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Leaching Chalcopyrite with High MnO_2 and Chloride Concentrations

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Abstract: Most copper minerals are found as sulfides, with chalcopyrite being the most abundant. However; this ore is refractory to conventional hydrometallurgical methods, so it has been historically exploited through froth flotation, followed by smelting operations. This implies that the processing involves polluting activities, either by the formation of tailings dams and the emission of large amounts of SO_2 into the atmosphere. Given the increasing environmental restrictions, it is necessary to consider new processing strategies, which are compatible with the environment, and, if feasible, combine the reuse of industrial waste. In the present research, the dissolution of pure chalcopyrite was studied considering the use of MnO_2 and wastewater with a high chloride content. Fine particles (−20 µm) generated an increase in extraction of copper from the mineral. Besides, it was discovered that working at high temperatures (80 °C); the large concentrations of MnO_2 become irrelevant. The biggest copper extractions of this work (71%) were achieved when operating at 80 °C; particle size of −47 + 38 µm, $MnO_2/CuFeS_2$ ratio of 5/1, and 1 mol/L of H_2SO_4.

Keywords: dissolution; $CuFeS_2$; chloride media; manganese nodules

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1. Introduction

The most abundant type of copper mineral is chalcopyrite [1–5]. Chalcopyrite has traditionally been treated by conventional pyrometallurgical techniques [6], which consist of flotation, smelting and refining, and electrorefining [7]. These techniques yield approximately 19 million tonnes per annum [8]. Despite the high level of copper production, there is concern about the environmental contamination resulting from the application of these techniques owing to SO_2 atmospheric emissions [9,10]. Because of this, it is necessary to study more environmentally friendly hydrometallurgical alternatives [11]. The slow copper extraction rate of conventional leaching from chalcopyrite in sulfur media makes commercial scale leaching economically unfeasible [12]. This may be due to the formation of a passive layer that forms on the surface of the mineral [13–15]. There have been numerous studies on dissolving copper from chalcopyrite [16–18]. However, none of these studies have obtained positive results working at ambient temperature and atmospheric pressure [19].

The polymetallic nodules are rock concretions formed by concentric layers of hydroxides [20]. Their high content of base, critical and rare metals makes them commercially interesting [21–23]. Their metal content includes high concentrations of Co, Ni, Te, Ti, and Pt, as well rare earth elements [24,25].

There have been few studies on acid leaching of chalcopyrite using marine nodules (MnO_2) as an oxidizing agent [26–29]. These studies showed that good copper dissolution rates of chalcopyrite can be obtained at room temperature, provided that the $MnO_2/CuFeS_2$ rate is high. Devi et al. [26,27] indicated that this is due to the galvanic interaction between chalcopyrite and MnO_2, the action of Fe^{3+}/Fe^{2+} ratio, and the formation of chlorine gas through the reaction between MnO_2 and HCl. Havlik et al. [28] showed that 4 mol/L of HCl and a 4/1 de $MnO_2/CuFeS_2$ ratio is optimal conditions to obtain good results at ambient temperature (54% of copper in 90 min).

The proposed reaction for chalcopyrite leaching with magnesium nodules is expressed as follows [29]:

$$CuFeS_{2(s)} + 2\,MnO_{2(s)} + 8\,H^{+}_{(aq)} + 5\,Cl^{-}_{(aq)} = 2\,Mn^{2+}_{(aq)} + 4\,H_2O_{(aq)} + CuCl^{-}_{2(aq)} + FeCl_{3(s)} + 2\,S^{0}_{(s)}\ \Delta G^0 = -202.6\ \text{kJ} \tag{1}$$

$$Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} = CaSO_{4(s)}\ \Delta G^0 = -28.0\ \text{kJ} \tag{2}$$

Equation (1) represents dissolving copper in a sulfur-chloride medium, owing to the use of sulfuric acid and the high presence of chloride (wastewater) in the system. Among the advantages of leaching in a chlorinated rather than sulphated environment is increased leaching kinetics, the generation of elemental sulfur and cupric and/or cuprous ions are stable in the form of chloride complexes. The Gibbs free energy of Equation (1), which negative, is spontaneous under normal conditions and forms a stable copper product and a non-polluting elemental sulfur residue. While the calcium in wastewater and the manganese nodules reacts with the sulfate in the system, forming Equation (2) which is spontaneous and more likely to occur under normal conditions with the elements present (higher affinity of sulfate for calcium than magnesium and manganese in solution), the calcium sulfate formed is insoluble because calcium precipitates when it comes in contact with sulfate, nitrates and other elements. Equation (1) shows a 2/1 $MnO_2/CuFeS_2$ ratio for leaching copper using manganese nodules as an oxidizing agent, which was initially proposed by Toro et al. [29], but the best conditions to leach copper is at a 4/1 $MnO_2/CuFeS_2$ ratio. The values of the Gibbs free energy were calculated using the software HSC 5.1.

Other investigations have reported the positive effect of the chloride concentration on chalcopyrite leaching [18,30–32]. Velasquez et al. [33] indicated that chloride ions play an important role in oxidizing copper and iron. The copper dissolution is improved with high chloride concentrations.

The level of energy consumed in industrial scale operations related to comminution processes, reactor design, and leaching residence time largely depend on the particle size of the working material [19]. Studies have found a positive effect of smaller particle size on chalcopyrite leaching owing to the large area of contact for leaching [34,35]. Skrobian et al. [36] conducted chalcopyrite leaching tests in agitating reactors, with the addition of 300 g/L of NaCl to all the reactors, but with different particle sizes (−40 µm, −80 + 60 µm and −200 + 100 µm) and a temperature of 100 °C. Their results indicate that particle size has a negligible effect on the copper dissolution rate from chalcopyrite.

Different researchers agree on the positive effects of higher temperature on copper dissolution from chalcopyrite in terms of substantially increasing dissolution velocity [37]. Ruiz et al. [17] used sulfate–chloride media for dissolve chalcopyrite of a particle size 12.3 µm, 20 g/L of acid, 35.5 g/L of chloride, a stirring rate of 1000 rpm and 0.3 L/min O_2 and obtained a copper dissolution rate of 90% in 180 min, with. Other studies of chalcopyrite leaching in chloride media and using oxidizing agents like cupric ions [30] and nitrates [38] have also reported good results in copper extraction at higher temperatures.

The scarcity of fresh water in arid zones is an economic, environmental and social problem [39,40]. The availability of water resources and the quality of potable water have decreased significantly owing to human activity, whose effects at the small-scale are significant for the entire basin [41]. Because of this situation the mining industry is driven to conserve the water it uses and minimize water discharges [41,42]. As well, conventional water resources that mining companies and communities compete for are limited [43]. Seawater has been shown to be a good alternative for mining, not only because of its positive effects on leaching owing to its chloride content, but also as a strategic and indispensable resource [40]. Another attractive alternative is using wastewater from desalination plants, not only because of the economic benefits, but also to avoid contaminating ocean waters [44].

There are few studies for the dissolution of chalcopyrite incorporating MnO_2 and chloride in the system [26–29], achieving positive results in the extraction of Cu at room temperature, mainly evaluating the concentration of MnO_2 in the system. Previously, Toro et al. [29] conducted an investigation in which they evaluated the use of wastewater with high chloride, seawater and manganese nodules contents, for the dissolution of chalcopyrite in an acidic medium. In this investigation, the effect on the concentration of MnO_2, chloride and agitation speed in the system was evaluated. The authors found that high levels of MnO_2 (4/1 and 5/1) allow potential values to be between 580 and 650 mV, favouring the dissolution of $CuFeS_2$, and preventing the formation of a passivating layer. However, no other fundamental variables have been evaluated to favor the dissolution of $CuFeS_2$. In the present research, we evaluated the use of wastewater with high chloride content, and MnO_2 present in manganese nodules as an oxidizing agent in leaching chalcopyrite. Also, wastewater with high chloride levels from a desalination plant was reused. The particle size and temperature were optimized.

2. Methodology

2.1. Chalcopyrite Sample

The chalcopyrite sample used in this study was the same as that used in the first part, published in Toro et al. [29]. The sample was taken selectively from a copper deposit (800 g) and then crushed in a porcelain mortar to avoid contamination. We removed the impurities by hand (with the help of a microscope). The homogenization of the material was done by sampling techniques, selecting a representative fraction of 40 g (20 g for chemical analysis and 20 g for mineralogical analysis). Through a mineralogical analysis using a Bruker brand X-ray diffractometer (Bruker, Billerica, MA, USA), automatic and computerized model of D8 determined that the sample has a purity of 99.9% as can be seen in Figure 1. Finally, a chemical analysis performed by means of an atomic emission spectrometry via induction-coupled plasma (ICP-AES) (AMETEK, SPECTRO, Boschstraße, Germany) determined 33.89% of Cu, 30.62% of Fe and 35.49% of S (See Table 1).

Table 1. Chemical analysis of chalcopyrite.

Component	Cu	Fe	S
Mass (%)	33.89	30.62	35.49

In addition, the sample was analyzed mineralogically using a Bruker brand X-ray diffractometer, automatic and computerized model of D8. In Figure 1, you can see the results of the analysis, from which it was obtained that the chalcopyrite mineral has a purity of 99.90%.

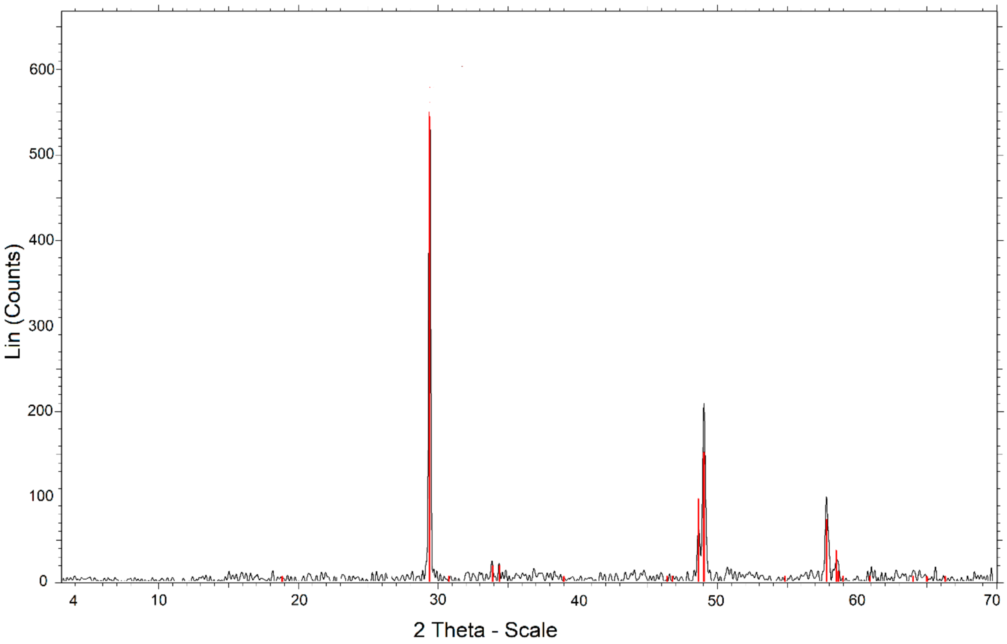


Figure 1. X-ray diffractogram for the chalcopyrite.

2.2. *MnO_2 (Manganese Nodules)*

The manganese nodules used in this study are the same as those used in the study by Toro et al. [29]. This sample was reduced in size with the use of a porcelain mortar until reaching a size range between −75 + 53 µm. This sample contains 15.96% of Mn. Table 2 shows the mineralogical composition. The sample was analyzed with a Bruker®tabletop M4-Tornado µ-FRX (Fremont, CA, USA). The interpretation of the µ-XRF data shows that the nodules were composed of fragments of preexisting nodules that formed their nucleus, with concentric layers that precipitated around the nucleus in later stages.

Table 2. Mineralogical Analysis of the Manganese Nodule.

Component	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3
Mass (%)	3.54	3.69	2.97	7.20	1.17	0.33	22.48	1.07	29.85	26.02

2.2.1. Reagent and Leaching Test

The sulfuric acid used for the leaching tests was P.A. grade (Merck, Darmstadt, Germany), purity 95–97%. We also work with the use of waste water from the Aguas Antofagasta Desalination Plant, which has a concentration of 39.16 g/L of chloride. Tables 3 and 4 shows the chemical composition of waste water and sea water.

Table 3. Chemical composition of waste water.

Compound	Concentration (g/L)
Fluoride (F^-)	0.002
Calcium (Ca^{2+})	0.8
Magnesium (Mg^{2+})	2.65
Bicarbonate ($HCO_3{}^-$)	1.1
Chloride (Cl^-)	39.16
Calcium carbonate ($CaCO_3$)	13

Table 4. Reference composition of seawater, with principal ions (Modified from Cisternas and Gálvez, [45]).

Solute	g/kg of solution
Na^+	10.781
Mg^{2+}	1.283
Ca^{2+}	0.412
K^+	0.399
Cl^-	19.353
$SO_4{}^{2-}$	2.712
$HCO_3{}^-$	0.105
Br^-	0.067
$CO_3{}^{2-}$	0.014
Total	35.146

Leaching tests were carried out in a 50 mL glass reactor with a 0.01 S/L ratio. A total of 200 mg of chalcopyrite ore, with the addition of different concentrations of MnO_2 (manganese nodules), was maintained in agitation and suspension with a 5 position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 800 rpm. Temperature was controlled using an oil-heated circulator (Julabo). The temperature range tested in the experiments was 25 to 80 °C. The tests were performed in triplicate, and measurements (or analyzes) were carried out on 5 mL undiluted samples using atomic absorption spectrometry with a coefficient of variation $\leq 5\%$ and a relative error between 5 to 10%. The pH levels and oxidation-reduction potential (ORP) of leaching solutions were measured with a pH-ORP meter (HANNA HI-4222 (HANNA instruments, Woonsocket, RI, USA)). The ORP solution was measured in a combination ORP electrode cell of a platinum working electrode and a saturated Ag/AgCl reference electrode.

In the previous study (Toro et al. [29]) the ratio of $MnO_2/CuFeS_2$, agitation rate, H_2SO_4 concentration, and chloride concentration were evaluated. Besides, the obtained residues were analyzed, but the formation of contaminating elements was not observed. However, no other fundamental variables were evaluated, and the performance in the extraction of Fe and Mn was not mentioned. For the reasons discussed above, the leaching of $CuFeS_2$ with MnO_2 and wastewater in the present investigation continues, evaluating the particle size and temperature.

2.2.2. Effect of Particle Size

In previous studies conducted by Devi et al. [27] and Havlik et al. [28], it was shown that high MnO_2 concentrations favour the kinetics of chalcopyrite dissolution. Recently, Toro et al. [29] indicated that when working on $MnO_2/CuFeS_2$ ratios of 5/1, attractive results were obtained for short periods. Based on previous background, the effect of the chalcopyrite particle size was evaluated by adding MnO_2 at different sulfuric acid concentrations over time under the conditions shown in Table 5.

Table 5. Experimental conditions for the study of the effect of chalcopyrite particle size.

Parameters	Values
Particle size (μm)	−75 + 53, −47 + 38, −20
Time (min)	5, 20, 40, 60, 80
H_2SO_4 (mol/L)	1, 2, 3
$MnO_2/CuFeS_2$ ratio	5/1

2.2.3. Effect of Temperature

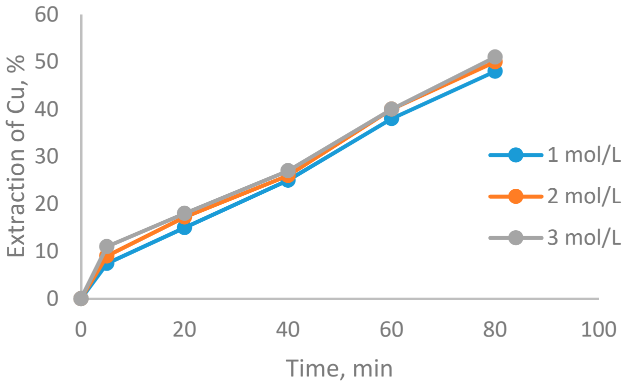
In the study conducted by Toro et al. [29], positive results were obtained when working at high ratios of $MnO_2/CuFeS_2$ (5/1). However, the effect of temperature was not evaluated to shorten leaching times or decrease MnO_2 concentrations.

This study investigated the effect of temperature (in which interval 25–80 °C) on the copper dissolution rate from chalcopyrite with the addition of MnO_2, working with a particle size of −47 + 38 µm, $MnO_2/CuFeS_2$ ratios of 2/1 and 5/1, 1 mol/L of sulfuric acid, 39.16 g/L of chloride (wastewater) and at a stirring speed of 800 rpm.

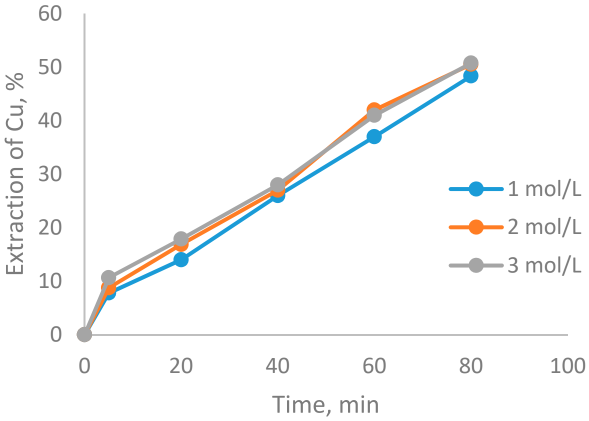
3. Results

3.1. The Effect of Particle Size on $CuFeS_2$ Dissolution

Figure 2 shows the effect on $CuFeS_2$ dissolution of particle size with the addition of MnO_2 (5/1 $MnO_2/CuFeS_2$ ratio, at different concentrations of H_2SO_4 and wastewater. It can be observed that no differences in copper dissolution rates can be obtained at particle size of −75 + 53 to −47 + 38 µm (Figure 2a,b). At small increases in the dissolution rate can be obtained by increasing the sulfuric acid concentration, with the best results obtained at 3 mol/L. This concurs with Skrobian et al. [36], who stated that particle size is irrelevant in chalcopyrite leaching in stirring reactors. However, the copper extraction rate increases with smaller particles (−20 µm), which could be due to the mechanical-chemical activation of the mineral resulting from extended milling [19], which Juhász and Opoczky [46] termed electrochemical activation. At this size, the concentration of H_2SO_4 is irrelevant.



(**a**)



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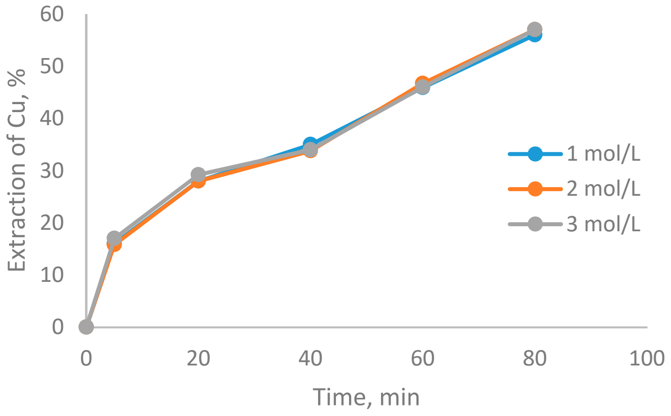
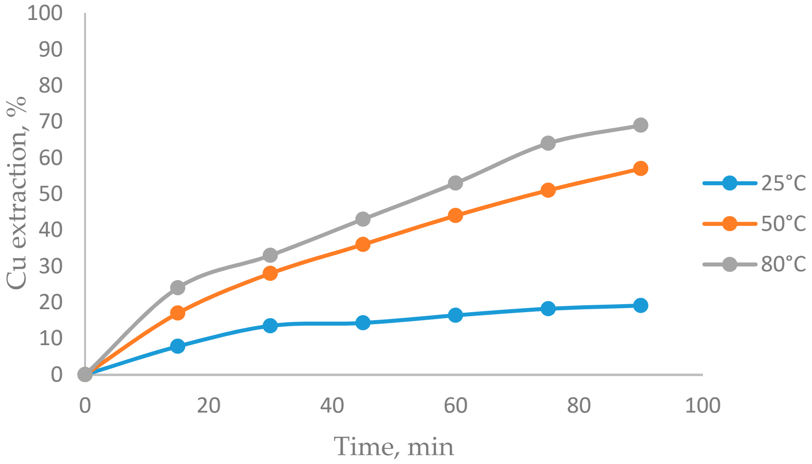


(**c**)

Figure 2. Effect of particle size and sulfuric acid concentration on copper dissolution. Particle size of: (**a**) −75 + 53 µm; (**b**) −47 + 38 µm; (**c**) −20 µm (acid concentration of 1, 2 and 3 mol/L and 25 °C).

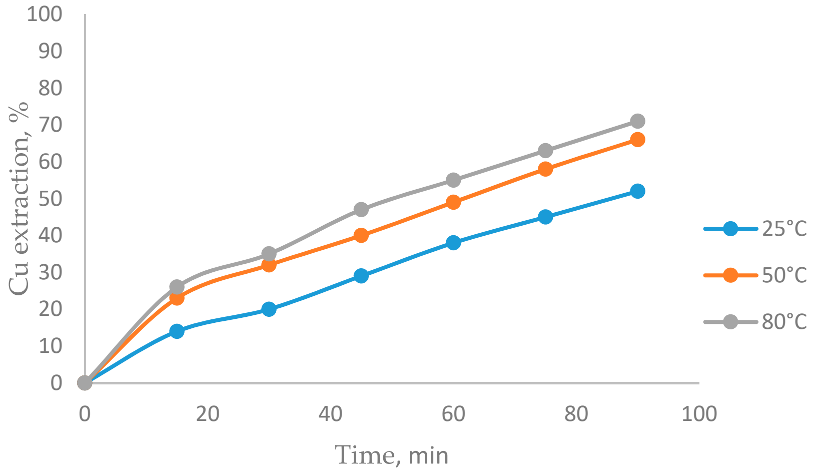
3.2. The Effect of Temperature on $CuFeS_2$ Dissolution

Figure 3 shows the effect of temperature and $MnO_2/CuFeS_2$ ratios on $CuFeS_2$ dissolution. Dutrizac [35] stated that it is difficult to precisely determine the effect of temperature on copper dissolution from chalcopyrite in chloride media, owing to the presence of small amounts of secondary copper mineralization that can affect data interpretation. However, this problem was avoided in this study by using pure chalcopyrite. It can be seen from Figure 3 that at high temperatures (80 °C), the extraction of copper in the system is greater, with similar results obtained with $MnO_2/CuFeS_2$ ratios of 2/1 and 5/1. It can also be seen that at ambient temperature there is a significant difference in Cu extraction (About 30%) at ambient temperature between $MnO_2/CuFeS_2$ ratios of 2/1 and 5/1. The potential values for the tests at room temperature were between 540 and 590 mV, which is within the potential range where the dissolution rate of the chalcopyrite is linear (550 and 620 mV), as Velásquez-Yévenes et al. [37] noted. The potential values in the tests at temperatures of 50 and 80 °C were between 610 and 660 mV, and yielded higher copper dissolution rates. This is because high concentrations of chloride can raise the range of potential values [34]. The pH levels ranged between −0.5 and 1.4 in all the tests.



(**a**)

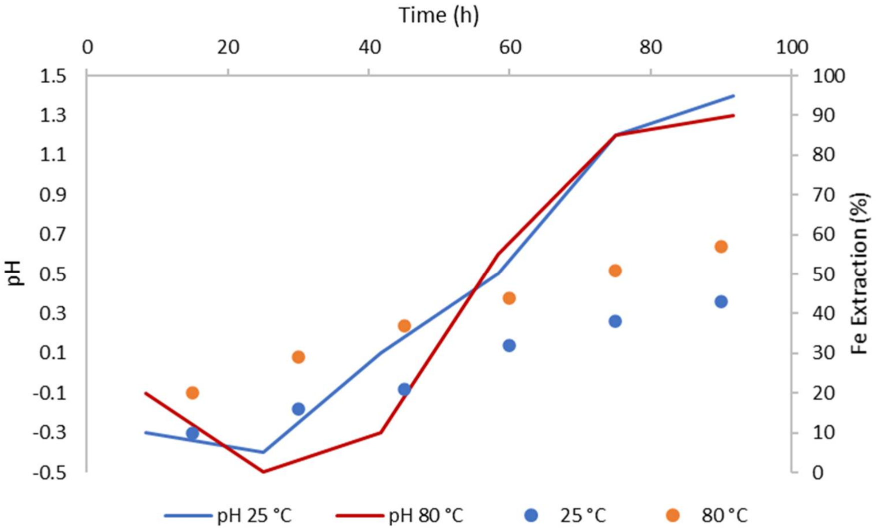
Figure 3. *Cont.*



(**b**)

Figure 3. Effect of the temperature on the dissolution of Cu from chalcopyrite at different ratios of $MnO_2/CuFeS_2$ (particle size of −47 + 38 µm, ratio $MnO_2/CuFeS_2$ of 2/1 (**a**) and 5/1 (**b**), H_2SO_4 concentration to 1 mol/L and 39.19 g/L of chloride).

Manganese nodules are composed of 29.85% MnO_2 and 26.02% Fe_2O_3, which are dissolved in the acidic environment. Figure 4a shows how the MnO_2 used as an oxidising agent for the dissolution of copper, where the Mn (IV) is reduced to Mn (II). Manganese has a high extraction at a temperature of 80 °C. The manganese dissolved in the PLS can be present in two forms, such as $MnSO_4$ or as $MnCl_2$, due to the effect of sulfuric acid and/or chloride, respectively. In Figure 4b, the iron (II) present in the chalcopyrite oxidises and slowly dissolves in an environment of high concentration of sulfuric acid and high level of chloride forming ferric chloride, which is positive since it is a compound that helps the copper solution from the chalcopyrite, and the kinetics of the iron solution increases with temperature. Regarding the pH, it can be seen that lowering the acidity in the Mn solution it does not decrease the dissolution of this element. While in iron, more positive results are presented in a more acidic environment.



(**a**)

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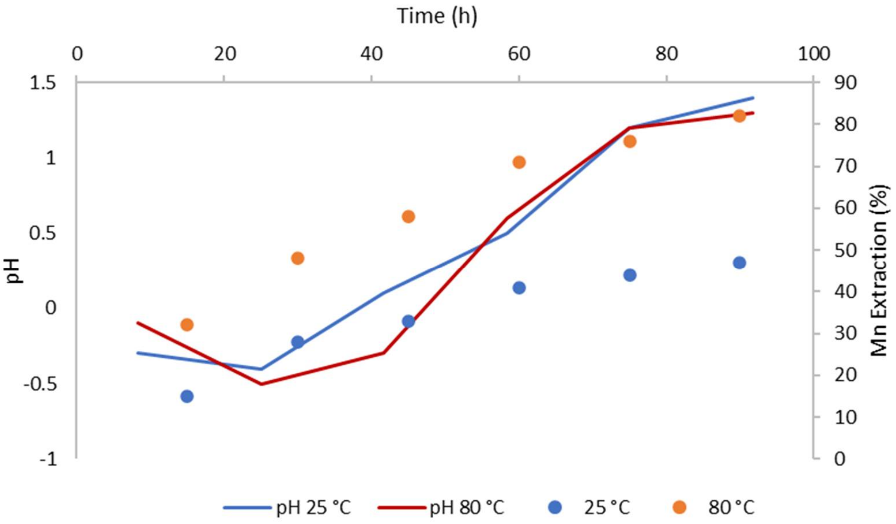

(**b**)

Figure 4. Dissolution of Fe and Mn over time from $CuFeS_2$ at room temperature (25 °C) and high temperature (80 °C) (**a**): Dissolution of Fe and its behavior at changes in pH; (**b**): Dissolution of Mn and its behavior at changes in pH).

In the big copper mining in Chile, the Fe and Mn present in the pregnant leaching solution (PLS) are considered as impurities, this because in the electro-obtaining process, the Fe reduces the efficiency of current. At the same time, the Mn generates corrosion in lead anodes. However, both impurities are controlled in metallurgical plants minimizing the problems that they could produce. Manganese and iron can be transferred to the electro-obtaining stage through physical drag generated by solvent extraction. To reduce the physical transfer of impurities, the plants must optimize the equipment to retain water trawlers in organic (A/O), in addition to adopting some operational practices like maintaining good organic quality through the treatment of organic with clay; avoid over agitation in the mixers; surfactant addition control; and maintain design parameters within the recommended range (linear speed, specific decantation flow, etc.). For the reasons stated, it is possible to apply this process at the industrial level through the conventional hydrometallurgical route (leaching, solvent extraction and electro-obtaining), since solvent extraction processes in Chile have solved this problem. Also, it works in several miners with the use of seawater or adding high concentrations of chloride in synthetic form.

4. Conclusions

This research presents the results of dissolving copper from chalcopyrite by adding MnO_2 as an oxidizing agent (manganese nodules) in a chloride medium (wastewater). As previously concluded by Devi et al. [26]; Devi et al. [27]; Havlik et al. [28] and Toro et al. [29], the addition of MnO2 and chloride in high concentrations generate a positive effect on the chalcopyrite solution. The main findings of this study are:

- There were no differences in copper dissolution rates at particle sizes between −75 + 53 and −47 + 38 µm. at different H_2SO_4 concentrations.
- Small particle size (−20 µm) increases $CuFeS_2$ dissolution kinetics, due to the mechanical-chemical activation of the mineral.
- Temperatures of 80 °C positively affect $CuFeS_2$ dissolution, while the MnO_2 concentration did not have a significant effect in the system.
- The biggest copper extractions in this research (71%) was obtained working at 80 °C, a particle size of −47 + 38 µm, a 5/1 $MnO_2/CuFeS_2$ ratio, and 1 mol/L of H_2SO_4.

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Conflicts of Interest: The authors declare no conflict of interest.

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