

IRON REMOVAL FROM LADEN BIOLEACHING SOLUTION BY PROCESSES OF SOLVENT EXTRACTION AND MAGNETITE SYNTHESIS

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ABSTRACT. Laden leach solution, generated from bioleaching of pyrometallurgical copper slags with a mixed culture of moderately thermophilic bacteria in a bioreactor, contains several base metals (Cu, Co, Zn) and a very high concentration of iron (33,9 g/L). Further processing of cobalt and zinc to the respective final products requires preparatory iron removal from the laden leach solution. The direct iron removal from that solution as goethite was unacceptable because of the significant co-precipitation of copper and cobalt from the solution. The main aim of this paper is to study magnetite (Fe_3O_4) synthesis as an approach for iron removal to a value-added product as a step of the processing of a laden solution generated due to the bioleaching of non-ferrous metals in a bioreactor. Ferrous iron oxidation to ferric state was efficient when the addition of H_2O_2 (30 %) was combined with maintaining the pH 3,1-3,3 with NaOH and air purging. Solvent extraction with 25 % D2EHPA and 7,5 % TBP dissolved in kerosene efficiently separated the dissolved iron and the base metals from the processed solution. However, in the presence of H_2 , the iron was stripped from the organic solvent with low acid consumption. The applied precise control of the chemical precipitation and oxidation processes at 50 degrees Celsius allowed the iron content (11,7 g/L) in the stripping solution to be removed efficiently as magnetite (Fe_3O_4). Based on the chemical content of iron, copper and sulphur, the synthesised nanoparticles of magnetite could be applicable in many sectors (steel, chemical, and electronics).

Keywords: iron, bioleaching, solvent extraction, magnetite

Introduction

Iron is the fourth most abundant chemical element in the Earth's crust, where it is a constituent of sulphides, hydroxides, carbonates, and silicates, mainly. The stable oxidation state of iron at acidic pH is ferrous iron (Fe^{2+}) which the ferrous-oxidising chemolithotrophic bacteria uses as a donor of electrons in their metabolism. On the other hand, ferric iron (Fe^{3+}), generated and released into the environment due to microbial activity, is a strong chemical oxidant towards sulphides, metals, and metalloids in their lower oxidation states. So, iron is paramount in biohydrometallurgy to process sulphide-enriched raw materials. The elaborated biohydrometallurgical methods are applied as *in situ*, *on-site* or *ex-situ* techniques depending on the factors such as the base metals' content and mineralogy and the raw material's quantity (Kaksonen et al., 2018). Regardless of the applied technique, the leach solutions laden with dissolved base metals are processed in the next stage by cementation, ion exchange or solvent extraction techniques (Sole, 2008; Sole et al., 2017). However, the iron removal stage from the processed stream is obligatory in a flow sheet due to the iron interference on the subsequent purification or the base metal recovery operations.

Some estimations showed that the global scale of copper, zinc, nickel and steel industries generates more than 9 million tons of soluble iron annually while processing their raw materials (Dutrizac, 1990). At the same, the demand for water-soluble iron salts on a global scale for sectors such as water treatment and agriculture is only about 10 percent of the amount mentioned above (Huang et al., 2015). Consequently, the precipitation of the excess dissolved iron and the disposal of the formed precipitates is the approach widely applied to the practice. Meanwhile, the global demand for iron increases and it is satisfied by mining a significantly bigger amount of iron from its primary sources. The iron removal from the laden leach solution needs the precise combination of oxidation and precipitation processes, enhancing the selective formation of

the relevant iron oxide. Factors such as temperature, pressure, Eh and seeding rate strongly affect the mineralogy of freshly formed iron precipitates and their properties as colour and sedimentation rate (Ismael and Carvalho, 2003).

The main aim of this paper is to study magnetite (Fe_3O_4) synthesis as an approach for iron removal to a value-added product as a step in the processing of a laden solution generated due to the bioleaching of non-ferrous metals in a bioreactor.

Materials and methods

Pyrometallurgical copper slags were leached continuously in a bioreactor (volume 5 L) with a mixed culture of *Sulfobacillus thermosulphidooxidans* and *Acidithiobacillus caldus* at pulp densities of 16 % and 55 °C to dissolve the non-ferrous metals, which have been capsulated in its structure (Georgiev et al., 2017). Next, a laboratory filter press carried out the separation of the residue from the laden leach solution. The laden leach solution had an acidic pH (~1,47) and contained 28530, 430, 2120, and 110 mg/L of iron, copper, zinc, and cobalt, respectively. The silicon concentration was 5480 mg/L, and it was removed by preliminary pH correction to 0,5, adding POLYSIL RM 1250 as a coagulant, and KCl and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as a flocculant, respectively. Finally, a filter press separated the gel ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) from the processed laden leach solution. The iron content in the leach solution was 27240 mg/L, of which 25200 mg/L was in a ferrous state (Table 1).

Iron oxidation and solvent extraction

The chemical oxidation was conducted in a reactor equipped with an overhead stirred at a stirring rate of 300 rpm at room temperature and with the serial addition of H_2O_2 (30 %), NaOH (12,5 M), maintaining the pH (3,1 – 3,3)

Table 1. Content of the laden leach solution after silica removal by flocculation/ precipitation

Index	Value
pH	0,48
Fe, mg/ L	27240
Cu, mg/ L	520
Zn, mg/ L	2280
Co, mg/ L	122,5
Mn, mg/ L	140
Si, mg/ L	105,5

and purging with air, which led to the formation of voluminous precipitates of ferric hydroxides with orange colour. Ferric iron hydroxides were redissolved by adding hydrochloric acid (30 %) and maintaining a pH of 1,1-1,2. A WTW pH meter with a pH-glass electrode measured the pH during the chemical oxidation process.

Di-(2-ethylhexyl)phosphoric acid (D2EHPA) (25 %) and tributyl phosphate (TBP) (7.5 %) were diluted in kerosene and used as an iron extractant and a modifier for better phase separation, respectively. The phosphoric acid in D2EHPA was saponified preliminary, adding NaOH (6,0 M) at 10,5 ml NaOH/ 100 ml 25 % D2EHPA. Iron extraction was studied at different Organic: Aqueous ratios (1: 1,25 to 1,25: 1) in a glass reactor equipped with a PTFE-coated four-bladed propeller stirrer at a stirring rate of 750 rpm for ten minutes. A glass funnel enhanced the easy separation of the iron-load organic phase from the raffinate. The efficiency of metal-solvent extraction from the laden leach solution and separation factor between iron and zinc were determined by a distribution coefficient (D) and a separation factor (β), respectively:

$$D = (M_{org}) / (M_{aq}) \quad (1)$$

$$\beta = D_{Fe} / D_{Zn} \quad (2)$$

where: (M_{org}) – the content of metal (iron or zinc) in the organic phase after the solvent extraction; (M_{aq}) – the content of metal (iron or zinc) in the aqueous phase after the solvent extraction; D_{Fe} , D_{Zn} – the distribution coefficient of iron and zinc, respectively.

The iron content (total and ferric state) was determined by its selective complexation with 5-sulfosalicylic acid at acidic and alkaline pH (Karamanev et al., 2002). The intensity of formed complexes was measured at the relevant wavelengths by a spectrophotometer MERCK SQ22.

Galvanic re-extraction of ferric iron

The galvanic re-extraction of iron from D2EHPA in the presence of H_2 was carried out in a three-necked glass reactor with a volume of 0,5 L. The process was realised at a ratio of organic (iron-loaded-D2EHPA) to aquatic (acidic solution) phase of 1,25 : 1. The reactor was closed, and the anaerobic conditions inside were created by purging with N_2 (with purity > 99,9 %) for 20 minutes. After that, the glass reactor was purged with H_2 , and by mixing three phases for ten minutes with a magnetic stirrer, the galvanic re-extraction of ferric iron was carried out. The temperature maintained during the process was 50 °C. Finally, the separation of the aquatic from the organic phase was carried out in a glass funnel. The total iron content on D2EHPA before the galvanic stripping and the residual iron content after that process was determined by

acidic extraction with 6N HCl at the same temperature and organic: aquatic ratio.

Magnetite synthesis

The magnetite was synthesised using the co-precipitation method (Gnanaprakash et al., 2007). The process was studied in a three-necked glass reactor with a volume of 0,5 L. The anaerobic conditions were created inside by purging with N_2 for 10 minutes. H_2O_2 (30 %) and NH_4OH (2,0 M) were used as solutions to carry out ferrous iron chemical oxidation and precipitation, respectively. The solution that contained Fe^{2+} was added to the reactor using a glass funnel in a regime of intensive mixing for 10 minutes. A magnetic stirrer maintained the rate of mixing (400 rpm) and the constant temperature (50°C). The separation of synthesised magnetite from the aquatic phase was carried out at a higher rate by a neodymium magnet with a tearing force of 965 N. Afterward, the particles were rinsed with water twice and dried in a heating box at 30°C. Magnetite particles were characterised by the X-ray diffraction method.

Results and discussion

Several chemical processes are applied nowadays in processing iron-contained pregnant leach solutions from mining and metallurgy at an industrial scale. The factors used for the processes' selection are the rate of particle sedimentation and the extent of co-precipitation of non-ferrous metals from the solution (Wang et al., 2011). The main products were jarosite and schwertmannite. Those processes are carried out at acidic pH, ambient temperature and atmospheric pressure and are suitable for solutions with higher concentrations of ferric ions. The main drawbacks of that approach are higher consumption of alkalisating agents, lower particle sedimentation rate and considerable co-precipitation of non-ferrous metals from the solution. For example, when the laden solution was neutralised to pH 3,5 and at 55 °C, the copper, zinc, and cobalt co-precipitation was 18,3 %, 28,7% and 21,6 %, respectively. The main advantage of the process is the low consumption of an alkalisating agent compared to the other iron removal methods. The main disadvantages are the lower iron content of formed phases (about 30 %), the higher exchangeable acidity and the significant co-precipitation of the non-ferrous metals (Dutrizac and Dinardo, 1983). For that reason, environmental legislation characterises those iron phases as toxic, and additional measures and control must be applied during their disposal and storage (Asokan et al., 2006). One of the approaches widely studied is based on iron precipitation to goethite or hematite as final products. The iron content of both phases is close to or higher than 50%, and they are used as pigments as an additive to a wide range of industrial products (Hedin, 2006; Marcello et al., 2008; Flores et al., 2012).

Different methods are used to synthesise magnetite, and considering the nature of the process involved, the methods could be divided into three groups: physical, chemical, and biological (Niculescu et al., 2022). Chemical methods are based on the formation of the nanoparticles through iron condensates interaction at the specific conditions of the experiment. Co-precipitation is one of the simplest and most widely used chemical methods for magnetite fabrication. It is based on the precipitation of ferric and ferrous iron hydroxides

in a basic solution. The main advantages of co-precipitation are high product yield, distinctive morphology and particle size distribution of the synthesised magnetite, and the method's simplicity, which enhance its easy upgrading to industrial scale.

A recent study showed that co-precipitation by magnetite synthesis could be applied directly during the acid mine drainage treatment in case of low concentrations of non-ferrous metals (Akinwekomi et al., 2020). Laden leach solutions generated due to the hydrometallurgical leaching of different raw materials contain significant concentrations of non-ferrous metals. Therefore, it needs the selective separation of iron in its stream before applying the magnetite synthesis method (Wang et al., 2011).

Iron oxidation and solvent extraction

Hydrogen peroxide oxidised ferrous iron in the laden leach solution with a higher rate up to the ferric content in the 4,5 – 5,0 g/ L range. After reaching that concentration, further chemical oxidation of ferrous iron stopped no matter the amount of the added oxidant. For that reason, the process of chemical oxidation was combined with the process of ferric iron precipitation by the serial addition of the chemical oxidants (hydrogen peroxide and molecular oxygen by air purging) and sodium hydroxide addition, respectively. It is well known that at room temperature and pH~3,5, goethite and schwertmannite are the main products of ferric iron hydrolysis (Flores et al., 2012). As a result, a voluminous precipitate with orange-brown colour was deposited in the lower part of the vessel.

The ferric iron separation from the non-ferrous metal ions is carried out at an industrial scale with a higher rate through ion exchange or solvent extraction processes. The experiments about ferric iron removal from acid mine drainage with ion-exchange resin LEWATIT MonoPlus TP 207 were very efficient (Georgiev et al., 2022). In that case, the resin was activated preliminary with hydrochloric acid. Therefore, it was a source of hydrogen ions consumed in the ferric iron minerals' re-dissolution when they were in contact. However, the experiment for the ferric iron separation from the laden leach solution with the type of ion exchange resin mentioned above was unsuccessful due to higher concentrations of iron and non-ferrous metals in the solution being processed. Therefore, ferric iron was removed by solvent extraction with D2EHPA/TBP dissolved in kerosene. The main advantages of the process are better ferric iron: non-ferrous metals separation, and the freedom to manipulate the number of phosphoric acid groups taking part in the ferric iron solvent extraction. In that case, the preliminary activation of D2EHPA was carried out with sodium hydroxide, which required the preliminary redissolution of ferric iron oxyhydroxides in the laden leach solutions before solvent extraction.

Organic to aqueous ratios strongly affect the solvent extraction efficiency of metals (Principe and Demopoulos, 2012). In that case, ferric iron transfer from laden leach solution to its stream by solvent extraction was studied in a narrow range of O : A ratio because of the delicate pH that had to be maintained. For example, if the equilibrium pH value during the extraction was higher than 1,6, a part of the ferric iron was hydrolysed, which required some extra acid addition for its dissolution. When the process was carried out at O : A of 1,25 : 1, the conditions for the ferric extraction were optimal, and its residual content in the raffinate was 103 mg/ L. In addition, the zinc co-extraction was carried out at a lower rate

which determined the value of the separation factor (β) between two metals higher than 11000 (Table 2).

Table 2. Effect of the organic to aqueous ratio on the iron and zinc solvent extraction with 25 % D2EHPA and 7.5 % TBP from the laden leach solution

Index	Organic: aqueous ratio		
	1,15:1	1,25:1	1,35:1
pH _{equilibrium}	1,09	1,22	1,41
Iron solvent extraction, D_{Fe}	47,4	276	508,5
Zinc solvent extraction, D_{Zn}	0,018	0,025	0,061
Separation factor, β	2633	11040	8336

Galvanic re-extraction of ferric iron

Phosphorous-containing organic extractants, such as D2EHPA and TBP, are used widely for the solvent extraction of ferric iron in hydrometallurgy (Ismael and Carvalho, 2003). The strong chemical bond between these extractants and ferric iron determines the higher selectivity and efficiency of such compounds at acidic pH and significant concentrations of non-ferrous metals in laden solutions being processed. Two different mechanisms carry out the backward process - the stripping process of iron. First, it could be realised with concentrated acid solutions, such as 4-6 N HCl. The main advantage is the higher rate of ferric iron transfer from the organic into the aqueous phase. That approach is applicable at an industrial scale if only the iron concentration builds up to more than 100 g/L in the stripped solutions. It makes it economically feasible to recover iron as hematite and hydrochloric acid by pyro-hydrolysis. Second, the ferrous iron strips from D2EHPA in the presence of a significantly lower amount of acid. Different reducing agents such as H_2 , Zn^0 , Fe^0 (Sun and O'Keefe, 2002), or hydrazine (Hang et al., 2008) carry out the preliminary ferric reduction to the ferrous state.

An experiment about iron stripping from loaded D2EHPA with 6 N HCl showed that the total iron content in the laden solution was 26675 mg/ L. That value was accepted as 100% for the re-extractable iron from the loaded D2EHPA. However, studies carried out by other researchers revealed that nearly 10% of iron could not be stripped at the maintained experimental conditions due to the strong chemical bond between ferric iron and D2EHPA (Principe and Demopoulos, 2012). For those reasons, this variant of the iron stripping from loaded D2EHPA, generated as a stage of processing of copper slag's laden solutions, would be unsuitable at an industrial scale due to the significant acid consumption. Therefore, the iron stripping would be economically feasible if ferric ions on the organic phase have been reduced preliminary to a ferrous state. The main advantage of H_2 compared to other widely used reducing agents (Fe^0 , Zn^0) was that the hydrogen ions produced due to the reduction process did not affect the chemical content or properties of the finally made ferric iron oxides.

The preliminary experiments have shown that 50 °C and 20 minutes were optimal for the galvanic reduction of ferric iron ions. The pH of the stripping solution strongly affects iron stripping. For example, the percent of iron stripped from the loaded D2EHPA increased steadily from 15395 to 26610 mg/L, increasing the solutions' acidity from 0,6 to 1,2 N (Table 3). So, the optimal acid content of the stripping solution was 1,0 M HCl, at which 26542 mg Fe/ L, or 99,5% of the re-extractable

iron from the loaded D2EHPA, were stripped to the acid solution. In addition, due to the galvanic stripping of ferric iron to a ferrous state, the colour of D2EHPA has changed from yellow-orange to colourless. The pH of the stripped solution was acidic (1,96), which enabled its long-term storage due to the suppression of ferrous iron chemical oxidation.

Table 3. Effect of the concentration of hydrochloric acid on the iron stripping efficiency from D2EHPA

Index	Concentration of HCl			
	0,6	0,8	1,0	1,2
Fe, mg/ L	15395	18511	26542	26610
Fe _{stripped} , %	57,7	69,4	99,5	99,8
pH at the end of the stripping	2,86	2,38	1,96	1,73

As a result, the ferric iron extraction improved at a higher equilibrium value. However, zinc co-extraction increased too. Therefore, it led to a lower separation factor (β) value between iron and zinc.

The residual 0,5% of re-extractable iron consisted almost entirely of iron in a ferric state. Therefore, it did not strip from the loaded D2EHPA at the experimental conditions maintained during the galvanic process (Table 4).

Three different approaches could be applied to improve the efficiency of galvanic and stripping processes – to increase the process's duration, the temperature at which the process is carried out, or the stripping solution with higher acidity being used. However, they all would determine higher operational costs when the method is applied at a larger scale.

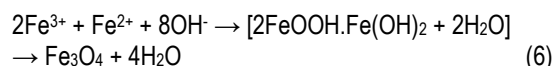
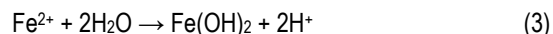
Table 4. Mass balance of iron during its stripping from D2EHPA with 1.0 N HCl at O: A = 1.25:1

Index	Stage of the iron extraction from D2EHPA	
	Galvanic stripping with H ₂ and 1.0 N HCl	Acidic re-extraction with 6N HCl
Fe ²⁺ , mg/ L	26503	21
Fe ³⁺ , mg/ L	39	112
Fe _{total} , mg/ L	26542	133
pH after re-extraction	1,96	- 1,21

Magnetite synthesis

Iron precipitation as magnetite depends strongly on the ratio Fe³⁺: Fe²⁺ being maintained during the synthesis. For example, when X ~ 0,33, (X = Fe³⁺/ Fe³⁺ + Fe²⁺), the main product of synthesis is green rust ((Fe₃⁽²⁺⁾Fe⁽³⁺⁾(OH)₈.(Cl.nH₂O)). The main product is goethite when X is ~ 1,0. When the value of X ranges around 0,66, magnetite synthesises dominates (Jolivet et al., 2004). The applied method of magnetite synthesis relies on the depositions of akaganeite (β -FeOOH) as an intermediate product. That process occurs when chlorides are in excess in the solution (Cornell and Schwertmann, 2004). Therefore, the method is applicable in biohydrometallurgy only when iron's removal technique, such as ion exchange or solvent extraction and stripping processes, is included in the laden leach solutions processing flowsheet. The following reactions (3 - 5)

occurred during the magnetite synthesis. Reaction 6 could be considered a summarised process of synthesis:



The value of X ~ 0,66 was maintained in the reactor by the separation in time of processes of ferrous iron oxidation and magnetite crystal growth. Firstly, ferrous iron ions hydrolysed to ferrous hydroxide precipitate with green colour because of the alkaline pH and the absence of oxygen (process 3). The formed particles had aged steadily, and their colour changed to pale grey. The second process was the partial oxidation of ferrous iron to a ferric state in the presence of a substance with oxidising properties (hydrogen peroxide). Finally, the particles transformed to akaganeite (β -FeOOH) (process 4). The main advantage of hydrogen peroxide is its liquid character which enables easy dosing of the needed amount to carry out the process. As a result of the oxidation, the colour of already formed nanoparticles changed immediately to orange, then steadily to dark brown and black. The final product was magnetite nanocrystals, which resulted from the reaction between ferrous iron hydroxides and already-formed akaganeite (reaction 5). That new phase was black-coloured and with distinguishing magnetic properties. Those particles were deposited only in the magnetic field's presence and resuspended back into the solution in its absence. Their complete sedimentation was observed after adding 0,1% oleic acid, which acted to them effectively as a flocculant.

The particle size distribution of magnetite nanoparticles strongly depended on the rate of oxidant addition and its mixing with precipitates already formed. Those factors determined the number, average size and morphology of the freshly formed nanoparticles, which could be controlled during the synthesis process (Ni et al., 2010; Fang et al., 2012).

The tested method removed iron very efficiently from the solution. For example, the residual iron concentration in the solution was below 0,5 mg/L, which was lower than the relevant permissible standards (Table 5). The particles reacting toward the magnetic field constituted 91,3% of all synthesised particles. Their reaction toward the magnetic field did not change after applying three washing and drying cycles.

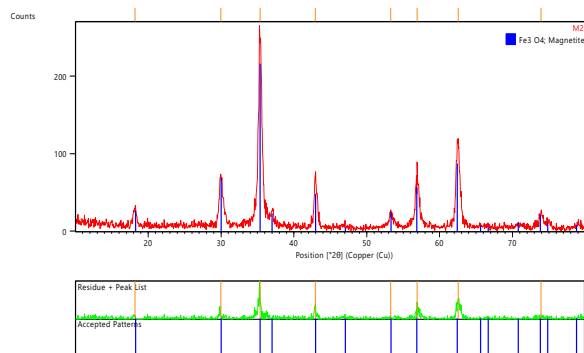
The X-ray diffraction technique revealed that 82% of the particles that have been separated with neodymium magnet consisted of magnetite (Figure 1).

Table 5. Mass balance of the magnetite synthesis process being tested

Index		Value
Fe, mg/L	before synthesis	26542
	after synthesis	< 0,5
Zn, mg/L	before synthesis	52,0
	after synthesis	< 0,5
Particles with magnetic properties (after drying), g		6,71
Particles with no magnetic properties (after drying), g		0,64

The synthesised magnetite nanoparticles revealed the presence of distinctive peaks at 35, 56, and 62 theta degrees and smaller peaks at 18, 30, 43, and 53. It was an evidence of their good orientation and pure crystalline nature. As such, the results obtained in this study agree with those from other studies (Bezdrozhev et al., 2017; Tipsawat et al., 2018).

It is well-known that goethite and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are other phases described as impurities formed during such methods for magnetite synthesis (Gnanapkarash et al., 2007). Other experiments about magnetite synthesis carried out at higher temperatures (60 - 80 °C) showed that its content reached up to 95 % of the iron precipitated phase.



Ref. Code	Score	Displ [°2θ]	Scale Fac.	Chem. Formula
98-018-3971	82	0,000	0,781	Fe ₃ O ₄

Fig. 1. X-ray diffraction analyses of precipitate being synthesised

Apart from maghemite and goethite, ZnO, MnO₂ and Mn₃O₄ are impurities if the treated solution contains higher concentrations of zinc and manganese. Regarding the chemical content (Table 6), synthesised nanoparticle magnetite could be a suitable iron resource for the steel industry, contrast agents in magnetic resonance imaging, catalysis, batteries or sorbents for pollutants removal (Niculescu et al., 2022).

Table 6. Chemical content of the synthesised magnetite

Index	Value
Fe, %	70,9
S, %	0,11
Zn, %	0,003

When synthesised magnetite's morphology, size and properties are controlled during the synthesis, the nanocrystals could be applicable in electronics and medicine (Zhang and Zhang, 2009; Ni et al., 2009). Similar methods could be used in practice as an alternative to the typical techniques for iron removal from acid mine drainage (Kefeni et al., 2015; Akinwekomi et al., 2020).

Conclusions

The main conclusion that can be drawn from this study: the sequential carrying out of chemical oxidation, solvent extraction, and galvanic stripping enables the iron separation from the multicomponent content of copper slag's laden leach solution. Therefore, iron could be removed to a value-added

product by magnetite synthesis instead of its deposition as technogenic wastes.

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