Article

Biodepression of Copper-Activated Pyrite with *Acidithiobacillus ferrooxidans* in Flotation with Fresh and Seawater

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Abstract: *Acidithiobacillus ferrooxidans* has been shown to be a good depressant of pyrite in freshwater and seawater flotation. However, the effect of these bacteria over copper-activated pyrite has not been studied. At the industrial scale, the activation of pyrite with copper is a common process that occurs because Cu^{2+} ions, released from other minerals, react with pyrite. This is a problem because Cu^{2+} ions facilitate the reaction of pyrite with the xanthate collectors, becoming hydrophobic and reaching the froth. In this study, microflotation experiments in a Hallimond tube were conducted to evaluate the depressant effect of *A. ferrooxidans* over non-activated and Cu-activated pyrite in freshwater and seawater flotation. The experiments were carried out at pH 4, 6, 8, 10 and 12 and pyrite was mixed with $CuSO_4$ at 2.5×10^{-5} and 5×10^{-5} M in order to activate its surface. Considering the results obtained in the microflotation tests, it is possible to conclude that *Acidithiobacillus ferrooxidans* is able to depress non-activated and Cu-activated pyrite at the entire pH range studied (4–12) in freshwater. On the other hand, the use of bacteria in flotation with seawater proved to be effective to depress non-activated and Cu-activated pyrite at pH 8 and 10 with better results achieved at pH 10. At this pH, the non-activated pyrite recovery dropped from 96% to 15%, and the recovery of Cu-activated pyrite dropped from 95% to 32% when the activation was carried out at 2.5×10^{-5} M, and from 87% to 50% when the activation was conducted at 5×10^{-5} M of $CuSO_4$. The XPS analysis showed that chalcopyrite and copper (II) hydroxide were formed on the pyrite surface when it is contacted with $CuSO_4$.

Keywords: flotation; seawater; freshwater; copper activation; pyrite; *Acidithiobacillus ferrooxidans*

1. Introduction

The activation of pyrite with copper represents a problem when processing copper sulfide minerals by flotation. The copper ions released from sulfide minerals present in the pulp are adsorbed on the pyrite surface, allowing it to react with the collector. As a result, pyrite appears in the froth, diminishing the quality of the concentrate. Pyrite reacts naturally with xanthate collectors at low pH with the formation of dixanthogen and iron-xanthate over its surface [1–3]. However, at high pH, the absorption of xanthate is not as significant as at low pH, so pyrite recovery is lower making possible its separation from copper sulfide minerals which are able to float at high pH values [2]. When Cu^{2+} ions are present in the pulp, pyrite recovery increases considerably even at high pH. For example, Leppinen [2] studied the activation of pyrite with copper between pH 4 and 12, and determined that the highest activation of pyrite occurs between pH 7 and 9, where recoveries of Cu-activated pyrite are significantly higher than non-activated pyrite.

Furthermore, Zhang et al. [4] studied the activation of pyrite with copper between pH 4 and 11 and established that the highest activation of pyrite with copper occurs between pH 6 and 10. The increase in pyrite recovery is attributable to the adsorption of Cu^{2+} ions over the mineral surface; it has been observed that Cu^{2+} absorption increase with pH in the range 2–7.5 [5]. Some of the products that form over the pyrite surface when it is exposed to Cu^{2+} are chalcopyrite and copper (II) hydroxide. Ejtemaei and Nguyen [6] determined by Cryogenic X-ray Photoelectron Spectroscopy (Cryo-XPS), that a layer of chalcopyrite ($CuFeS_2$-type) on the pyrite surface is formed when it is contacted with copper sulfate ($CuSO_4$). Weisener and Gerson [7] showed, by angle resolved X-ray photoelectron spectroscopy (ARXPS), the presence of Cu^{1+} and Cu^{2+} over pyrite. They determined that the Cu^{2+} ions are adsorbed on the pyrite surface and then reduced to Cu^{1+} and, as the reaction proceeds, a $Cu(OH)_2$ layer on the mineral surface is formed. The xanthate collectors react with the Cu-activated pyrite-forming copper (I) xanthate and dixanthogen, making its flotation possible [2,4].

In Chile, the consumption of seawater in mining has increased considerably in recent years and it is expected to continue to increase. In 2010, the consumption of seawater without desalination was $0.11\,m^3/s$ which increased to $1.84\,m^3/s$ in 2019 [8]. This is relevant, considering that pyrite presents a higher activation with copper on seawater flotation compared to freshwater, due to the oxidation of chalcopyrite, which causes a higher extraction of copper [9].

The bacterium *Acidithiobacillus ferrooxidans* has been studied as a pyrite depressant in flotation with freshwater and seawater showing good results [10–17]. However, the effect of bacteria as a depressant of Cu-activated pyrite has not been investigated. In the present study, the use of *A. ferrooxidans* as a depressant of Cu-activated pyrite in freshwater and seawater is evaluated.

Bioflotation has not been carried out on an industrial scale in Chile, so in order to evaluate its use it is necessary to take into consideration the activation of pyrite with copper, which is a common problem that occurs in flotation systems. In seawater, this problem is greater because chalcopyrite oxidizes and releases copper ions that react with pyrite. Because the use of natural seawater is becoming relevant in flotation process, it is necessary to evaluate if bacteria are capable of depressing copper-activated pyrite in flotation with seawater.

2. Materials and Methods

2.1. Mineral Preparation

The pyrite used in this study was hand-picked from the central zone of Chile, and was prepared in a sequential crushing and sieving process. The mineral was dry screened between mesh # 70 and # 400 (212 μm and 37 μm), cleaned with 6N hydrochloric acid solution to remove the oxidized species from the surfaces, and washed with distilled water to remove the remaining acid. The purity of the pyrite was determined by quantitative X-ray diffraction using a Bruker D8 powder XRD and it was higher than 99%.

2.2. Microorganisms Preparation

The bacterium used was *Acidithiobacillus ferrooxidans* strain ATCC19859. The bacteria were grown at 30 °C in a sterile basal medium at pH 1.6, the bacterial composition is presented in Table 1. The sterile medium was inoculated with an active inoculum of *A. ferrooxidans*. Iron sulfate heptahydrate ($FeSO_4·7H_2O$) was used as the substrate. All experiments were carried out with fresh bacteria, harvested on the third day of incubation. At the end of the incubation, the solution containing the cells was filtered using Whatman 42 filter paper to remove iron precipitates. The filtrate was then centrifuged at 12,000 rpm for 20 min in a Sorvall RC-5B refrigerated Superspeed Centrifuge, at 5°. The pellet obtained was re-suspended in a sulfuric acid (H_2SO_4) solution at pH 2. The re-suspended cells were filtered using a 0.22 μm Millipore membrane in order to obtain iron-free cells without metabolites. Finally, the cells retained in the membrane were re-suspended in pH 2 H_2SO_4

solution. The bacterial concentration was monitored by direct counting with an Axio. Lab. A1 Zeiss microscope using a Neubauer counter.

Table 1. Composition of the *A. ferrooxidans* culture medium.

Reagent	Chemical Formula	Molecular Weight	Concentration (g/L)
Ammonium sulfate	$(NH_4)_2SO_4$	132.14	0.4
Potassium hydrogen phosphate trihydrate	$K_2HPO_4 \cdot 3\,H_2O$	228.23	0.056
Magnesium sulfate heptahydrate	$MgSO_4 \cdot 7\,H_2O$	246.48	0.4
Iron sulfate heptahydrate	$FeSO_4 \cdot 7\,H_2O$	278.02	14.85

2.3. Seawater Preparation

The seawater used in this study was artificial seawater prepared according to Kester et al. [18]. The composition of the artificial seawater is presented in Table 2.

Table 2. Composition of artificial seawater [18].

Salt	Molecular Weight	Concentration (g/kg of Distilled Water)
NaCl	58.44	23.926
Na_2SO_4	142.04	4.008
KCl	74.56	0.677
$NaHCO_3$	84.00	0.196
KBr	119.01	0.098
H_3BO_3	61.83	0.026
NaF	41.99	0.003
$MgCl_2 \cdot 6H_2O$	203.33	10.83
$CaCl_2 \cdot 2H_2O$	147.03	1.52
$SrCl_2 \cdot 6H_2O$	266.64	0.024

2.4. Flotation and Bioflotation of Cu-Activated Pyrite

Flotations and bioflotations were carried out in a 100 mL Hallimond tube at different pH values (4, 6, 8, 10 and 12) with freshwater (distilled water) and artificial seawater. The experiments were conducted at room temperature, which was approximately 20 °C. Figure 1 shows a flowsheet of the bioflotation experimental procedure. Copper (II) sulfate anhydrous ($CuSO_4$) with a molecular weight 159.61 g/mol was used to activate pyrite with copper. First, 1 g of pyrite was contacted with 18.5 mL of water and 1 mL of $CuSO_4$ solution with a concentration of 0.5×10^{-3} M or 1×10^{-3} M for 5 min. Subsequently, 0.5 mL of bacterial suspension with a concentration of 1.2×10^{10} bacteria/mL was added to carry out the bioconditioning of the mineral. The biocontitioning was conducted for 15 min. After that, 150 μL of sodium isopropyl xanthate solution with a concentration of 6.3×10^{-3} M was added and agited for 5 min with the mineral at the desired pH. The concentration of sodium isopropyl xanthate corresponds to a collector dosage of 150 g/ton of mineral which is the dosage of industrial operations. Then, flotation was conducted by blowing nitrogen at a flow rate of 35 mL/min for 5 min. Finally, floatable and non-floatable fractions were separately collected, filtered, dried and weighed. Flotations without microorganisms were performed in the Hallimond tube in the same way as the bioflotations but without bio-conditioning. In all experiments, the pH was adjusted using a potassium hydroxide (KOH) solution or sulfuric acid (H_2SO_4). All experiments were conducted in duplicate.
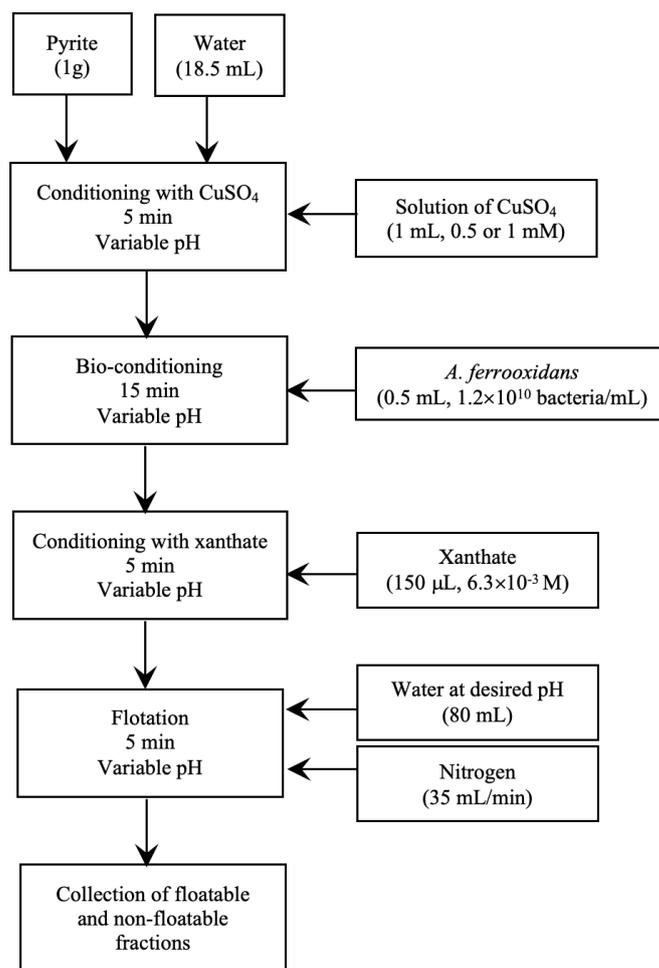
Figure 1. Flowsheet of experimental bioflotation procedure.

2.5. X-ray Photoelectron Spectroscopy

In a beaker, 10 g of the mineral was contacted with 190 mL of water (fresh or seawater) and 10 mL of $CuSO_4$ solution at 0.5×10^{-3} M or 1×10^{-3} M obtaining a concentration of 2.5×10^{-5} M or 5×10^{-5} M, respectively (the same concentration as the flotation experiments). It was agitated for 5 min at pH 10. The pH was adjusted by adding KOH. Then, the slurry was filtered, dried in a oven at 30 °C and analyzed by X-ray photoelectron spectroscopy (XPS) to corroborate the formation of Cu-species, like chalcopyrite ($CuFeS_2$) and copper (II) hydroxide ($Cu(OH)_2$)) over the pyrite surface. As a control, samples of pyrite previously mixed with pure freshwater (distilled water) and artificial seawater, were analyzed.

3. Results and Discussion

3.1. Flotation and Bioflotation of Cu-Activated Pyrite

Figure 2 shows the results of the pyrite flotation in freshwater without *A. ferrooxidans* at different concentrations of copper sulfate ($CuSO_4$). Without $CuSO_4$ (squares), the recoveries of pyrite were between 80% and 88% at the pH range 4–10, and 59% at pH 12. Pyrite normally has a good floatability with a xanthate collector at low pH, due to the formation of dixanthogen and iron xanthate compounds which render the mineral hydrophobic [1,2]. At 2.5×10^{-5} M of $CuSO_4$ (triangles), the recoveries of pyrite increased to values between 88% and 92% at pH range 4–10, and 79% at pH 12. When the pyrite was conditioned at 5×10^{-5} M of $CuSO_4$ (circles), the recoveries increased even more, reaching values between 94% and 95% at pH range 4–10, and 96% at pH 12. It is clear that the addition of $CuSO_4$ produced an increase in the recoveries indicating the activation of pyrite with

copper ions. It has been determined that the collector xanthate reacts with the Cu-activated pyrite, forming copper (I) xanthate and dixanthogen on the surface of the mineral, thereby increasing its flotation [2,4].
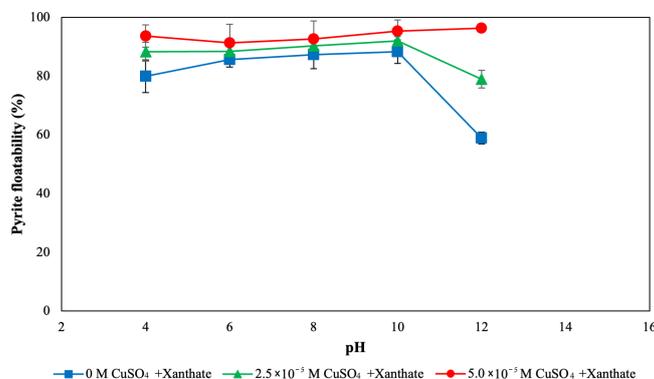

Figure 2. Recovery of pyrite conditioned with different concentrations of $CuSO_4$ in freshwater. The concentration of xanthate in the conditioning was 4.7×10^{-5} M.

Figure 3 shows the effect of *A. ferrooxidans* in the recovery of pyrite at different concentrations of $CuSO_4$ in freshwater. Without $CuSO_4$ (squares), the recoveries were between 10% and 38% at the entire pH range studied (4–12). These recoveries are very low compared to the results without *A. ferrooxidans* shown in Figure 2, indicating that the bacteria are able to depress pyrite. The depressant effect of *A. ferrooxidans* on pyrite has also been reported by other authors and is attributable to the adhesion of the bacteria to the mineral [10–15,19]. At 2.5×10^{-5} M (triangles) and 5×10^{-5} M (circles) of $CuSO_4$, the recoveries of pyrite were slightly greater than without $CuSO_4$ at all pH values, showing the effect of the copper activation. However, these values are low compared to the results without bacteria, indicating that *A. ferrooxidans* is able to depress Cu-activated pyrite.
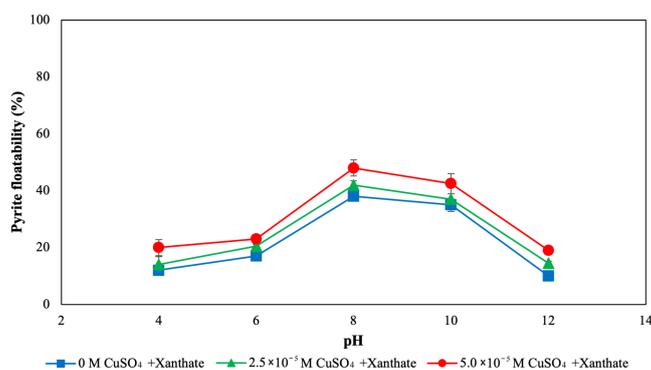

Figure 3. Effect of bacterium *A. ferrooxidans* on the recovery of pyrite conditioned with different concentrations of $CuSO_4$ in freshwater. The concentration of *A. ferrooxidans* and xanthate in the conditioning was 3×10^8 bacteria/mL and 4.7×10^{-5} M, respectively.

The results of pyrite flotation in artificial seawater at different concentrations of $CuSO_4$ without *A. ferrooxidans* are presented in Figure 4. Without $CuSO_4$ (squares), the recoveries of pyrite were between 92% and 96% at the pH range 4–10, and 37% at pH 12. At 2.5×10^{-5} M of $CuSO_4$ (triangles), the recoveries were between 95% and 96% at the pH range 4–10, and 46% at pH 12. At 5×10^{-5} M of $CuSO_4$ (circles), the recoveries were between 87% and 95% at the pH range 4–10, and 42% at pH 12. The activation of pyrite with copper is not seen as clearly as in freshwater since the recoveries were similar at all $CuSO_4$ concentrations in the entire pH range. This may be due to the presence of cations in seawater that absorbs preferencially on the pyrite instead of Cu^{2+}. A selectivity sequence for some cations is

$Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > Ag^+ > Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+$ [20]. The artificial seawater has Sr^{2+} and Ca^{2+}, which absorb preferentially over copper.
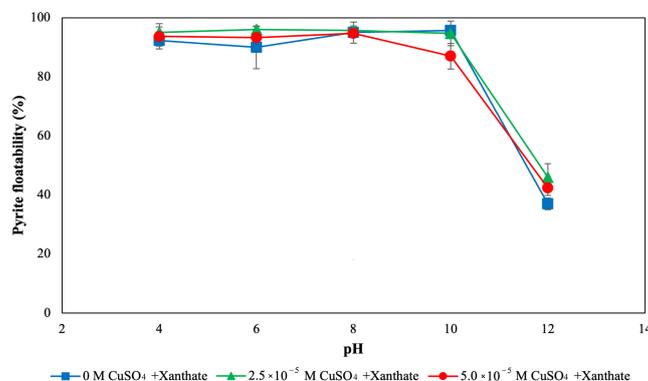

Figure 4. Recovery of pyrite conditioned with different concentrations of CuSO$_4$ in artificial seawater. The concentration of xanthate in the conditioning was 4.7×10^{-5} M.

Figure 5 shows the effect of *A. ferrooxidans* in the recovery of pyrite at different concentrations of CuSO$_4$ in artificial seawater. Without the presence of CuSO$_4$ (squares), the recovery was 24% at pH 8, and 15% at pH 10, which are very low values compared to the results without bacteria shown in Figure 4, where the recoveries were approximately 100%. Meanwhile, at pH < 8, the bacteria were not able to depress pyrite. It has been reported that *A. ferrooxidans* is a good pyrite depressant in actual seawater at pH 8 [17]. At 2.5×10^{-5} M of CuSO$_4$ (triangles), the recovery of pyrite was 81% and 32% at pH 8 and 10, respectively. At 5×10^{-5} M of CuSO$_4$ (circles), the recovery of pyrite was 80% and 50% at pH 8 and 10, respectively. Therefore, *A. ferrooxidans* is more effective to depress non-activated pyrite than Cu-activated pyrite. Regardless, the bacteria are able to depress Cu-activated pyrite, especially at pH 10.
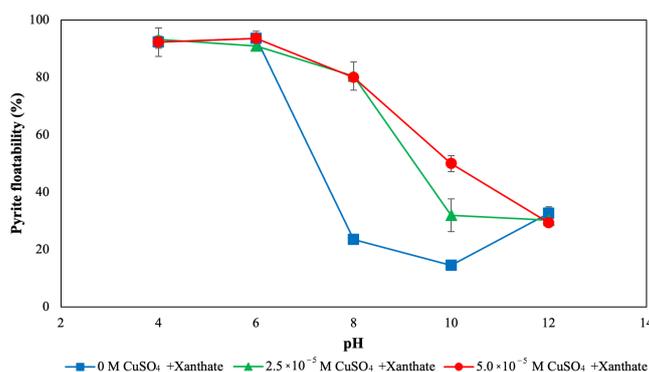

Figure 5. Effect of bacterium *A. ferrooxidans* on the recovery of pyrite conditioned with different concentrations of CuSO$_4$ in artificial seawater. The concentration of *A. ferrooxidans* and xanthate in the conditioning was 3×10^8 bacteria/mL and 4.7×10^{-5} M, respectively.

3.2. X-ray Photoelectron Spectroscopy

Figures 6 and 7 show the XPS spectrum of pyrite conditioned at 0, 2.5×10^{-5} M or 5×10^{-5} M of CuSO$_4$ in freshwater and seawater, respectively. Both figures have peaks of carbon, oxygen, copper, iron and sulfur. The spectra revealed an overlapping of the signals in both cases and lower intensity in the samples mixed with freshwater (Figure 6) compared to samples mixed with seawater (Figure 7). Both figures show a typical spectrum of Cu2p for chalcopyrite and copper hydroxide with approximate bond energies of 938 eV, for the case 2.5×10^{-5} M and 5×10^{-5} M of CuSO$_4$. These results agree with those of

Ejtemaei and Nguyen [6] and Weisener and Gerson [7], who also determined the presence of chalcopyrite and copper hydroxide by contacting pyrite with $CuSO_4$. On the other hand, the Fe2p spectra are observed, which coincide with the peaks related to pyrite and chalcopyrite in both types of sample (freshwater and seawater). Two strong peaks corresponding to Fe2p3/2 and Fe2p1/2 are observed at approximately 707 and 719 eV, respectively. These are related to coordinated Fe atoms in the structure of chalcopyrite and pyrite, consistent with the results of other authors [21]. Finally, the peaks of S2p3/2 are present in both samples, at approximately 162.4 and 163.3 eV. The position of the S2p3/2 peak for the disulfide species (S_2^{2-}) has been reported to be 162.48 eV [22], which is consistent with the first peak obtained, while the second peak has been reported as S_n^{2-} and which, has been detected on the surfaces of oxidized pyrite [23].

A. ferrooxidans has been shown to be selective to depress pyrite in the presence of chalcopyrite [11]. Therefore, the selectivity of the bacteria in systems with this mineral and Cu-activated pyrite must be evaluated, since one of the products that forms on the pyrite surface is chalcopyrite.
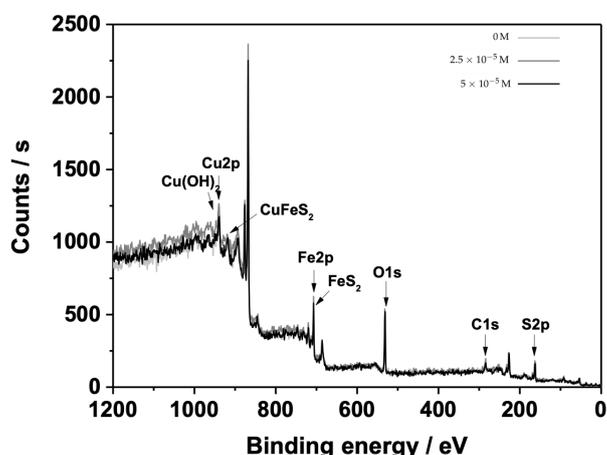

Figure 6. XPS spectrum of pyrite conditioned at 0 M, 2.5×10^{-5} M or 5×10^{-5} M of $CuSO_4$ in freshwater at pH 10.
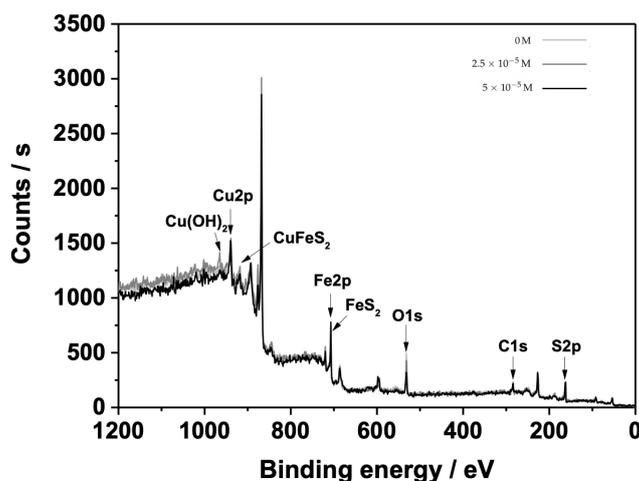
Figure 7. XPS spectrum of pyrite conditioned at 0 M, 2.5×10^{-5} M or 5×10^{-5} M of $CuSO_4$ in artificial seawater at pH 10.

4. Conclusions

The microflotation experiments in freshwater showed that *A. ferrooxidans* is able to depress non-activated and Cu-activated pyrite at the entire pH range studied (4–12), with better results achieved at pH 4, 6 and 12. In seawater flotation, the bacteria were able to depress non-activated and Cu-activated pyrite at pH 8 and 10, with the better results obtained at pH 10. At this pH, non-activated pyrite recovery dropped from 96% to 15% by pre-conditioning with *A. ferrooxidans*, while Cu-activated pyrite recovery dropped from 95% to 32% and from 87% to 50% at 2.5×10^{-5} and 5×10^{-5} M of $CuSO_4$, respectively. XPS analysis showed that chalcopyrite and copper (II) hydroxide form on the surface of pyrite both in freshwater and seawater when in contact with $CuSO_4$.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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