–4 (Neculita, et al. 2007). The sulfate concentration ranges from 100 to 5000mg/L (Kolmert and Johnson 2001). Metal-rich mine wastewater is generated due to accelerated oxidation of iron pyrite (FeS_2) and other sulfide minerals during mining activities (Tsukamoto and Miller 1999). AMD exerts negative on environment by changing water quality: adding metals to aquatic ecosystems, altering water chemistry, decreasing the amount of oxygen available for aquatic organisms, precipitation of metals (ferric hydroxide, aluminum hydroxide etc.), leading to reduced availability of light to aquatic ecosystems (Tsukamoto and Miller 1999).

The rate and degree by which AMD pollutes can be increased by the action of certain bacteria which can contaminate drinking water, disrupted growth and reproduction of aquatic plants and animals; and have corroding effects on parts of infrastructures such as bridges. It is not only an ecological concern to the states but an economic concern as well. The significance of the pollution caused by heavy metals is based on three basic reasons: - (1) they are not biodegradable, so they remain indefinitely in the environment, unless transported to other environments; (2) they can be retained by organic tissues through bioaccumulation and then transmitted to other species in a higher level of the tropic chain, thus causing biomagnifications (Kolmert and Johnson 2001); (3) heavy metals can be either essential or not for life. Some of them such as copper, zinc and manganese are necessary micronutrients for some plants and animals, but they can become lethal above certain concentration levels. However, organisms need these metals within an optimal concentration.

AMD generation is one of the most serious types of water pollution, by its nature, extent and difficulty of resolution, as well as the economic costs of traditional remediation. The water bodies affected by this pollution are characterized by their acidity, as well as the high content

of sulfates and heavy metals on the water and the metals content on the sediments. The range of damage by AMD is from sublethal alterations by very weak pollution, which is associated with problems of bioaccumulation and biomagnification to lethal alteration, which associated with the disappearance of the river fauna and loss of water resources by becoming unusable for human, agricultural or industrial use.

Some environmental impacts of AMD are as follows: -

- Because of how corrosive it is, acidic stream water damages infrastructure such as culverts, bridges, and stormwater pipes.
- Drinking water becomes contaminated. Groundwater can be affected, impacting local water wells.
- Waters with a very low pH can support only severely reduced animal and plant diversity. Fish species are some of the first to disappear. In the most acidic streams, only some specialized bacteria survive.
- Any recreational potential (e.g., fishing, swimming) and scenic value for streams or rivers affected by acid mine drainage are greatly reduced.

1.2 Strategic metals in AMD

Acid mine drainage can be highly contaminated by some strategic metals such as copper and zinc, which are widely used nowadays as is indicated for example in table 1. Thus, it can be viewed as a metal secondary source for metals recovery. The importance of some main metals present in AMD are following described

1.2.1 Copper

Copper and its compounds have a very wide range of properties that make them very useful for many applications. Excellent corrosion resistance, good conductivity of electricity and heat is combined with strength and ductility, which are a few of the properties that copper, and its alloys have (Agarwal, et al. 2010). Copper is normally the most cost-effective electrical conductor. Even if silver is a better conductor, it is generally too expensive to use (Agarwal, et al. 2010). Copper metal is widely used because it has several essential properties for different technological applications, such as use in electrical materials and construction, transportation, and industrial machinery parts, which are produced at a higher rate every year. According to world annual data of mining per capita, 19 939 825 metric tons of copper totally produced per year (based on data of 2017 year) (Reichl and Schatz 2019).

There are two main methods employed worldwide to process copper ore for metal production: pyrometallurgical and hydrometallurgical methods (Younger, et al. 2002). Pyrometallurgical processing is extraction and purification of metals by processes involving the application of heat, roasting, or heating in air without fusion, transforms sulfide ores into oxides, the sulfur escaping as sulfur dioxide, to gas. Hydrometallurgy is a method for obtaining metals from their ores. It is a technique within the field of extractive metallurgy involving the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual material (Hiskey 2000).

Table 1: Application of copper in various areas (Hiskey 2000)

Type of market	Copper consumption [million Ibs]	Examples
Construction	2,233	Wiring, heating/refrigeration, & plumbing
Electrical & Electronics	978	Power utilities, cell phones, computers, lighting, & anything with an on/off switch
Consumer & General Products	627	Currency, cookware, household appliances, coins, etc.
Transportation Equipment	982	Airplanes, cars, trucks, trains, etc.
Industrial Equipment	378	Manufacturing machinery, on-site equipment, off-highway vehicles, & transmission lines

Copper is a naturally occurring element, which is presents in the earth's crust, in ocean, and rivers. The sources of copper range from minute trace amounts to rich mine deposits. Copper is an essential element, meaning that all plants, fish and animals need copper to function properly.

According to European Copper Institute, the amount of copper naturally present in the Earth's crust is at a concentration of about 67 parts per million, while most mines operate with copper concentrations of between 0.2 and 0.8 % (w/w) (Younger, et al. 2002). Some of the richest ore bodies are in central to southern Africa and: - can contain 5–6% copper (Lossin 2005).

Copper yield comes from primary sources using hydrometallurgical processes, being a highly developed technology, accounts for about 20% of the world's copper production and till now

a major part of the total copper production (Lossin 2005). Though, copper production from primary sources was outpaced by the global demand for the metal which is expected to continue to grow at a rate of 3.5% over the next few years (Agarwal, et al. 2010). Hence, the recovery of copper from the secondary sector and other waste streams is gaining importance as it cuts down the load on primary sources and presents the solution to the waste disposal problem. The pyrometallurgical route is also found suitable for processing low grade ores and secondary/wastes in the environmentally friendly way.

1.2.2 Zinc

Zinc is an important base metal required for various applications in metallurgical, chemical and textile industries. According to world annual data of mining per capita, 12 527 486 metric tons of zinc totally produced per year (based on data of 2017 year) (Reichl and Schatz 2019).

It is mainly recovered from primary sulfide concentrates. However, according to Jha, et al. (2001), approximately 30% of global zinc production arises from recycling. The growing interest in secondary zinc materials as a valuable resource, and stricter environmental legislation that controls dumping of these hazardous materials, has increased interest in their recycling (Martı́n, et al. 2002). Zinc is also recovered from different secondary resources: - zinc ash, zinc dross, flue dusts of electric arc furnace and brass smelting, automobile shredder scrap, rayon industry sludge etc. which contain different levels of impurities depending on their sources (Younger, et al. 2002). Those materials could be used to recover metallic values, or they may be disposed of. But, the disposal of such materials besides being polluting is now becoming expensive because of increasingly stringent environmental protection regulations. Furthermore, the chemical nature of these dust particles is such that they are classified as hazardous waste. The toxicity is mainly due to the presence of different metals: - lead, cadmium, arsenic, chromium etc. (Matthew, et al. 2014). In view of the above, there has been an increasing interest in developing processes for the recovery of zinc from other secondary sources/wastes. Recovery of zinc from a secondary source, should produce a less residue which could be recycled or safely disposed-off without affecting the environment.

Usually, pyrometallurgical and hydrometallurgical processes are employed for treating such secondary sources. A major drawback of the pyrometallurgical method is high energy requirement and need of dust collecting/ gas cleaning system (Cole and Sole 2003). The presence of chloride and fluoride salts in the dust causes severe corrosion problems and necessitates the use of expensive alloys as construction materials. The hydrometallurgical

processes are more environmentally suitable and economical to treat even low zinc containing materials on small scale. It is possible to process secondary materials containing different impurities. Different hydrometallurgical processes developed on bench, pilot and commercial scale are described in the literature (Cole, et al. 2005). The metal from the leach solution is recovered by different methods such as precipitation, crystallization, solvent extraction, ion exchange, electrowinning etc. (Cole, et al. 2005; Gibert, et al. 2004).
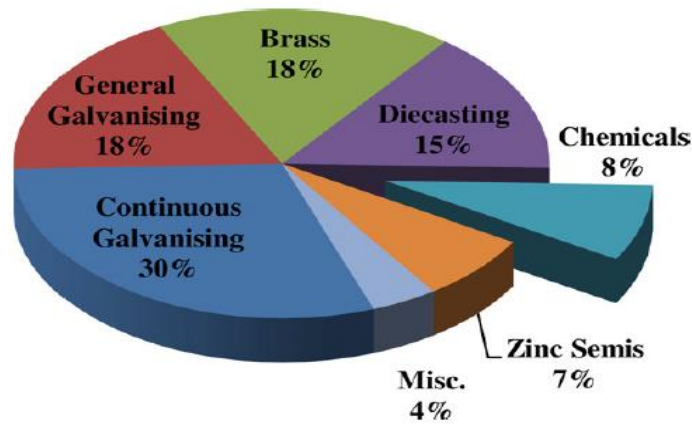
Figure 1: Various uses of zinc metals (Moezzi, et al. 2012)

Most zinc ores occur as the sulfide and, as such, are amenable to upgrading by flotation. The traditional treatment route includes smelting of the concentrates followed by hydrometallurgical processing to produce electrolytic zinc metal. Limitations imposed by this approach have led to the search for alternative purely hydrometallurgical routes for the processing of both ore and concentrate. Direct ore processing could also enable the economic exploitation of some complex ores that yield low upgrading recoveries. Hydrometallurgical processing of concentrates would avoid the generation of sulfur dioxide gas and would be more flexible with respect to the grade of feed material that is treatable. The inclusion of solvent separation step in potential process flowsheets could also accommodate difficult-to-treat concentrates, such as those with high lead or halide contents Integration with Bioleaching An interesting approach to the hydrometallurgical treatment of sulfides is the use of bacterial leaching for solubilizing the valuable metals. Under different conditions, the application of bioleaching to sulfide materials can generate leach liquors with zinc concentrations ranging from 50 to 120 g/L (Martı́n, et al. 2002). The main impurities in such streams typically include copper, iron, cobalt, nickel, cadmium, calcium, and magnesium. Following a bulk iron-removal step (typically by precipitation), LLE has been successfully used to produce ultrapure electrolytes suitable to produce Special High Grade (SHG) zinc cathode from a variety of bioleach liquors (Buslaeva, et al. 2009; Dı́az, et al. 1994). It is

significant to notice the high lead and chloride contents of some of these materials, which render conventional processing difficult. The recycling of these secondary zinc sources is becoming increasingly important, as zinc-containing materials are classified as hazardous and environmental legislation prohibits dumping of this material. Direct recycling tends to be costly and can deleteriously affect the operation of the primary plant. Several pyrometallurgical processes have been implemented for the treatment of secondary materials (Dı́az, et al. 1994), however, these generally are only efficient for a constant composition feed and need to have a high production capacity to be economically viable. Some materials are not amenable to treatment by this route, and environmentally acceptable discharges are not always assured.

1.3 Liquid-liquid extraction (LLE)

LLE, also called solvent extraction, SX, is a separation technique that can be used to separate compounds. When applied to the separation of metals from metal-bearing aqueous solutions; it is performed in two main steps: extraction and stripping processes as outlined in Figure 2.
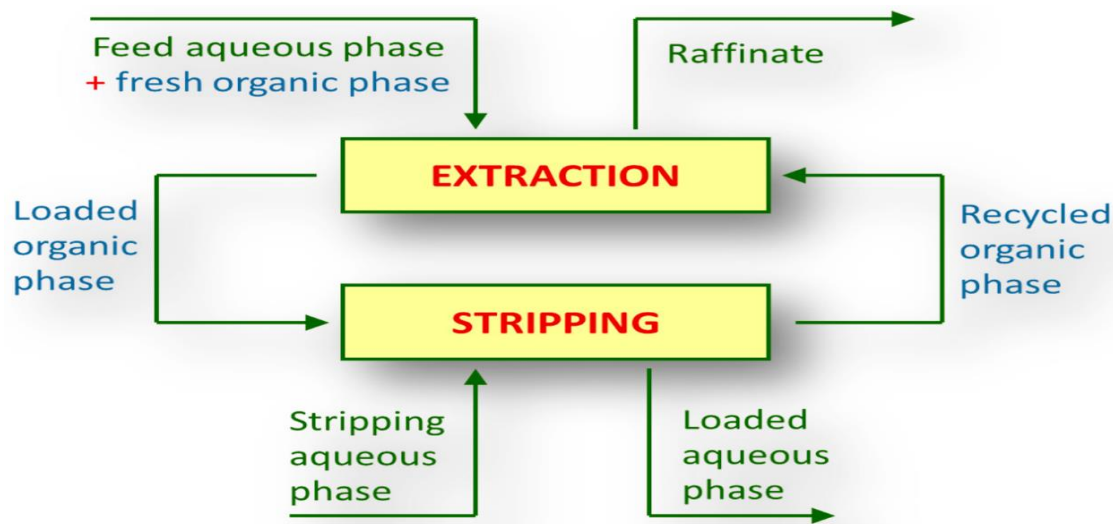
Figure 2: Liquid-liquid extraction and stripping scheme applied for metals recovery (Paiva 2017)

LLE is a separation process consisting of the transfer of a solute from one solvent to another, the two solvents being immiscible or partially miscible with each other (Berk 2013). As in all extraction processes, LLE comprises a step of mixing (contacting) followed by a step of phase separation. It is important to consider both steps in the selection of solvents and modes of operation (Berk 2013). Thus, while vigorous mixing is favorable to the transfer of the extractable from one solvent to the other, it may also impair the ease of phase separation by forming emulsions (Owusu 1998). The solvent that is enhanced in solute is called extract. The feed solution that is drained in solute is called the raffinate. In the extraction process the

transference is from the aqueous to the organic solvent and the solvent that becomes enriched with solute(s) (referred as "Loaded organic phase in Figure 2) is called the extract while the feed solution that is depleted in solute(s) is called the raffinate.

Stripping is the opposite of extraction: the transference of mass is from organic to aqueous phase. It is the removal of the extracted solute from the organic phase to more stable medium for further processing or analysis. The conditions employed depend upon solute (s) and the extraction system and are such that they promote the reversal of extraction. High-purity single solutes may be obtained in aqueous phase streams of 'stripping' processes.

Distribution ratio; is the ratio of the analytical concentration of a substance in the organic phase to its analytical concentration in the aqueous phase, normally at equilibrium.

The distribution of the concentration of solute between two immiscible solvents can be described by the distribution ratio "D".

$$D = \frac{[A]_{Org}}{[A]_{Aq}} \qquad (1.1)$$

Where [A] represents the stoichiometric or formal concentration of a substance A and the subscripts Org and Aq refer to the organic and aqueous phases respectively.

In LLE, modifier is an important reagent in some cases. It used to make clear phase separation and to avoid emulsification. Modifier is a substance that is added to a solvent to improve its properties e.g. by increasing the solubility of an extractant, changing interfacial parameters or reducing adsorption losses. According to Bonnesen, et al. (2000), the effect of oxygen-containing diluents (modifiers), such as alcohols, ethers, and ketones, on the extraction of Cu with LIX65N/n-heptane and LIX-65N/xylene57 has been investigated. The distribution of Cu decreases with addition of the modifier, as a result of the formation of an intermolecular complex between extractant and modifier (Yoshizuka, et al. 2007; Bogacki, et al. 2000).

LLE plays an important role in multistep chemical processing and has advantages such as low energy consumption when compared to distillation as well as suitability for purification of thermally sensitive compounds. It is one of the capable methods to separate valuable metal ions from diluted effluents.

1.3.1 Extractants and Diluents in LLE

An extractant in LLE is a substance primarily responsible for the transfer of a solute (metal in this work) from one phase (usually aqueous) to the another (usually organic). The extractant should be completely dissolved in a suitable organic diluent and both are the organic solvent (Agarwal, et al. 2010). The solvent composed by the extractant and diluent should be immiscible with the aqueous phase. The extractant may react with the solute by several ways: solvation, chelation and ion pair formation, thus extracting the specie of interest from the aqueous phase to the organic phase. Extraction performance is strongly dependent on the characteristics of an extractant. The extractant and the extraction process should obey to the following requirements (Owusu 1998): -

1. High capacity for the species that has to be extracted

2. High selectivity to the species of interest

3. High ability of an the extractant to remove the solute of interest from the aqueous feed phase into the organic phase.

4. High ability of the extractant–solute species to be stripped from the loaded organic to new purified aqueous strip.

5. Rapid kinetics of extraction and stripping.

6. Stability of the extractant.

7. No side reactions.

8. No irreversible or degradation reactions.

9. Low solubility of the extractant in the aqueous phase.

10. Low coextraction of water.

11. Extractant should be easily regenerated.

12. Extractant should have suitable physical properties, such as density, viscosity, and surface tension.

13. Low toxicity for biological systems and low corrosivity.

14. Reasonable price at industrial applications.

Liquid-liquid extraction with chelating agents as selective extractants is an important process for wastewater treatment as well as for commercial separation and recovery of metals from aqueous solutions of different compositions (Agarwal, et al. 2010).

Extraction of metal ions from aqueous solution is a potential method for the concentration, separation and preparation of high purity metal. It releases up the possibility of using poor

mineral resources, semi-finished products and industrial waste containing small quantities of the metals in it.

Currently the other interesting option for extractants is using ionic liquids as extractants. Ionic liquids are 'designer solvents' composed entirely of ions. Ionic liquids show unique properties such as nonvolatility, thermal stability, nonflammable nature, lower reactivity, strong ability to dissolve a large variety of organic and inorganic compounds (Didier, et al.2013). Their physicochemical properties are controllable by changing discrete cations and anions (Sun, et al. 2012). With brilliant technical potential, tunable compounds can be developed as functionalized ionic liquids containing certain functional groups. Most results have been obtained by using ionic liquids as diluents (Atanassova, et al. 2002; Belova, et al. 2012), while during the exploration of the extraction of rare earths, more and more work has been reported on designing ionic liquids as highly efficient extractants (Rout, et al. 2012; Rout and Binnemans 2014). Ionic liquids (ILs) have generated substantial interest across a wide variety of engineering applications, with their use as media for green synthesis (Buslaeva et al. 2009). CO_2 capture, removal of fermentation products and pharmaceuticals (Pereira, et al. 2010), and appearing to be especially promising as solvents or extractants for liquid–liquid extraction (Rout, et al. 2012 and Cieszynska and Binnemans 2010) and hence, for supported liquid membrane processes (Kulacki and Shermata 2008). For industrial liquid–liquid extraction applications it is necessary to consider the long-term behavior of the IL used, specially its stability (Kulacki and Shermata 2008; Torrecilla, et al. 2009).

Ionic liquids having low volatility, flammability and greater stability, have been used as solvents (Matthew, et al. 2014). The recent trend in liquid−liquid extraction is to use them as extractants (Cieszynska 2010). Zinc and iron for example extracted from chloride media using trihexyl (tetradecyl) phosphonium chloride (Cyphos IL 101) and trihexyl (tetradecyl) phosphonium bis (2,4,4-trimethylpentyl) phosphinate (Cyphos IL 104) (Cieszynska and Binnemans 2010).

Effective Ionic liquid used for Iron extraction is the combination of two commercial extractants, trioctylmethylammonium chloride (Aliquat 336) and bis 2, 4, 4-trimethylpentyphosphinic acid (Cyanex 272) rather than using them separately (Cieszynska and Binnemans 2010).

A diluent is a diluting agent used to dissolve the extractant in the organic phase and to reduce the viscosity of the extractant. Diluents also help to reduce the tendency of the emulsification of the extractant. Similarly, they improve the dispersion and coalescence properties of the solvent. The diluent must be a good solvent for the extractant and the extracted species. It

must have a very low solubility in the aqueous phase, a low volatility, a high flash point, a low surface tension, and it must be economic and readily available. It is often assumed that the diluent merely acts as a solvent for the extractant and that it has no active role in the extraction process. Though, the diluent can have a large effect on the distribution ratios (Marcus 1998). The extraction of the metal to the organic phase is influenced by the physical properties of the diluent: density, viscosity, dielectric constant and solubility parameters (Reichardt 2003). In general, aromatic diluents have higher densities than aliphatic diluents, which may impede the dispersion and coalescence. The polarity of the diluent has a considerable effect on the extraction efficiencies. The average degree of polymerization increases with a decrease in polarity of the diluent and the presence of polymeric forms decreases the loading capacity of the extractant. Diluents affect the solvation of the extractant and, hence, its extractive properties (Marcus 1989).

In many cases, the distribution ratios cannot be correlated to the physical properties of the diluent, even though many attempts have been made to do so (Taube 1959, 1960; Healy 1961).

The more polar diluents cyclohexanone, chloroform and 1-octanol exhibited the lowest distribution ratios.

1.3.2 Liquid-liquid extraction of copper

Table 2: Summary of some selected extractants and suitable diluents for copper extraction, pH and the reference used for the detail description

Extractant	Diluent	Target metal	pH	Reference
Acorga M5640	Solvesso 100	Cu (II)	1.75	Algucil et al., 2004
LIX 984N	kerosene	Cu (II)	0.53-0.71	Sridhar et al., 2009
LIX 84-I and LIX 622N	kerosene	Cu (II)	1.3	Sengupta et al., 2007
LIX 84	kerosene	Cu (II)	2	Parija and Blaskar., 2000
LIX 622 and LIX 64N	kerosene	Cu (II)	1.3	Whewell et al., 1979
Kelex100	Isoctanol	Cu (II)	0.24	Bogacki et al., 2000
Acorga M5640	Shell Sol D70	Cu (II)	N/A	Agarwal et al., 2012
Almine LM	Kerosene	Cu (II)	0.5-3.5	Marchese et al., 1995

| Stable sandwich - SLM | Cu (II) | 2.5 | Wang et al., 2015 |

The liquid-liquid extraction of copper is usually carried out with hydroxyoxime extractants and β-diketones (Agarwal, et al. 2010). The most widely used copper extractants, recognized by their usual selectivity, are hydroxyoxime-type organic acids as is the case of Acorga M5640 and Lix-extractants (Owusu 1998). Among these reagents, alkylsalicylaldehyde derivatives are the most used, being able to extract copper from sulphate acidic media (Agarwal, et al. 2010). The equilibrium reaction of copper (II) ions using these extractant has attracted interest and relatively recently several models have been proposed (Alguacil, et al. 2004). According to Agarwal, et al., (2012), Acorga M5640 was designed to optimize metallurgical performance relative to ketoxime- based extractants while providing protection against nitration. Designed to protect against oxidative degradation, it reduces extractant consumption and improve operational reliability (relative to conventional extractants) when oxidizing conditions are present and therefore enabling technology ensures high-quality organic is returned to the solvent extraction circuit (Alguacil, et al. 2004). Diluents are mainly used as solvents for extraction of metals and must be suited for the selected extractants, the effect of diluents on the solvent extraction of metal ions has been studied for copper (Whewell, et al. 1979; Wionczyk and Apostoluk 1997; Mitchell and Banks 1969; Alguacil, et al. 1987; Cai, et al. 2016; Mountcastle, et al. 1971).
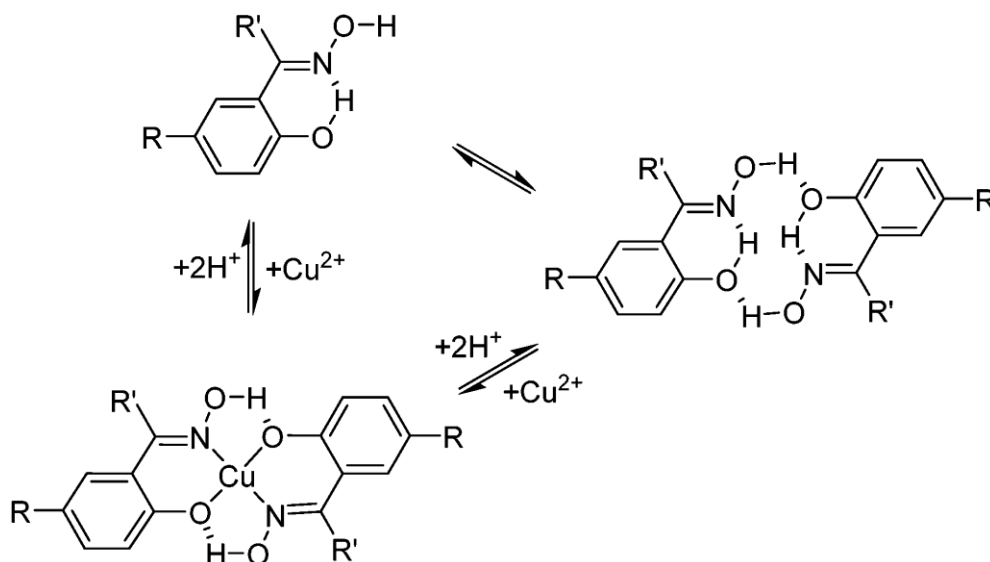
Figure 3: Pre-organisation of phenolic oxime extractant (Acorga) ligands formation and the pseudo-macrocyclic structures of their Cu(II) complexes (Matthew, et al. 2014).

1.3.3 Liquid-liquid extraction of Zinc

According to Cole and Sole (2003) and Deep and Carvalho (2008), various kinds of extractants are used in liquid-liquid extraction processes aiming to; concentrate and purify zinc from the leaching solutions, such as; Di-(2-ethylhexyl) phosphoric acid (D2EHPA), TBP, Bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and the synergistic of D2EPHA and Cyanex 272. Among the reagents used, organophosphorous acid based extractants play a significant role in extraction of zinc. D2EHPA was successfully applied as an excellent selective extractant for zinc (Daryabor, et al. 2017). For example, Kongolo, et al. (2003) studied the ability of D2EHPA for extraction of zinc from sulphate solution achieved by oxidative leaching of copper smelter slag and the obtained results indicated that about 90% zinc can be extracted with 20% (w/w) D2EHPA in kerosene at 25 °C, using a aqueous organic ratio (A/O) = 1 and pH = 3. As another example, Pereira, et al. (2007) reported that D2EHPA diluted in kerosene is an effective solvent for extraction of zinc from phosphoric acid solution (~94.9%) and industrial effluents (~98%), respectively. Cyanex 272 is another alternative extractant, which has effectively been used to extract and concentrate the zinc (Ali, et al. 2006).

The synergistic use of both extractants (D2EHPA and Cyanex 272) for LLE of zinc has been studied and proved to increase the efficiency (Tahereh, et al. 2017). According to their study, 59.01% extraction performance of zinc was achieved from synthetic zinc sulfate solution prepared in laboratory at (Conditions: 25 °C, pH 3, agitation rate of 450rpm, contact time of 25min by using the synergistic of 80% (v/v) D2EHPA and 20% (v/v) Cyanex 272. 42% of zinc extraction was achieved using a mixture of 15% (v/v) D2EHPA and 5% (v/v) Cyanex 272 from sulfate leach solution at 23 °C and at pH 3 (Ahmadipour, et al. 2011). They also employed TBP as modifier and found that TBP has no influence on the recovery. Although many studies have been performed to develop reagents for the selective extraction of zinc from leachates, the information on solvent extraction of zinc from sulphate solution derived from leaching of the mixed sulfide-oxide samples and the synergistic effects of extractants such as TBP, D2EHPA and Cyanex 272 are limited and hence requires more detailed investigations.

Further studies on LLE of zinc and its optimization has also been employed for the purification of zinc from acidic leach solutions obtained from the secondary sources (Anderson and Reinhart 1979; San Lorenzo, et al. 1982; Diaz, et al. 1994; Lindermann, et al. 1994; Jha, et al. 2001). The process is found suitable for selective extraction of zinc from secondaries, environmentally safer, techno economically feasible and flexible to fit several

secondaries (Diaz, et al. 1994). The impurities that commonly occur in zinc process include iron, copper, manganese, cobalt, and nickel (San Lorenzo 1982). Iron is one of the most troublesome impurities in zinc processing (Lindermann, et al. 1994; Jha, et al. 2001). According to Anderson and Reinhart (1979) iron is quantitatively extracted by organophosphorus extractants and forms more stable complexes than those of zinc. Lindermann, et al. (1994), has investigated methods of overcoming the iron co-extraction problem in zinc extraction circuits. Verbeken, et al. (2000) have demonstrated an electroreduction process for stripping iron from D2EHPA. The strip liquor, comprising 2 M H_2SO_4, is continuously recycled via an electrochemical cell where iron (III) is reduced to iron (II) (Diaz, et al. 1994; Xue, et al. 2001).
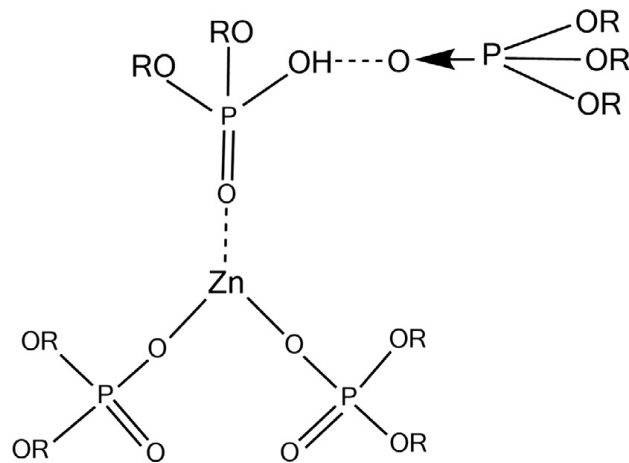
Figure 4: The possible structure of the extracted complex of zinc with D2EPHA and TBP (Azizitorghabeh, et al. 2016)

1.4 Scope of the study

This study was performed in the framework of METALCHEMBIO project which aims to employ liquid-liquid extraction methods in combination with biological processes (based on plants and bacteria) to investigate the extraction and recovery of metals from different contaminated metals-bearing wastewaters, including highly concentrated AMD.

There is a major increase of gross demands for copper and zinc as the result of their increasing utilization in current technologies and a lack of new primary sources for these metals (Lossin 2005; Agarwal, et al. 2010, 2012; Jha, et al. 2001; Matthew, et al. 2014; Younger, et al 2002; Alguacil, et al. 2004) Therefore, it is urgent to develop and/or optimize environmentally friendly and cost effective; selective processes for their recovery from secondary sources.

There are several methods such as; oxidative precipitation, metal reduction methods such as Cu cementation, solvent extraction (SX), sulfide precipitation (SP), reverse osmosis (RO), evaporation, ion exchange (IX), electrowinning/electroplating, electrowinning with solvent extraction or ion exchange, solvent extraction with ion exchange that have been employed for the recovery of metals from the secondary sources (acid mine drainage) to increase their supply and to make the wastewater environmentally friendly (Matthew, et al. 2014; Ahmadipour, et al. 2011; Pius, et al. 2017).

LLE is one of the metal separation process employed to recover metals from secondary sources. Copper was recovered from synthetic sulfate leach solution by LLE using Acorga M5640 in Solvesso 100 diluent (Alguacil, et al. 2004), and from real and synthetic sulfate solution using LIX984N, LIX622N and LIX64 extractants in kerosene (Sengupta, et al. 2007; Parija and Bhaskara 2000; Sridhar, et al. 2009). Iron was extracted from synthetic and real metallic sulfate solution by LLE using Aliquat 336, Cyanex 272, Cyphos 101,104 and AliCy extractants (Verbeken, et al. 2000; Azizitorghabeh, et al. 2016; Alguacil, et al. 1987) and from chloride and ammoniacal solutions (Alguacil, et al. 1987; Keppler, et al. 2012; Perez, et al. 2010). LLE of zinc from synthetic sulfate solution was achieved by using D2EPHA, TBP, Cyanex 272 and the synergistic mixture of two extractants (Tahereh, et al. 2017) and from chloride and ammoniacal content real and synthetic wastewater (Gallardo, et al. 2008; Bogacki, et al. 2000; Cai, et al. 2016; Dalton and Quan 1993; Diaz, et al. 1994)

In this study LLE of copper, iron and zinc were tested to evaluate and compare their efficiencies using several selected known commercial and ionic liquid extractants based on a bibliographic review for the state of the art of copper, iron and zinc recovery from this type of real wastewater (AMD) for the first time. The optimization of selected extractants in terms

of; concentration, kinetics, isotherms, loading capacity and reutilization was investigated. The stripping using different stripping agents was also tested and optimized.

1.5 Objective of the study

The general objective of this work was to test and optimize the recovery of strategic metals from a highly contaminated AMD; by liquid-liquid extraction processes. Therefore, the specific objectives of this study were (i) to review and list the main commercial extractants able to remove copper and zinc from metals bearing wastewaters, (ii) to investigate the efficiency of promising extractants to extract these metals from a sample of the highly contaminated AMD (iii) to evaluate promising stripping agents able to remove these valuable metal ions from the loaded organic phases or able to specifically remove other metals eventually co-extracted with them, (iv) to estimate maximum capacities of selected extractants and (v) to test the reutilization of the selected extractants in successive extraction and stripping cycles.

In this study, LIX-extractants (LIX 622, LIX 54, LIX 864 and LIX 622N), Acorga M5640, just D2EPHA, the synergistic of D2EHPA and Cyanex 272 the commercial ionic liquid, Cyphos 104 and a home-made ionic liquid composed mixtures of Aliquat 336 and Cyanex 272 (AliCY) extractants in diluents of Kerosene, Toluene, Shell sol D70 and shell GTL and using the modifiers Octanol and TBP were tested. Stripping agents, such as H_2SO_4, HNO_3, HCl, $C_2H_2O_4$ (Oxalic acid), $(NH_4)_2SO_4$ and distilled water were also attempted.

2. MATERIALS AND METHODS

2.1 AMD collection

The sample used in this work was collected on 25 October 2018 from São Domingo's mine located in south east Portugal, on the left margin of Guadiana River, near the Spanish frontier, namely from a small dam located beside the ruins of two reactors from the old sulfur factories of Achada do Gamo known to have AMD highly concentrated due to continuous accumulation and evaporation cycles along the years (Figure 5). The all vast area of mining activities, from the mine to the site where the ore was processed at the Achada do Gamo factories and the large heap deposits in the surrounding areas, depicts a significant environmental footprint, the most prominent concern being related to AMD and subsequent release of hazardous elements on soils and waters: acidity, sulphate and metals (mainly Al, Fe, Cu, Zn and Mn) (Neculita, et al. 2007; Sheremata and Kuyucak 1996).

A   B
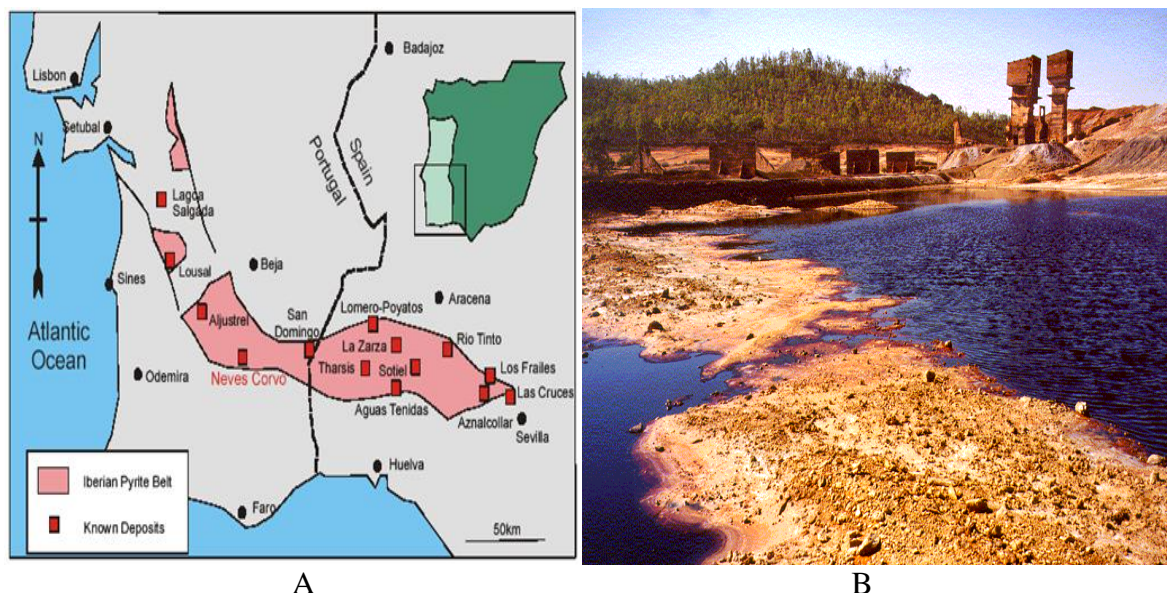
Figure 5:– A) Domingos mine in the Iberian Pyrite Belt (from https://www.sec.gov/Archives/edgar/data/1377085/000120445907001642/lundintechrep.htm) ; B) Photo of the AMD sampling site at Achada do Gamo lagoon with pH <2 waters.

2.2 Liquid-liquid extraction procedures

The extraction experiments were carried out by mixing specified volumes of AMD (aqueous phase) and diluted extractants (organic phases) at room temperature (25 ± 2 ºC), with mixing conditions varying according to the different organic phases being tested and to the objectives of each experiment. Larger volumes (10 to 70 mL total (both phases)) were mixed in 100 mL round bottom flasks using magnetic stirrers and smaller volumes (2 to 10 mL total) were mixed in centrifuge tubes shaken in the horizontal position to increase the contact surface using an orbital shaker, in both cases with rotation speeds in the range of 250 to 600 rpm to

ensure the maximum mass transfer and during 1 to 60 minutes depending on the objective. The volume ratio of aqueous to organic phase A/O varied for the extraction isotherms and some extractant/metal ratios tested but was kept at 1:1 for the other equilibrium experiments. The concentration of the extractant in the organic phase was in the range of 5 to 30% (v/v). Afterwards, in the experiments with larger volumes the phases were separated using separating funnels having capacity of 100 mL and in the cases with smaller volumes transference pipettes were used to collect both phases separately. The initial (raw AMD) and final (AMD after the LLE test) concentrations of Cu, Fe, Zn and Mn in the aqueous phases were determined by FAAS and the concentration of Al by MP-AES and the concentrations of these metals in the organic phases were computed by mass balance. The pH in the aqueous phase was also measured, using a pH/E Meter GLP 21 (Crison).

2.2.1 LLE to extract copper from AMD

2.2.1.1 Screening of extractants

Commercial extractants

Several known commercial extractants selected based on a bibliographic review for the state of the art of LLE of copper were tested to evaluate and compare their efficiencies for copper recovery from this type of AMD for the first time: Acorga M5640 (formerly from Cytec, which was acquired by Solvay), LIX 54, LIX 622, LIX 622N, LIX 864 formerly from Cognis, which was acquired by BASF In this experiment, 15% (v/v) of each extractant diluted in a kerosene-like diluent called Shell GTL with 3% (v/v) of Tributyl phosphate (TBP) as a modifier were tested in duplicates using a A/O of 1:1 and with a contact time of 30 minutes with magnetic stirring.

Ionic liquids

In addition, following the current trend of trying to profit of the advantages of ionic liquids, the ionic liquid Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos 104) and the bifunctional home-made ionic liquid trioctylmethylammonium/2,4,4-trimethylpentyl phosphinate synthesized from the two commercial extractants trioctylmethylammonium chloride (Aliquat 336) and bis 2,4,4-trimethylpentyphosphinic acid (Cyanex 272), thus called AliCy (Fortuny, et al. 2012) or A336/Cy272 (Devi 2016) were also tested for the first time with this type of metals bearing wastewater.

In the experiment with Cyphos 104, a 0.04M concentration % (v/v)) diluted in Toluene was tested without any modifier in duplicates using a A/O of 1:1 and with a contact time of 30 minutes with magnetic stirring. In the experiment with AliCy, two home-made solutions were

tested: one with both extractants diluted in kerosene and another with both extractants diluted in a kerosene like solvent called Shell Sol D-70. In the case of Aliquat 336, octanol was added to a concentration of 10% (v/v) to facilitate the dilution of this highly viscous extractant; yet its complete dilution was achieved just after overnight contact at room temperature. Devi (2016) determined the loading capacity of 0.1 M AliCy for copper to be 1.71 g/L using aqueous synthetic solutions of copper (II) sulphate pentahydrate. Therefore, in this work it was estimated that 0.3M AliCy would be enough to extract the 4.6 g/L of copper in the AMD using a A/O of 1:1. To prepare AliCy the procedures described by Fortuny, et al. (2012) were followed with minor modifications: equimolar concentrations of Aliquat 336 and Cyanex 272 (0.3M each in this work) in organic solvent were mixed and two times successively washed for 10 minutes with an aqueous solution of 0.5M $NaHCO_3$ in a A/O ratio of 1:1, using vigorous stirring in bottom round flasks kept open to allow the release of large amounts of CO_2 emitted when mixing, and using separation funnels to separate the washing solution from the AliCy. In order to replace the Cl^- anion from Aliquat 336 and the H^+ from the Cyanex 272, $HNaCO_3$ 0.5 M is added with vigorous shaken to promote the ALiCY formation.

The reactions involved in the process could be:

$R_4NCl + HCy \longrightarrow R_4NClHCy$

$R_4NClHCy + NaHCO_3 \longrightarrow R_4NCy + CO_2\uparrow + NaCl + H_2O$
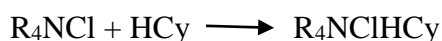
The LLEs of copper form the AMD with the two home-made AliCy ionic liquids (one in kerosene and the other in Shell Soll D-70) were tested in duplicates using a A/O of 1:1 and with a contact time of 30 minutes with magnetic stirring.

In neither these sets of screening experiments, with the commercial extractants or with the ionic liquids, stripping of metals from the organic phases was tested.

2.2.1.2 LLE of copper from AMD with selected extractant – Acorga M5640

Among all the extractants tested in the screening experiments, Acorga M5640 revealed the best results to recover copper from this type of AMD, when combining both criteria of extraction efficiency and specificity.

Acorga M5640 is a mixture of 5-nonyl-2-hydroxybenzaldoxime the active compound (Figure 6) with a modifier, a fatty ester, 2,4,4-trimethyl 1,3-pentanediol di-isobutyrate, diluted in petroleum distillate hydrotreated light. Agarwal, et al. (2012), determined the content of active reagent of Acorga M5640 by using the maximum uptake of copper to be at 57%,

which is in the range of 30-60% documented the product's Material Safety Data Sheet (MSDS).
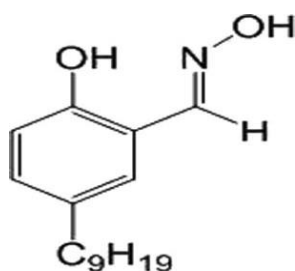
Figure 6: Structure of the active reagent (5-nonyl-2-hydroxy-benzaldoxime, MW = 263.38 g/mol) of Acorga M5640 (Agarwal, et al. 2010).

Several experiments were carried out to characterize the LLE of copper from such a highly concentrated AMD using Acorga M5640, aiming to determine optimal conditions and limits for the process:

- to optimize the efficiency of copper extraction, increasing concentrations of Acorga M5640 (10%, 20% and 30% (v/v), in a kerosene like solvent called Shell GTL with 2.5% octanol as a modifier, where tested in triplicates using a A/O of 1:1 and with a contact time of 1 hour with magnetic stirring.

- a first round of stripping tests with 0.1M H_2SO_4, 0.1M HNO_3, 0.1M HCl and distilled H_2O, was carried out in duplicates using a A/O of 1:1 and with a contact time of 1 hour with magnetic stirring.

- a second round of stripping tests with 1M H_2SO_4, 2M H_2SO_4, 1M HNO_3 and 2M HNO_3 was carried out in duplicates using a A/O of 1:1 and with a contact time of 1 hour with magnetic stirring.

- the reutilization of the organic phase was tested in five successive cycles of extraction and stripping, using always the same organic phase (30% Acorga M5640 in Shell GTL with 2.5% of modifier octanol) but new AMD and new stripping solution (2M H_2SO_4) in each cycle, in triplicates, with a A/O of 1:1 and with a contact time of 1 hour with magnetic stirring.

- to estimate the maximum loading capacity of copper on the organic phase, increasing A/O ratios (1:1, 2:1, 3:1, 4:1, 5:1 and 6:1) were carried out in duplicates, using 30% Acorga M5640 in Shell GTL plus 2.5% of octanol, with a contact time of 1 hour with magnetic stirring.

- to confirm the maximum capacity estimated in the previous experiment, three consecutive cycles of extraction without stripping were carried out in triplicate, using always the same organic phase (30% Acorga M5640 in Shell GTL with 2.5% of modifier octanol) but using

new AMD in each cycle, in triplicates, with a A/O of 1:1 and with a contact time of 1 hour with magnetic stirring.

- to estimate the maximum loading capacity of copper on the 2M H_2SO_4 stripping solution, consecutive cycles of extraction and stripping steps were carried out in triplicate, using always the same stripping solution but using new organic phases (30% Acorga M5640 in Shell GTL with 2.5% of modifier octanol) loaded with copper, with a A/O ratio of 1:1 and with a contact time of 1 hour with magnetic stirring.

- to study the kinetics of copper extraction from this AMD different contact times (1, 5, 15, 30, 60 min) with magnetic stirring were tested in duplicates, using 30% Acorga M5640 in Shell GTL plus 2.5% of octanol with a A/O of 1:1.

2.2.2 LLE to extract iron from AMD

2.2.2.1 Screening of extractants

Although none of both ionic liquids tested revealed good results for copper extraction in the previous screening tests, the results obtained with the home-made ionic liquid called AliCy revealed specificity to extract iron from this type of AMD (shown in results and discussion section). In addition, among the commercial extractants screened, LIX 54 also exhibited this feature. This specificity for iron extraction is very important to allow further recovery of zinc, another valuable metal highly concentrated in this type of AMD. Indeed, the most known commercial extractants to recover zinc from metals bearing wastewaters (e.g. D2EHPA and Cyanex 272) have the drawback of co-extracting iron. (Azizitorghabeh, et al. 2016; Perez de los Rios, et al. 2010).

Therefore, aiming to test the capacity to recover iron from copper-free AMD, the 0.3M home-made AliCy (both AliCy solutions previously prepared with kerosene and with Shell Sol D70 mixed in a 1:1 ratio) and 15% (v/v) LIX 54 solutions in Shell GTL and in Shell Sol D70 were further tested in duplicates using copper-free AMD (collected after LLE with Acorga 5640 / Organic phases) with A/O ratios of 1:5 and with a contact time of 30 minutes with magnetic stirring.

2.2.2.2 LLE of iron from copper-free AMD with selected extractant – AliCy

Among the two extractants tested in the screening experiments, the home-made AliCy revealed the best results to recover iron from the copper-free AMD, when combining both criteria of extraction efficiency and specificity.

Therefore, several experiments were carried out aiming to test and optimize the recovery of iron from the copper-free AMD collected after LLE with Acorga 5640:

- to optimize the efficiency of iron extraction, decreasing A/O rations of copper-free AMD / 0.3M home-made AliCy in kerosene (1:1, 1:5, 1:10 and 1:15) were tested in duplicates with a contact time of 30 minutes with magnetic stirring.

- a round of stripping tests with 2M H_2SO_4, 2M HNO_3, 2M HCl, 2M $C_2H_2O_4$ (Oxalic acid), 2M $(NH_4)_2SO_4$ and distilled water was carried out in duplicates using A/O ratio of 1:1 and with a contact time of 30 minutes with magnetic stirring.

2.2.3 LLE to extract zinc from AMD

2.2.3.1 Screening of extractants

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) has been successfully applied as an excellent selective extractant for zinc from different types of metals bearing waters (Healy 1961; Tahereh, et al. 2017). Moreover, it has been proven that synergistic extractions with D2EHPA and other extractants is an important variant that can be used to increase the extraction and separation of zinc (e.g. Ahmadipour, et al. 2011; Azizitorghabeh, et al. 2016). More recently, Tahereh, et al. (2017) reported that a mixture with 80% D2EHPA and 20% Cyanex 272 exhibited the best ratio for a synergistic effect to extract zinc from a sulphate leach liquor obtained from a sulfide-oxide based tailing sample.

Therefore, since the AMD generated at the São Domingos mining area is also a sulphate leach liquor, an experiment was carried out in duplicates to test the extraction of zinc from the AMD sample collected for this work using just D2EHPA (0.9M in kerosene with 3% TBP) and using a synergistic mixture of 80% (v/v) of a 0.9M D2EHPA solution (in kerosene with 3% TBP) and 20% of a 0.9M Cyanex 272 solution (in kerosene with 3% TBP) (making 0.72M D2EHPA and 0.18M Cyanex 272 in kerosene with 3% TBP), with a A/O ratio of 1:1 and a contact time of 30 minutes with magnetic stirring.

2.2.3.2 LLE of zinc from copper-free and iron-free AMD with selected extractant - synergistic mixture of 0.72M D2EPHA and 0.18M Cyanex 272

The LLE tests with a synergistic mixture of 0.72M D2EHPA and 0.18M Cyanex 272 revealed better results for the recovery of zinc from copper-free AMD water than the LLE tests just with 0.9M D2EHPA, in terms of extraction efficiency and specificity.

Therefore, several experiments were then carried out aiming to test and optimize the recovery of zinc from the copper-free and iron-free AMD:

- to test the efficiency of zinc extraction, LLE tests were carried out in duplicates using a mixture of 0.72M D2EHPA and 0.18M Cyanex 272 in kerosene with 3% TBP as extractant and a copper- free and iron-free AMD successively collected after LLE with Acorga 5640

and LLE with AliCY as the aqueous phase, with a contact time of 30 minutes with magnetic stirring.

- a stripping test with 2M H_2SO_4 was carried out in duplicates using a A/O of 1:1, with a contact time of 30 minutes with magnetic stirring.

2.3 Reagents and Equipment

The standards used to build the calibration curves for metals analysis by flame atomic absorption spectroscopy and microwave plasma atomic emission spectroscopy were prepared from standard stock reagents with concentrations of 1000 ± 2 mg/L: Fe, Cu, Zn and Al (Certipur Merk); Mn (AA Panreac).

A magnetic stirrer (Hei-Tec; Heidolph) was used for the extraction and stripping experiments. The stripping reagents were prepared from HCl (37%, Analytical reagent grade, Fisher Scientific), HNO_3 (65%, Merck Kommanditgesellschaft auf Aktien), H_2SO_4 (96%, Pronalab) and deionized water.

A flame atomic absorption spectrophotometer (FAAS, novAA 350, Analytik Jena, Jena, Germany) was used to analyze the concentrations of Fe, Cu, Zn and Mn, while a microwave plasma-atomic emission spectroscopy (MP-AES, Agilent Technologies, 4200) was used to determine the concentration of Al in the aqueous phases before and after extraction, as well as in the stripping solutions. Glass pH electrode (VWR, SJ) was used for pH measurements. A centrifuge (Hettich ROTOFIX 32A) was used for separation of solid and liquid phases.

3. RESULTS AND DISCUSSION

3.1 Initial AMD characterization

The AMD used in this work was collected in the inactive Sao Domingos Mine, in southeastern Portugal close to the border with Spain. This mine is in the Iberian Pyrite Belt (IPB), one of the largest metallogenetic provinces of massive polymetallic sulfides in the world, and the mining activity in this region goes back thousands of years and has been very intense in the last two centuries, having produced considerable amount of residues which deteriorate the environment of the mining areas and surroundings, mainly due to acid mine drainage (AMD) (Álvarez-Valero, et al. 2008; Pérez-López, et al. 2008). The sulfide oxidation processes are producing AMD leachates, a source of pollution rich in sulfates, iron, copper, zinc, aluminum and manganese, and hence a threat to the ecologic equilibrium. It is a subject of great environmental concern as acid mine water flows through several kilometers downstream of the mine and reaches a river, causing its partial pollution (Abreu, et al. 2010). The sample used in this work was collected from a small dam beside the ruins of two reactors from the old sulfur factories of Achada do Gamo. A brief characterization of this AMD sample was done, and their results are shown in Table 3.

Table 3: Initial characterization of the Acid mine drainage (AMD) sample from Mina de São Domingos (Pond next to the sulfur factory ruins at Achada do gamo) collected in 25/10/2018.

Parameter	Average	Standard Deviation*	Units
[Cu]	4603	69	
[Zn]	2589	31	
[Fe]	55240	367	
[Mn]	123.9	0.2	mg/L
[Al]	6221	125	
[SO_4^{2-}]	157200	-	
pH	1.19	-	Sorensen scale
Eh	469	-	mV

* Technical standard deviations for three readings made for metals analysis with FAAS and MP-AES systems.

The initial concentration of AMD sample (Table 3) was highly concentrated. A study by Ballester, et al. (2016) shows that AMD collected from São Domingos mine, Mértola was also highly concentrated, however, the tested parameters have lower concentrations compared to the present result. The high concentration of the present result might be due to evaporation,

sampling site, sampling time or successive cycles of accumulation. Similar suggestions were given from previous studies, they suggested that, the extremely high level of pollution measured and its variation from this site is due to successive cycles of accumulation and evaporation (Matos, et al. 2004; Álvarez-Valero, et al. 2009; Pérez-López, et al. 2008; Mateus, et al. 2011).

3.2 Screening of extractants to extract copper from AMD

3.2.1 Commercial extractants

Under the same conditions, commercial extractants such as, LIX 622N, LIX 54, LIX 864, LIX 622 and Acorga M5640 in Shell GTL were tested for the first time recover copper from such a highly concentrated AMD sample collected from São Domingos mine. The results of extracted Cu, Al, Zn, Fe and Mn for the different extractants are presented in Figure 7. Among the five tested extractants, Acorga M5640 and LIX 622 were specific to extract just copper while LIX 864, LIX 54 and LIX 622N co-extracted zinc and iron. $85 \pm 1\%$ of the initial copper was extracted from the aqueous phase to the organic phase containing Acorga M5640 and $37 \pm 4\%$ was extracted with LIX 622 (Figure 7). LIX 54 (a β-diketone derivative) looks like preferable to extract iron than copper from this AMD sample just $2 \pm 1\%$ of copper was extracted using LIX 54, but $20 \pm 1\%$ of iron was co-extracted.

The comparison of test data shows that extraction systems using the hydroxy oxime reagents like Acorga M5640 are preferred over the one with β-diketone reagent (Alguacil, et al. 2004; Marchese, et al. 1995). The authors investigated the extraction of copper using Acorga M5640 from synthetic wastewater prepared by adding desired quantity of standard copper sulfate solution which had a pH adjusted to 2.5. Katarzyna and Tomasz (2013) and Lili, et al. (2018), also investigated the extraction of copper from prepared copper sulfate solutions with very low pH. They also chose hydroxy oxime-based reagents as the best extractant based on a few criteria: good stability of reagent, no propensity towards emulsion formation, low number of extraction stages and low amount of acid needed in stripping stage.

In another example, Moore, et al. (1999) demonstrated that, the ester modified Acorga M5640 provided the highest copper recovery of all the reagents tested at the same reagent strengths in synthetic solutions containing copper sulfate in deionized water and pH < 2.

That is, the results obtained in this work, revealing that Acorga M5640 ensures better copper recovery from a real highly concentrated AMD (Figure 7) are consistent with results achieved by other authors with synthetic waters.

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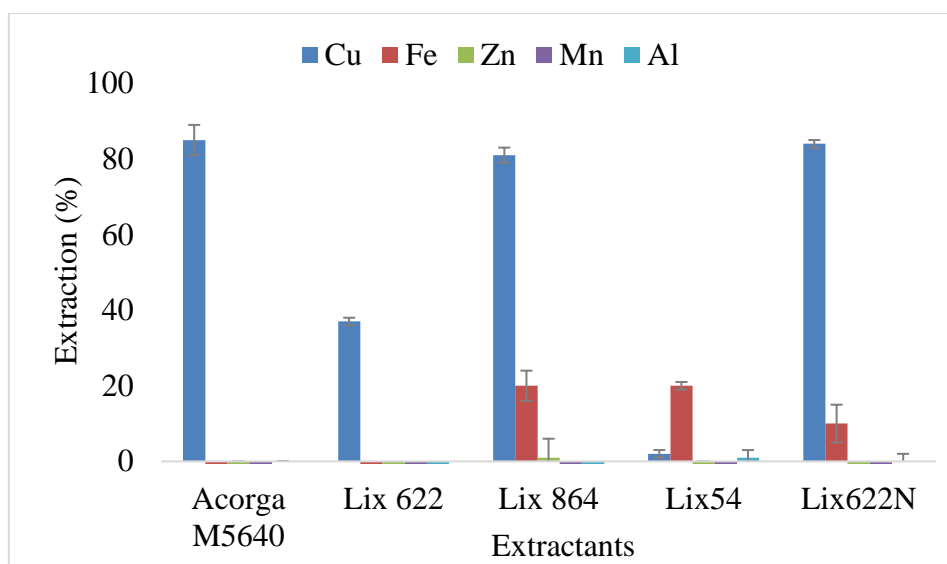
Figure 7: Screening of extractants for copper separation from AMD, with 15% (v/v) of each extractant diluted in Shell GTL + 2.5% (v/v) octanol and using an A/O = 1/1 and a contact time of 30 minutes at room temperature (25 ± 3 ℃). Results are averages of 3 replicates and the error bars are standard deviations.

3.2.2 Ionic liquids

To compare the extraction ability of two ionic liquid as extractants diluted in organic solvents, the home-made AliCY (A336/Cy272) prepared as described in the Materials and Methods section and Cyphos 104, were tested (Figure 8).

The AliCY (A336/Cy272), either diluted in kerosene or in Shell Sol exhibited higher extraction efficiency towards iron (18 and 35%) rather than copper (4 and 11%), while the Cyphos 104 showed almost no extraction ability for the metals tested under this study.

Regarding AliCy, the results achieved in this work with real AMD water confirm the results obtained by Devi (2016) using synthetic solutions containing copper and other metals in sulfate medium. The author reported a novel solvent extraction process for extraction and separation of copper from other base metal ions using A336/Cy272 (a synonymous of AliCy) in kerosene even though it extracted preferentially iron over copper.

On another hand, Cyphos IL 104 has been reported for the extraction of different metal ions such as Zn, Pd, Co, Ni, Fe, Ga from chloride solutions (Perez de los Rios, et al. 2010). Yet, Devi (2016) when focusing on the recovery of gallium found that 0.005 M Cyphos IL 104 diluted in Toluene co-extracted (11.3%) copper from a synthetic binary solution containing 0.001 M of each of both metals Ga (III) and Cu (II) in 3M HCl. In this study 0.04 M Cyphos IL 104 was tested to extract copper from AMD for the first time and only 4 ± 2 % was extracted.

According to Keppler, et al. (2012), a broad application of ionic liquids in extraction processes is limited by their relatively high cost, still largely unknown toxicity and long-term stability. The costs of some recently developed ILs, for example, [Aliquate 336] is lower in making their application more attractive (Keppler, et al. 2012). Moreover, fundamental knowledge regarding biodegradability, aquatic toxicity, or in general the environmental fate of ionic liquids is still needed, in order to estimate the potential of the ionic liquid-based technology. Moreover, the distinct water solubility of ILs strongly influences their stability as extracting agents, their reusability and their environmental impact (Keppler, et al. 2012).
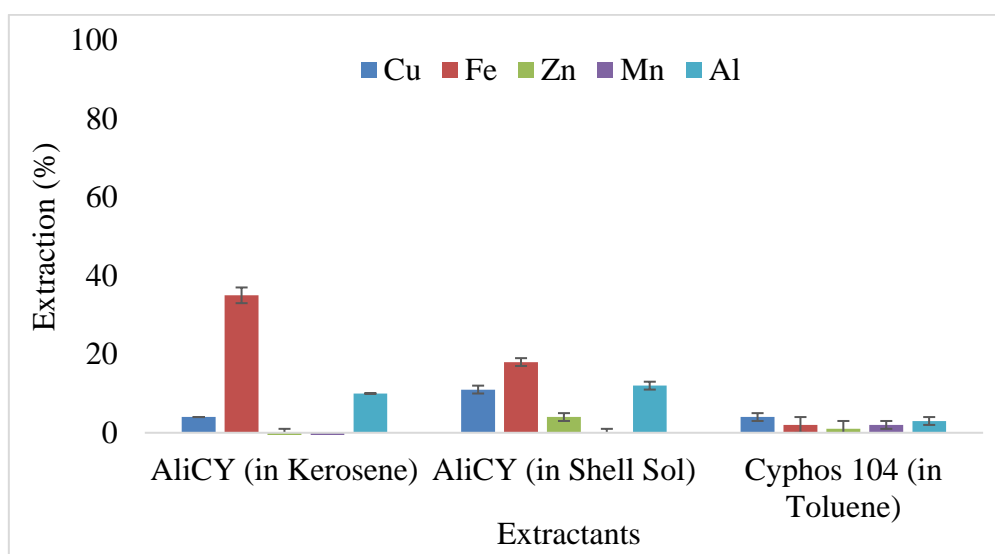
Figure 8: Extraction efficiency of 03M methyltrioctyl/decylammonium bis 2,4,4-(trimethylpentyl) phosphinate ionic liquid (ALiCY IL) in Shell Sol D70 and in Kerosene, and 0.04 M Cyphos 104, in toluene, using an A/O = 1/1 and a contact time of 30 minutes at room temperature (25 ± 3 ºC). Results are averages of 2 replicates and the error bars are mean absolute deviations.

3.3. Optimization with extractant selected for copper - ACORGA M5640

Based on the results obtained in section "3.2 Screening of extractants to extract copper from AMD", the extractant Acorga M5640 was selected for the subsequent experiments to optimize and characterize the extraction of copper from the AMD collected at São Domingos mine. The efficiency of examined systems was estimated considering few parameters, namely organic phase loading, concentration of copper in the raffinates, recyclability of the organic phase (contained Acorga M5640) and contact time. All obtained results of each parameters will be discussed in upcoming sections.

3.3.1 Extractant/copper ions ratios

The effect of Acorga M5640 concentration on the extraction and separation of copper was investigated (Figure 9). The copper extraction percentage enhanced significantly from 45.0 ±

2% to 96.0 ± 3% as Acorga M5640 concentration increased from 5% to 30% (v/v) in the organic phase. With 30% (v/v) Acorga M5640 (0.57 mol/L of the active compound (5-nonyl-2-hydroxy-benzaldoxime), 4.55g/L (0.072 mol/L) of copper was extracted, which makes a 8/1 ratio of active compounds to copper ions. In fact, this is a third of the 24/1 ratio reported for the optimal Acorga M5640 concentration of 20% (v/v) using an aqueous phase with 1 g/L Cu at pH 1.4 by Agarwal, et al., (2010). According to Agarwal, et al. (2010), in both cases (real metallic sulfate solution containing 1.17g/L of Cu and synthetic solution containing 1.0g/L of Cu) followed similar trends, the maximum extraction of copper achieved with 20% (v/v) Acorga M5640 at pH 1.35. They obtained 99% extraction efficiency in real sulfate leach solution, which was the same values as obtained from synthetic solution in their study.

The results of Alguacil and Alons (2005), concerning extraction of copper from Iberfluid solution containing 0.16M of Copper at pH 2.0, 0.72 M of Acorga M5640 was the optimum condition.
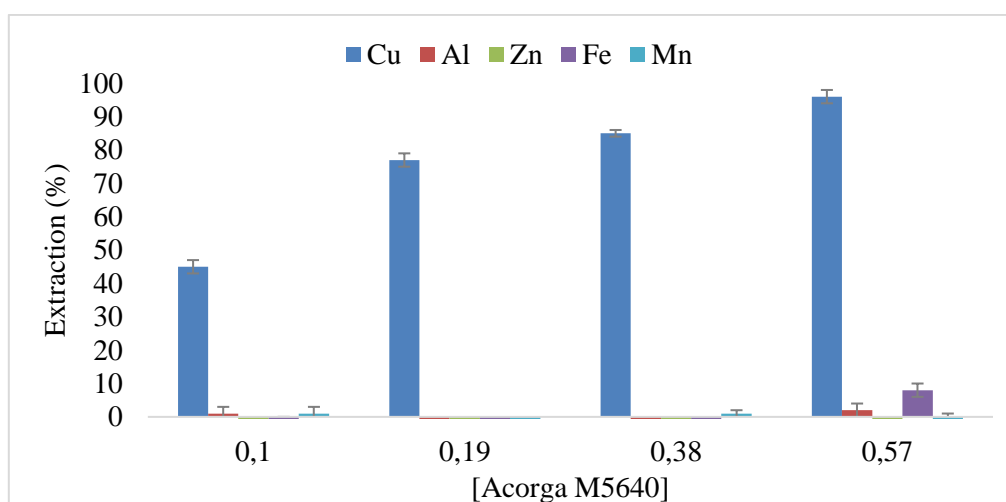
Figure 9 : Extraction efficiencies of Acorga M5640 at concentrations: 5, 10, 20 and 30 % (v/v) (0.1 M, 0.19 M, 0.38 M and 0.57 M, respectively), diluted in Shell GTL + 2.5 % (v/v) octanol, using an at A/O = 1/1 and 60 minutes contact time at room temperature (25 ± 3°C). Results are averages of 3 replicates and the error bars are standard deviations.

3.3.2 Contact time (kinetics)

The effect of different contact times on the extraction of copper from the sample of AMD from São Domingos mine was studied using 30% (v/v) Acorga M5640 (Figure 10). The maximum extraction of copper was reached after approximately 15 minutes, when more than 96% of copper was transferred into the organic phase. These results are in accordance with previous studies performed by other authors with synthetic waters. According to Sridhar, et al. (2009), the extraction equilibrium of copper was achieved after 10 minutes using Acorga M5640 in the prepared copper sulfate synthetic wastewater.

In another example, according to Alguacil and Alons (2005), equilibrium of copper extraction from aqueous solutions which contained 1 g/L copper by 10% (v/v) Acorga M5640 in Iberfluid, was generally reached within 10 minutes of contact and beyond this no further improvement was achieved. Such fast kinetics of extraction is critical to guide industrial production (Duan, et al. 2017). However, even if over 96% copper extraction was already reached at 15 minutes, 60 minutes was used in subsequent experiments to ensure the optimum equilibrium.
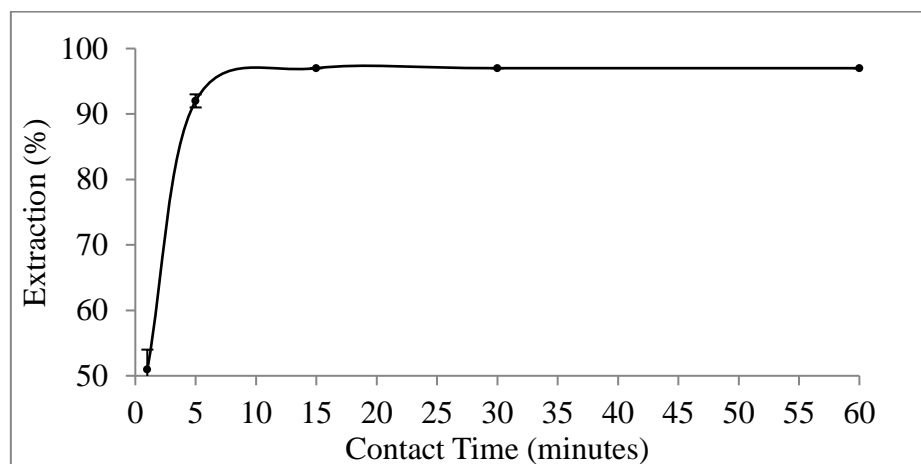
Figure 10 : Copper extraction efficiency of 30% v/v ACORGA M5640 in Shell GTL + 2.5 % (v/v) octanol, using an A/O = 1/:1 and (different contact times:- 1, 5, 15, 30 and 60 minutes) at room temperature (25 ± 3°C). Results are averages of 2 replicates and the error bars are mean absolute deviations.

3.3.3 Estimation of the maximum loading capacity of copper on the organic phase

The loading capacity of copper extracted from the sample of AMD collected at São Domingos mine to 30% (v/v) Acorga M5640 was determined by plotting the equilibrium isotherm for copper extraction with increasing quantities of copper available in the LLE (Figure 11). The results reveal excellent extraction performance of copper from AMD to the tested organic phase with a saturating capacity of 16.15 g/L of copper.

The obtained result (16.15 g/L) at equilibrium isotherm for copper extraction using 30% (v/v) Acorga M5640 is attractive compared to the previous study. For example, Agarwal, et al. (2008) was reported that, 7.64g/L of copper was loaded to the organic phase at O/A ratio of 1/4 from copper bleed stream.
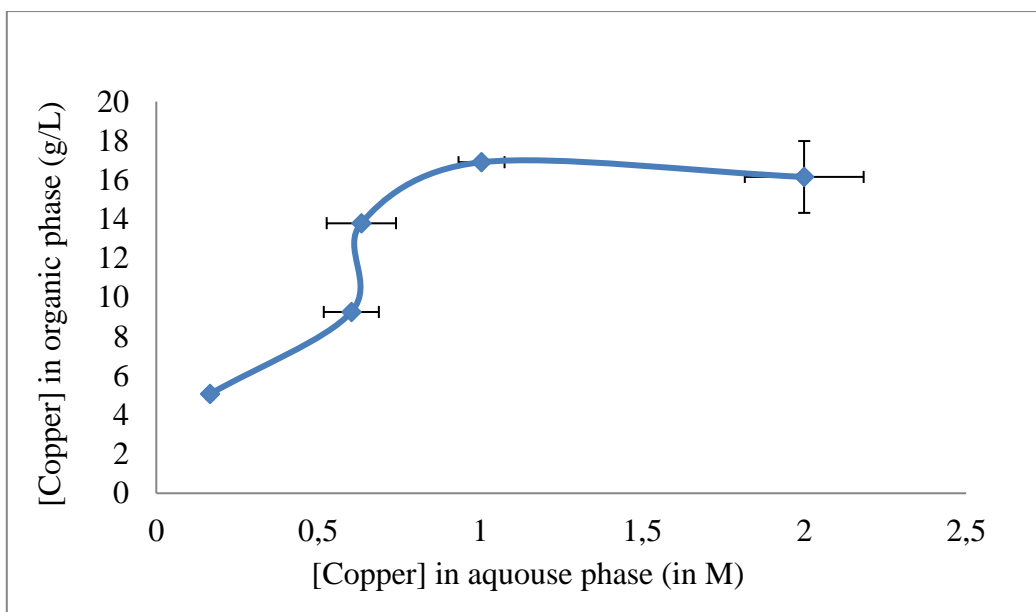
Figure 11 *:* Isotherm at equilibrium for the extraction of copper, build with different A/O ratios (1/1 to 5/1) using 30% (v/v) Acorga M5640 in Shell GTL + 2.5 % (v/v) octanol and, contact time of 60 minutes at room temperature ($25 \pm 3^{\circ}$C). Results are averages of 2 replicates and the error bars are mean absolute deviations.

3.3.4 Building up copper concentration in the organic phase

To confirm the loading capacity determined in the previous experiment carried out to build the isotherm of extraction capacity and test successive cycles to build up copper concentration in the organic phase, three consecutive cycles of extraction without stripping were carried using always the same organic phase but new AMD in each cycle (Table 4). The results confirm the capacity of accumulating concentrations up to the 16 g/L of copper in 30% (v/v) Acorga M5640 in Shell GTL + 2.5 % (v/v) octanol by performing successive cycles of extraction from AMD collected at São Domingos mine, without stripping.

Table 4 : Copper concentrations at equilibrium in three consecutive cycles of extraction without stripping, using the same organic phase (30% Acorga M5640 in Shell GTL with 2.5% octanol) but new AMD in each cycle, with an A/O = 1/:1 and 60 minutes contact time at room temperature ($25 \pm 3^{\circ}$C). Results are averages of 3 replicates ± standard deviations.

Cycle	[Copper] in final organic phase (g/L)	[Copper] in final aqueous phase (g/L)
1	$5,06 \pm 0,02$	$0,17 \pm 0,01$
2	$11,53 \pm 0,02$	$0,345 \pm 0,007$
3	$16,111 \pm 0,007$	$0,64 \pm 0,03$

3.3.5 Stripping agents for copper

Different stripping agents were examined for the re-extraction of copper from loaded organic phases (Figure 12 and 13). First it was verified that, sulfuric acid had higher net transfer capacity than nitric acid, hydrochloric acid and deionized water (Figure 12). Then, it was observed that 2M H_2SO_4 was effective for re-extracting all copper extracted from the São Domingos AMD sample to the organic phase composed of 30% (v/v) Acorga M5640 in Shell GTL + 2.5% (v/v) octanol (Figure 13).

The contact of Acorga M5640 with nitric acid degrades the active substance of the extractant, on the other hand, sulfuric acid is not as oxidizing agent as nitric acid and is widely used as stripping reagent in copper liquid-liquid extraction (Alguacil and Alons 2005). In fact, according to Alguacil and Alons (2005), Acorga M5640 is a strong extractant for copper removal and H_2SO_4 is the best stripping agent to strip the net copper from the organic phase.

The copper decomplexation at the stripping interface given by Eq. (3) (Sengupta, et al. 2007).

$$CuR_{2(org)} + 2H^+_{(aq)} + SO^{2-}_{4(aq)} \leftrightarrow Cu^{2+}_{(aq)} + 2HR_{(org)} + SO^{2-}_{4(aq)} \tag{3}$$
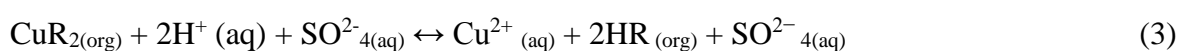
Figure 13 illustrates the variation of copper stripping percentage after a period of 1hour at different H_2SO_4 concentrations. When the concentration of H_2SO_4 increased from 1M to 2M, the transport percentage of copper was increased from 95% to 99%. By considering the stripping efficiency of copper, 2M H_2SO_4 was selected as the optimal concentration of sulfuric acid in the stripping solution for subsequent investigations.

Similar results were published by Sengupta, et al. (2007), showing that 2M H_2SO_4 was the optimum condition to strip all copper loaded in organic phase to the aqueous stripping phase.
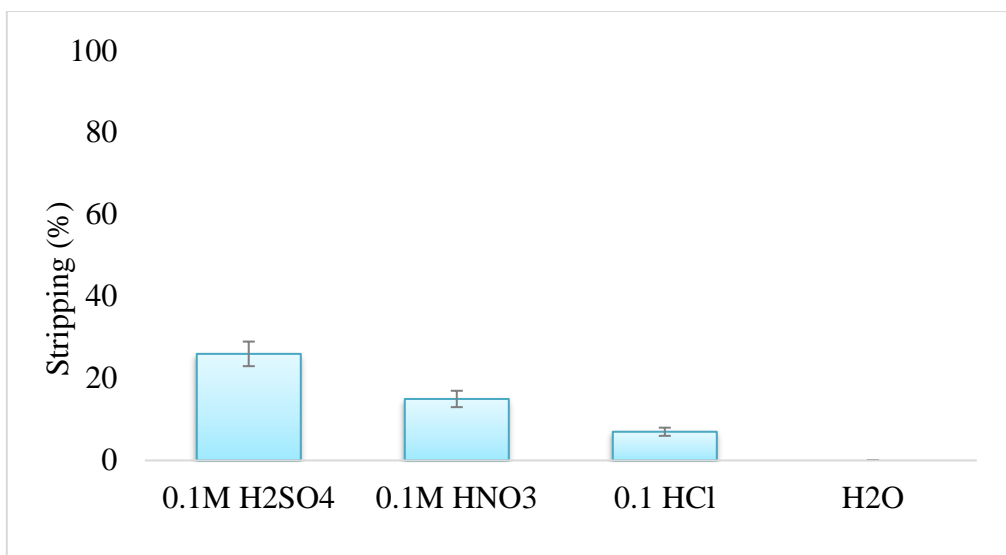
Figure 12 : Copper stripping efficiency of sulfuric acid, nitric acid and hydrochloric acid at 0.1M and of distilled water from an organic phase of 10% (v/v) Acorga M5640 in Shell GTL + 2.5% (v/v) octanol, with an A/O = 1/1and contact time of 60 minutes at $25 \pm 3^{\circ}C$. Results are averages of 2 replicates and the error bars are mean absolute deviations.
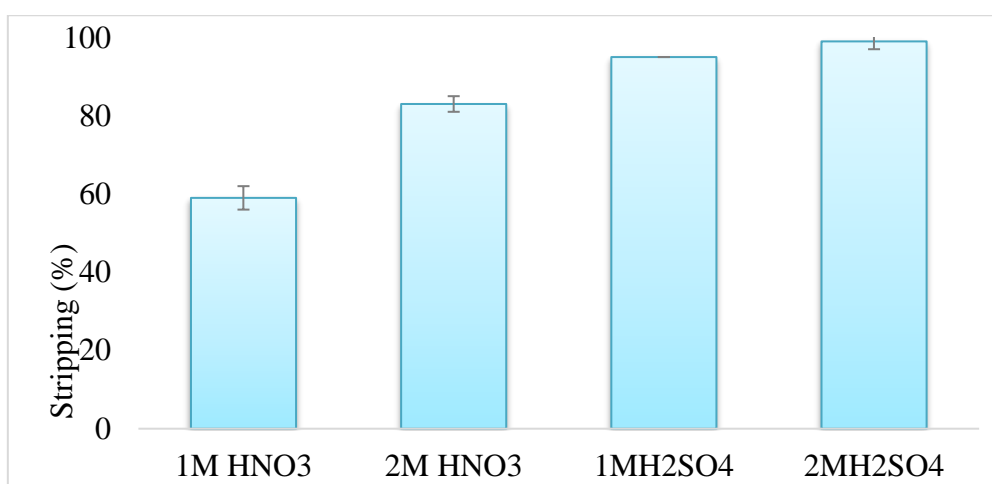
Figure 13 *:* Copper stripping efficiency of nitric acid and sulfuric acid at 1M and 2M concentrations from the organic phase of 30% (v/v) Acorga M5640 in Shell GTL + 2.5% (v/v) octanol, with an A/O = 1/1 and contact time of 60 minutes at $25 \pm 3^{\circ}C$. Results are averages of 2 replicates and the error bars are mean absolute deviations.

3.3.6 Maximum loading capacity of copper on the 2M H_2SO_4 stripping solution

To estimate the maximum loading capacity of copper in the 2M H_2SO_4 stripping solution, consecutive cycles of extraction and stripping were carried out using always the same stripping solution, but new organic phases loaded with copper (Table 5). Copper contained in the final stripping of fourth cycle reached 46 ± 3 g/L. The obtained result revealed good loading capacity of copper in the 2M H_2SO_4 stripping solution initially had 4.6g/L of copper compared to Agarwal, et al. (2008) study with initially had 6.74g/L of copper. Agarwal, et al. (2008) was reported that the maximum loading capacity of copper from organic phase contained LIX 84 initially had 6.74g/L of Cu at fourth cycle was found to contain 57.19 g/L of Cu in stripped solution.

Table 5*: Copper concentrations in the initial organic phase and final stripping solution in four consecutive cycles of extraction and stripping using always the same stripping solution but new organic phases (30% Acorga M5640 in Shell GTL + 2.5% (v/v) octanol) loaded with copper, with an A/O ratio of 1/1 and with a contact time of 60 minutes at room temperature (25 ± 3ºC). Results are averages of 3 replicates $\pm$ standard deviations.

Cycle	[Copper] in initial organic phase (g/L)	[Copper] in final stripping solution (g/L)
1	5.56 ± 0.07	5.3 ± 0.5
2	16.11 ± 0.03	21 ± 3
3	13.8 ± 0.1	35 ± 2
4	15 ± 2	46 ± 3

3.3.7 Reutilization of the organic phase

Figure 14 reveals the effect of reusing the extractant Acorga M5640 in successive cycles of extraction and stripping. After five extraction cycles, the copper extraction efficiency remains almost unchanged. In the first cycle, the copper extraction percentage was $97 \pm 1\%$, while in the fifth cycle it was $94 \pm 2\%$. In the extraction process, the phase disengagement time is short, the phase interface is clear, and no emulsification occurs. Therefore, the extractant Acorga M5640 has excellent reuse performance and can be recycled at least 5 times, according to this experiment and potentially much more times, which is an important feature in industrial applications for the extraction of copper from AMD. It is worth noting that the above conclusions were obtained at laboratory scale and play a guiding role in practical industrial applications. Further studies are also intended to be carried out to test the overall

process of copper recovery from AMD. In practical application, the stability and recycling of the extractants are the most important required factors (Alguacil, et al. 2004).
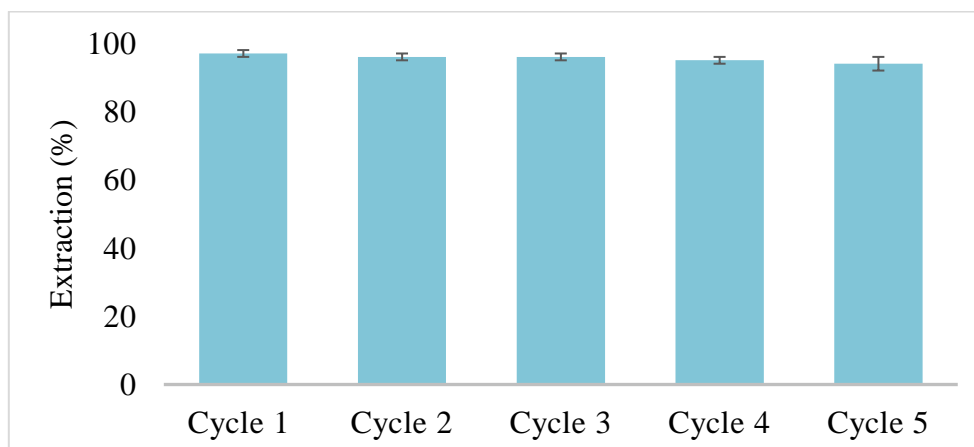
Figure 14: Five successive cycles of extraction and stripping, using always the same organic phase (30% (v/v) Acorga M5640 in Shell GTL + 2.5% (v/v) octanol) but new stripping solution (2M H_2SO_4), with an A/O = 1/1, and a contact time of 60 minutes at room temperature $25 \pm 3^{\circ}C$. Results are averages of 3 replicates and the error bars are standard deviations.

3.4 Screening of extractants to extract iron from copper-free AMD

As observed in the previous section, copper can be specifically extracted from AMD using Acorga M5640, but to extract the second strategic metal (zinc) after copper removal difficulties are expected because of iron co-extraction. Iron causes a problem because, it forms very strong complexes with zinc-extractants and will be co-extracted with zinc, severely compromising zinc extraction efficiency. This long-known problem can be overcome if the iron is selectively removed before zinc recovery. An effective way to do this is by raising the pH to precipitate iron. However, in this way there is generally a percentage of zinc (although small) which also precipitates. In addition, in the case of the AMD from the São Domingos mine, it is expected that the rise of pH also leads to the precipitation of aluminum. Thus, it seems interesting to explore extractants selective for iron, so that this metal can be recovered rather than just removed.

Some studies have shown selectivity for iron over zinc in sulfate media by ionic liquid extractants and a bis benzimidazole-based extractant (Dalton, et al. 1992; Dalton and Quan 1993; Cupertino, et al. 1996). In this work, the results obtained in the screening tests with raw AMD revealed zinc selectivity of the commercial extractant LIX 54 and the home-made ionic liquid AliCy, though with relatively low extraction efficiencies for the extractant and iron concentrations tested with A/O ratios of 1/1 (Figures 7 and 8). Therefore, further tests were

performed to extract iron from copper-free AMD (after extraction of copper with Acorga M5640) with both these extractants but using A/O ratios of 1/5 (Figure 15).

AliCy shows a better extraction capacity of iron ($60 \pm 2\%$), though some aluminum is co-extracted ($13 \pm 2\%$), then LIX 54 in Shell GTL or in Shell Sol (34 or 26% iron extraction respectively). Therefore, LIX 54 was phased out from further experiments.

According to Perez de los Rios, et al., (2010), some ionic liquid extractants operate very efficiently without a ligand complexing metal ion such as methyltrioctylammonium salt (Aliquat 336). In fact, many phosphonium ILs used for iron extraction are based on widely known and applied Cytec Industries extractants such as trialkylphosphine oxides or Cyanex 272 (Campos, et al. 2008a; Gallardo, et al. 2008; Guibal, et al. 2008).
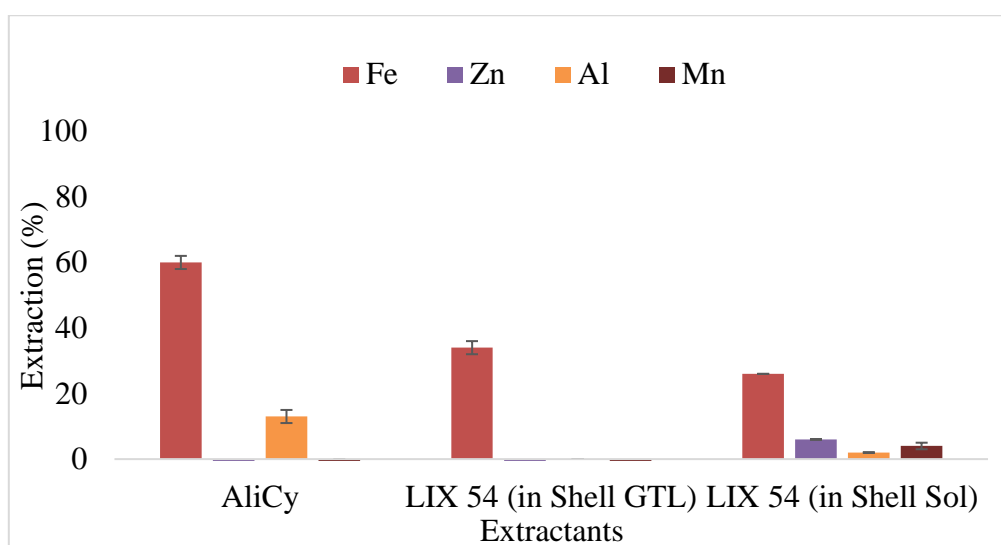
Figure 15: Extraction efficiency from copper-free AMD obtained after extraction with Acorga M5640 (with 55.2 ± 0.3 g/L Fe, 6.2 ± 0.1 g/L Al, 2.59 ± 0.03 g/L Zn and 123.9 ± 0.2 mg/L Mn), using 0.3M AliCY (both AliCy solutions previously prepared with kerosene and using with Shell Sol D70 described in Materials and methods mixed in a 1:1 ratio) and 15% (v/v) LIX54 in Shell GTL as well as 15% (v/v) LIX 54 in Shell Sol D70 with an A/O = 1/5 and 30 minutes contact time at room temperature (25 ± 3^0C). Results are averages of 2 replicates and the error bars are mean absolute deviations.

3.5 Optimization with extractant selected for iron - AliCy

3.5.1 Extractant/iron ions ratios

The extraction efficiency of iron using 0.3 M AliCy with an A/O = 1/5 (Figure 16) was higher than in the previous screening tests in which 0.3M AliCy was also used but with an A/O = 1/1 (Figure 15). Yet, some iron remained in the aqueous phase (~40%). Therefore, aiming to achieve extraction of all iron, decreasing A/O ratios of copper-free AMD / 0.3M home-made AliCy in kerosene (1/1, 1/5, 1/10 and 1/15) were tested (Figure 16).

Total iron extraction was achieved at A/O = 1/10, with an extraction efficiency of 94 ± 3%; that is, with a ratio of 3 mol of extractant AliCy per 1 mol of iron ions. This makes an iron concentration of 52 ± 0.2 g/L in the final organic phase; which has 10 times the volume of the aqueous phase. However, some degree of co-extraction of the other main metals in AMD was observed with all A/O ratios tested. With the 1/10 ratio, the co-extraction percentages were 16 ± 7% of the initial zinc, 16 ± 1% of the initial aluminum and 11 ± 1% of the initial manganese; which makes the following concentrations in the final organic phase: 40 ± 20 mg/L Zn, 99 ± 6 mg/L Al and 13 ± 1 mg/L Mn.

Nur, et al. (2012) study indicates that, the optimal extraction efficiency of iron (86%) using ionic liquids [C4mim] [NTf2] from the aqueous solutions prepared using 20mg/L of iron in ultrapure water was obtained when the ratio of the aqueous solution volume to the ionic liquid volume (Vaq/VIL) was 1/20.
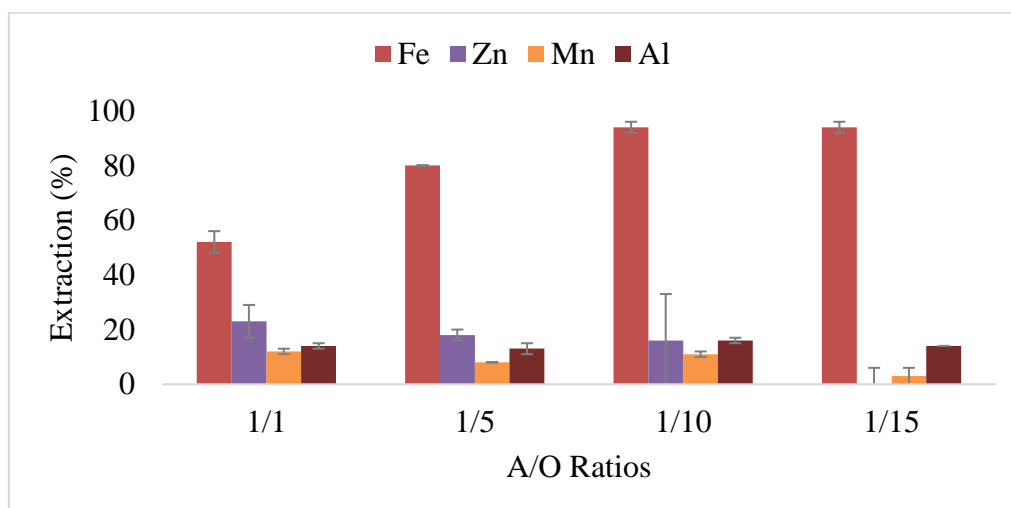
Figure 16: Metals extraction efficiency from copper-free AMD obtained after extraction with Acorga M5640 (with 55.2 ± 0.3 g/L Fe, 6.2 ± 0.1 g/L Al, 2.59 ± 0.03 g/L Zn and 123.9 ± 0.2 mg/L Mn), using 0.3M AliCY in kerosene at different A/O ratios (1/1, 1/5, 1/10, 1/15). Results are averages of 2 replicates and the error bars are mean absolute deviations.

3.5.2 Stripping agents for iron

Stripping tests were carried out with a mixed organic phase of 0.3M AliCy in kerosene (prepared as described in the Materials and methods section) loaded with iron (collected from previous experiments) using different stripping agents (Figure 17). Best stripping efficiency (91 ± 9%) was achieved with 2M H_2SO_4.

According to Pius, et al. (2017), the stripping percentage of iron from loaded organic solutions containing Aliquat 336 were 99.4% using 0.3M $Na_2S_2O_3$ stripping agent and 21.0%

using 0.1M H_2SO_4. They used Aliquat 336 in Kerosene for the extraction process from synthetic solutions of 5.0M iron chloride.

Since the stripping process is designed to recover the metal and ensure that the ionic liquid can be reused (Guibal, et al. 2008), further experiments are necessary to test the reusability of AliCy in kerosene in successive cycles of iron extraction and stripping with 2M H_2SO_4.
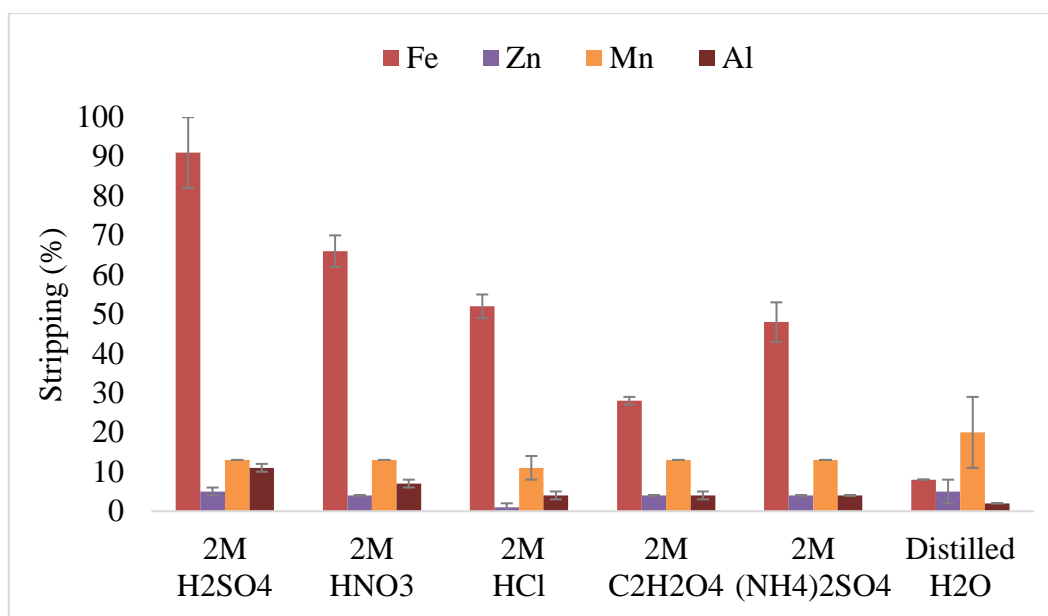
Figure 17: Iron stripping efficiency of 2M H_2SO_4, 2M HNO_3, 2M HCl, 2M $C_2H_2O_4$ (Oxalic acid), 2M $(NH_4)_2SO_4$ and distilled water, from an organic phase of 0.3M AliCy in kerosene loaded with 5189 ± 0.2166 mg/L iron, 40 ± 20 mg/L Zn, 99 ± 6 mg/L Al and 13 ± 1 mg/L Mn, using an A/O = 1/1 and a contact time of 30 minutes at room temperature. Results are averages of 2 replicates and the error bars are mean absolute deviations.

3.6 Alternative process to remove iron from copper-free AMD – pH adjustment

Iron forms very strong complexes with zinc-extractants and will be co-extracted with zinc, severely compromising zinc extraction efficiency. As an alternative process to remove iron from copper-free AMD prior to zinc extraction, pH adjustment method was investigated (Figure 18).

Iron precipitation was 96% at pH 5.0 and 99% at pH 6.0. As expected, aluminum co-precipitated with iron and was 84% and 99% precipitated at pH values 5.0 and 6.0, respectively. Regarding zinc, the second target metal to be extracted from AMD after copper, it was 31% and 32% precipitated at pH values 5.0 and 6.0, respectively, with total precipitation achieved just at pH 10. Manganese precipitation pattern with pH adjustment was similar to that of zinc. Yet, this metal is not reported as causing problems to zinc recovery by LLE processes. Taking these findings into account, a pH value between 5.0 and 6.0 can be chosen in the treatment of copper-free AMD from São Domingo's mine obtained after copper

recovery, to allow further recovery of the zinc still remaining in solution after pH adjustment (~69% of the initial 2.59 ± 0.03 g/L Zn).

These results are in accordance with the previously published data. It is known that iron begins to precipitate at pH > 4 and total precipitation occurs at pH 6 (e.g. Kuyucak and Sheremata 1996; Xinchao, et al. 2005), while zinc precipitates with values pH > 7 (e.g. Kuyucak and Sheremata 1996).
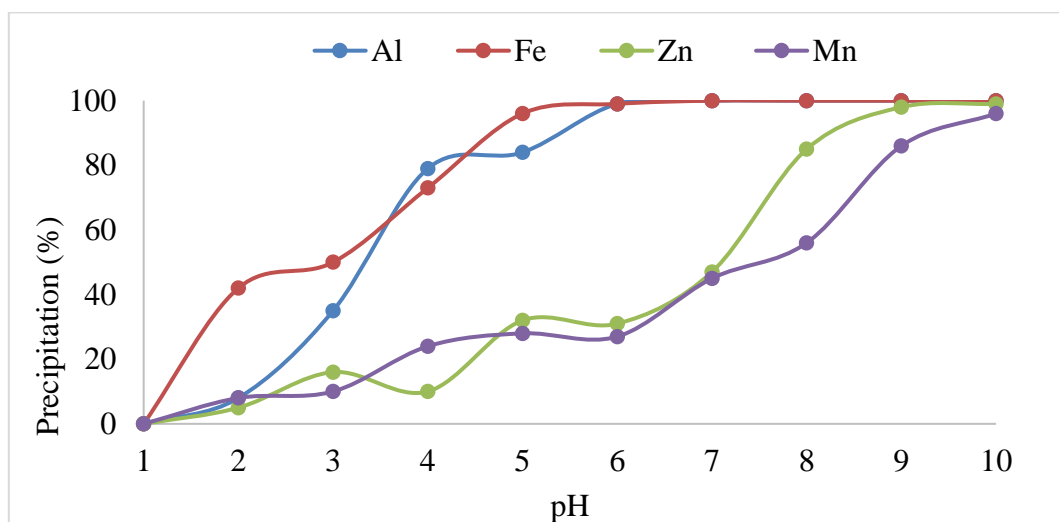
Figure 18: Precipitation efficiency of metals from copper-free AMD obtained after extraction with Acorga M5640 (with 55.2 ± 0.3 g/L Fe, 6.2 ± 0.1 g/L Al, 2.59 ± 0.03 g/L Zn and 123.9 ± 0.2 mg/L Mn) through pH adjustment by addition of NaOH

3.7 Screening of extractants to extract zinc from copper-free AMD

LLE of zinc from the copper-free AMD using 0.9M D2EHPA (30% (v/v)) diluted in kerosene with 3% TBP was tested on one side and a synergistic mixture of 80% (v/v) of a 0.9M D2EHPA solution plus 20% (v/v) of 0.9M Cyanex 272 solution, both diluted in Kerosene with 3% (v/v) TBP (making 0.72M D2EPHA and 0.18M Cyanex 272 in kerosene plus 3% TBP) was tested on another side (Figure 19).

The percentage of zinc extracted using sole D2EPHA was 45 ± 1% and using a synergistic mixture of 80% D2EHPA plus 20% Cyanex 272) was 57 ± 2%. On the contrary, it was observed that, 40% iron was co-extracted using sole D2EPHA, but when the synergistic mixture was used only 33% of iron was co-extracted. It can be concluded that the co-extraction percentage of iron higher when sole D2EPHA is used than using the synergistic mixture of 80% D2EHPA with and 20% Cyanex 272. Other studies also confirm that the synergistic mixture of D2EHPA and Cyanex 272 is better to extract zinc than using sole D2EPHA from sulphate leach liquor, obtained from the sulfide-oxide based tailing sample (Tahereh, et al. 2017; Azizitorghabeh, et al. 2016).

Figure 19: Extraction efficiency from copper-free AMD after extraction with Acorga M5640 (with 55.2 ± 0.3 g/L Fe, 6.2 ± 0.1 g/L Al, 2.59 ± 0.03 g/L Zn and 123.9 ± 0.2 mg/L Mn) using just 0.9M D2EHPA in kerosene with 3% TBP and using a synergistic mixture of 0.72M D2EHPA plus 0.18M Cyanex 272 in kerosene with 3% TBP, with an A/O ratio of 1/1 and a contact time of 30 minutes at room temperature. Results are averages of 2 replicates and the error bars are mean absolute deviations
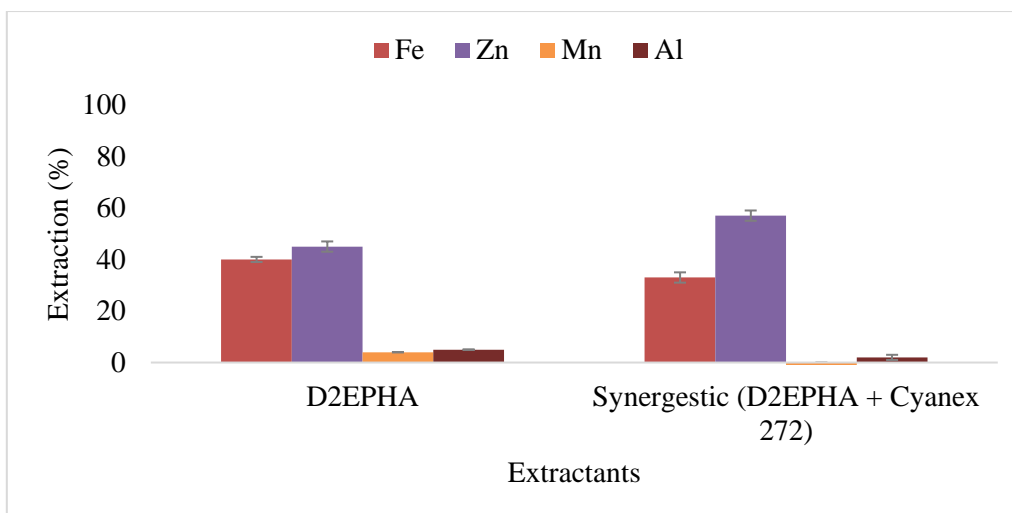
3.8: Optimization with extractant selected for zinc - 80% D2EHPA + 20% Cyanex 272

3.8.1: Extraction of zinc from copper-free and iron-free AMD

The synergistic mixture of 0.72M D2EHPA plus 0.18M Cyanex 272 revealed better results regarding extraction efficiency and specificity for the recovery of zinc from copper-free AMD than using just 0.9M D2EHPA, however, co-extraction of iron occurred in both cases (Figure 19). Therefore, that same mixture was further tested to extract zinc from copper-free and iron-free AMD (Figure 20).

With this tested ratio of 18 mol of D2EHPA plus 4.5 mol of Cyanex 272 per 1 mol of zinc ions, just 51 ± 2% of zinc was extracted, which corresponds to 1.32 ± 0.05 g/L of zinc in the final organic phase. Thus, further tests with higher extractant/zinc ions ratios are necessary to determine best conditions to recover this metal from AMD collected at São Domingos mine. On the other hand, though just 7 ± 2% of aluminum was extracted, the concentration of this metal in the organic phase at equilibrium is relatively high (0.4 ± 0.1 g/L) because its initial concentration in the aqueous phase was high (6.2 ± 0.1 g/L).

Jiménez, et al. (2014) invistigated that, the use of the mixture of Cyanex 272 and D2HEPA is better than the extraction with Cyanex 272 and D2HEPA alone. They used synthetic solution of sulfuric leach liquor containing 1.65 g/L zinc dissolved in deionized water. At pH 2.0 and

the organic phase composed from synergistic mixtures of 50% Cyanex 272 and 50% D2EHPA diluted with kerosene were 60% zinc extracted.
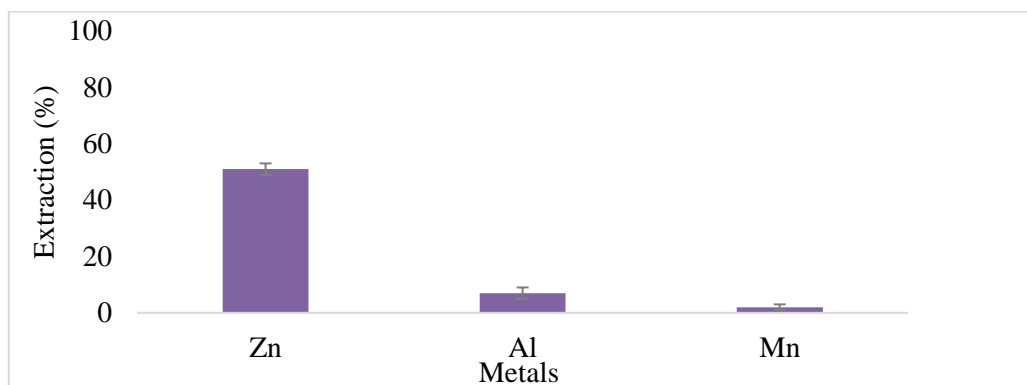
Figure 20: Extraction efficiency from copper-free and iron-free AMD after successive extractions with Acorga M5640 and with AliCy (with 6.2 ± 0.1 g/L Al, 2.59 ± 0.03 g/L Zn and 123.9 ± 0.2 mg/L Mn) using a mixture of 0.72M D2EHPA and 0.18M Cyanex 272 in kerosene with 3% TBP with an A/O = 1/1 and a contact time of 30 minutes at room temperature. Results are averages of 2 replicates and the error bars are mean absolute deviations

3.8.2 Stripping agents for zinc

Ahmadipour, et al. (2011) reported that 2M H_2SO_4 is an efficient solution to strip out zinc from organic phases with synergistic mixtures of D2EHPA plus Cyanex 272. Therefore this was the only agent tested in this work for the stripping of zinc from the synergistic mixture of D2EPHA (0.72M) and Cyanex 272 (0.18M) in kerosene plus 3% TBP loaded with zinc extracted from copper-free and iron-free AMD from São Domingos mine (Figure 21).

In fact, that organic phase was also loaded with a considerable concentration of aluminum due to $7 \pm 2\%$ co-extraction of aluminum (Figure 20). Thus, this light metal was also analyzed in the stripping tests. $99 \pm 0\%$ of zinc was stripped readily using 2M sulfuric acid, while just $1 \pm 0\%$ of aluminum was stripped, which corresponds to 1.31 ± 0.05 g/L of zinc and 0.004 ± 0.001 g/L of aluminum in the final stripping solution. Meaning that it is possible to obtain relatively highly pure zinc solutions. Nevertheless, it is worth to note that making successive cycles using the same organic phase would lead to aluminum accumulation which at a certain point would cause a decay in zinc extraction efficiency. Thus, further research is necessary aiming to avoid aluminum co-extraction to the synergistic mixture of D2EHPA plus Cyanex 272 in kerosene, or to find an efficient scrubbing agent to remove aluminum from this organic phase before stripping of zinc. Another simple option is the adjustment of pH to a value between 5 and 6 after the extraction of iron with AliCy and before the extraction of zinc with D2EHPA.
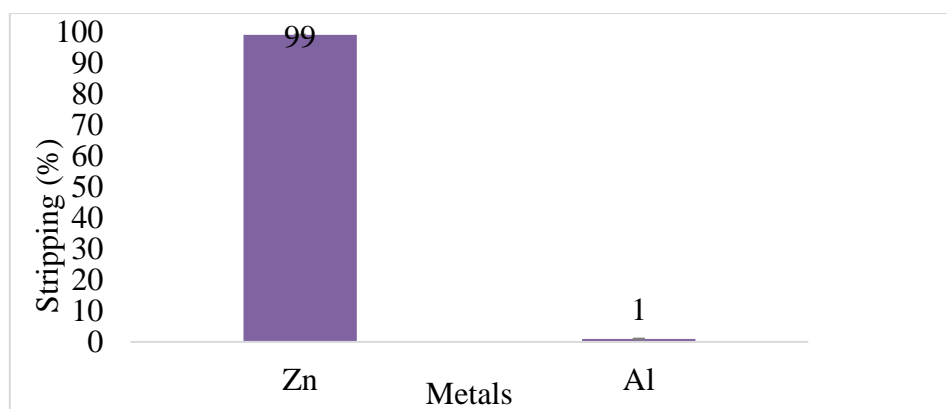
Figure 21: Zinc stripping efficiency of 2M H_2SO_4 from an organic phase of 0.72M D2EHPA and 0.18M Cyanex 272 in kerosene with 3% TBP loaded with 1.32 ± 0.05 g/L zinc and 0.4 ± 0.1g/L aluminum, using an A/O = 1/1 and a contact time of 30 minutes at room temperature. Results are averages of 2 replicates and the error bars are mean absolute deviation.

3.9 Proposed process for the separation of copper, iron and zinc from AMD

Based on the results discussed in the previous sections, it is possible to propose a process using Acorga M5640, AliCY and a synergistic mixture of 80% D2EPHA and 20% Cyanex 272, all diluted in kerosene, for the separation of copper, iron and zinc from AMD collected at the São Domingos mine, aiming the recovery of these metals in highly pure solutions.

A flow diagram summarizing the main steps of the proposed process is shown in the Figure 22.
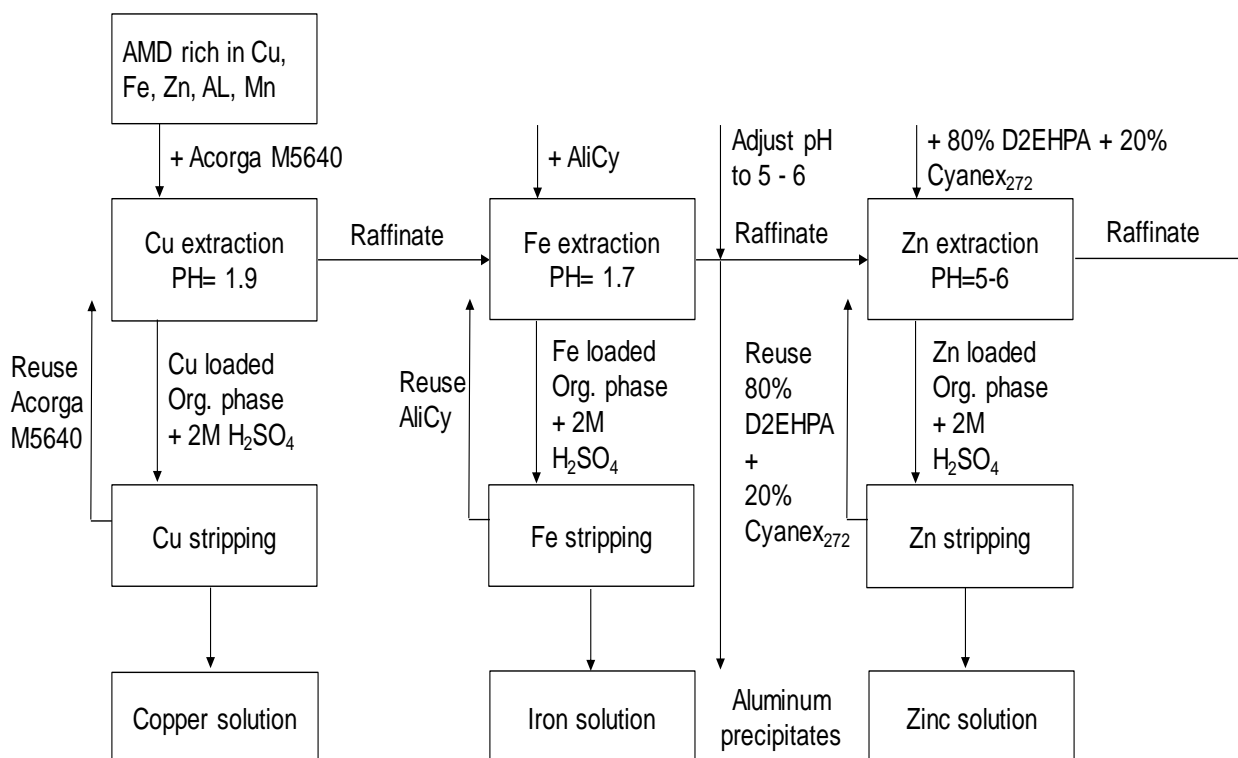
Figure 22: Flow diagram for the extraction and stripping of copper, iron and zinc from AMD collected at Mina de São Domingos.

4. CONCLUSIONS

The results obtained in this work allow to suggest three LLE processes that can be sequentially applied for the separation of copper, iron and zinc from AMD collected at the São Domingos mine, aiming the recovery of these metals in highly pure solutions.

The LLE of copper from highly contaminated AMD from São Domingos mine (55.2 ± 0.3 g/L Fe; 6.2 ± 0.1 g/L Al; 4.60 ± 0.07 g/L Cu; 2.59 ± 0.03 g/L Zn and 123.9 ± 0.2 mg/L Mn) was tested using five different extractants (Acorga M5640, LIX 622, LIX 864, LIX 54 and LIX 622N) and two ionic liquids (AliCy and Cyphos 104 IL) diluted in organic solvents. Acorga M5640 was the most efficient and at 30% (v/v) dilution in Shell GTL plus 2.5 % (v/v) octanol was suitable for the complete extraction of copper from AMD, which makes an 8/1 ratio of its active compound (5-nonyl-2-hydroxy-benzaldoxime) to copper ions. The kinetics of extraction with such 30% (v/v) Acorga M5640 dilution allows total copper extraction with a contact time of 15 minutes. On another hand, a maximum loading capacity of 16 g/L Cu in the organic phase was determined by the isotherm at equilibrium and was confirmed by successive extraction cycles. Regarding the complete re-extraction of copper from the organic phase, among four stripping agents tested (H_2SO_4, HNO_3, HCl and H_2O), a 2M H_2SO_4 solution was confirmed to be the best option. This solution allowed the accumulation of copper at least to a concentration of 46 ± 3 g/L. Moreover, this 30% (v/v) Acorga M5640 organic phase was recycled 5 times in successive extraction stripping cycles, revealing excellent reuse performance.

Extraction of iron from copper-free AMD was attempted by using the ionic liquid AliCy and the extractant LIX 54, both diluted in organic solvents, and the former was selected as the most efficient. Complete iron removal was obtained with AliCy diluted in kerosene plus 3% TBP with a 3/1 ratio of AliCy's ion pairs to iron ions and the stripping of iron was achieved also using 2M H_2SO_4. As an alternative for iron removal from copper-free AMD prior to zinc extraction, pH adjustments were tested, and it was found that iron precipitated completely at values between 5 and 6 while ~70% of zinc remained in solution.

Finally, it was found that a synergistic mixture of 80% D2EHPA and 20% Cyanex 272 was more efficient to extract zinc from copper-free and iron-free AMD than just D2EHPA, using the same organic solvent as diluent in both cases. Although just partial extraction of zinc (~50%) was achieved with 18/1 and 4.5/1 ratios of D2EHPA and Cyanex 272 to zinc ions, respectively, all extracted zinc was stripped using once again a 2M H_2SO_4 solution.

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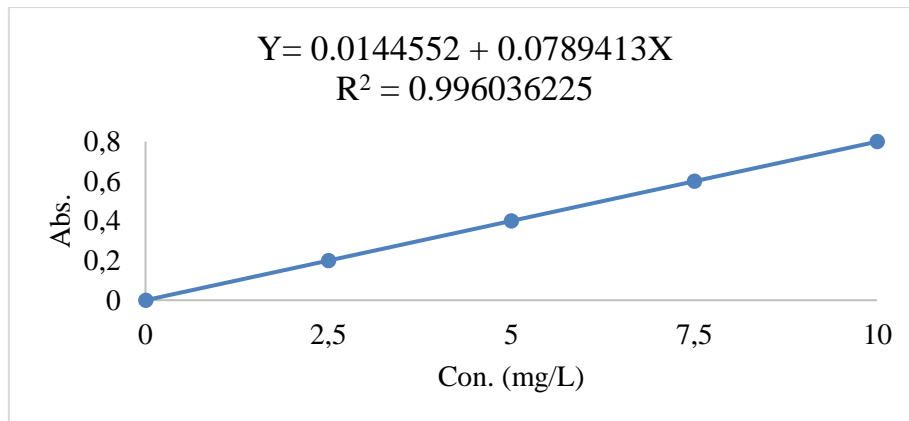
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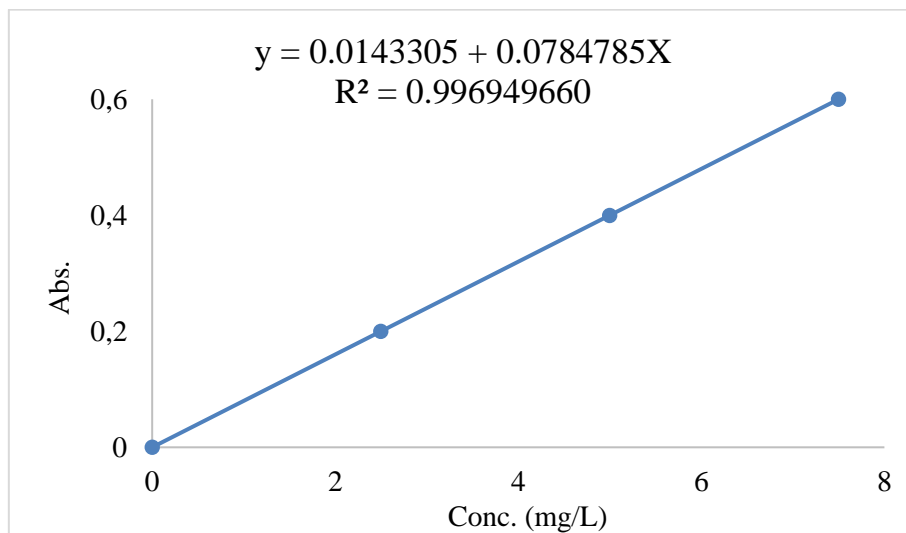
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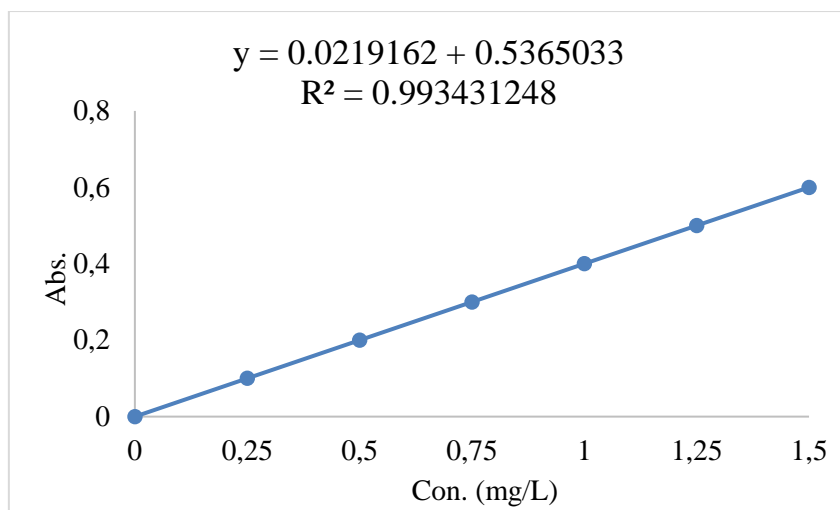
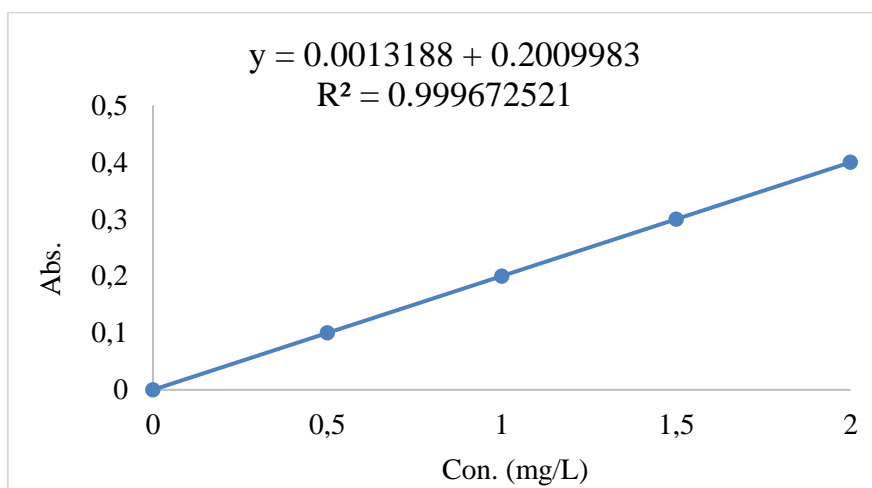**APPENDIX**

    1. Calibration curve for copper analysis

$$Y = 0.0144552 + 0.0789413X$$
$$R^2 = 0.996036225$$

2. Calibration curve for iron analysis

$$y = 0.0143305 + 0.0784785X$$
$$R^2 = 0.996949660$$

3. Calibration curve for zinc analysis

y = 0.0219162 + 0.5365033
R² = 0.993431248

4. Calibration curve for Manganese analysis

y = 0.0013188 + 0.2009983
R² = 0.999672521

5. Calibration curve for Aluminum analysis

Correlation coefficient = 0.99987