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# Assessment of the floatability of chalcopyrite, molybdenite and pyrite using biosolids and their main components as collectors for greening the froth flotation of copper sulphide ores



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## ABSTRACT

Biosolids and representative compounds of their main components – humic acids, sugars, and proteins – have been tested as possible environment-friendly collectors and frothers for the flotation of copper sulphide ores. The floatability of chalcopyrite and molybdenite – both valuable sulphide minerals present in these ores – as well as non-valuable pyrite was assessed through Hallimond tube flotation tests. Humic acids exhibit similar collector ability for chalcopyrite and molybdenite as that of a commercial collector (Aero 6697 promoter). Biosolids show more affinity for pyrite. The copper recovery (85.9%) and copper grade (6.7%) of a rougher concentrate obtained using humic acids as main collector for the flotation of a copper sulphide ore from Chile, were very similar to those of a copper concentrate produced by froth flotation under the same conditions with a xanthate type commercial collector. This new and feasible end-use of biosolids and humic acids should be new environment-friendly organic froth flotation agents for greening the concentration of copper sulphide ore. Now, further research is needed in order to scale current laboratory assays to operational mining scales to determine efficiencies to industrial scale.

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#### 1. Introduction

Chile bases its economic growth on natural resources exploitation, which makes it vulnerable to the impacts of climate change (ECLAC, 2010). Economic and industrial development has brought environmental and social consequences for communities inhabiting near industrial operating sites (Subramanian and Kawachi, 2004). A case of interest is the mineral processing industry, particularly the copper minerals industry.

Currently, both copper oxides and sulphide ores are actually being exploited in Chile, but sulphide ores predominate over the oxides (Bulatovic, 2007; Cochilco, 2012). Chalcopyrite (CuFeS<sub>2</sub>) is the main copper sulphide mineral in these ores, which also contain varying amounts of non-valuable and undesired pyrite (FeS<sub>2</sub>) (Bulatovic, 2007). Another mineral species associated with copper sulphide ores is molybdenite (MoS<sub>2</sub>), which has a high commercial value. On an industrial scale, copper sulphide ores are concentrated via froth flotation processes (Ata, 2012; Farrokhpay, 2011; Rahman et al., 2013).

According to statistics from the Copper Chilean Commission (Cochilco, 2013), in the year 2012 Chilean copper industry had an annual handling capacity to concentrate around 450 million tonnes of copper sulphide ore by froth flotation, and produced 3.7 million tonnes of fine copper. It is expected that in 2021 the fine copper production will reach 6.8 million tonnes with an installed capacity projected to process 1200 million tonnes of copper sulphide ore. This enormous capacity of ore processing could potentially cause continuous environmental impacts, throughout the release of huge solid waste deposits such as tailings storage facilities, sterile piles, and lixiviation piles, among others. Based on copper cycle assessment all steps of mineral processing are highly energy-intensive and generate hazardous waste materials (McLellan and Corder, 2012; Memary et al., 2012; Moors et al., 2005).

Different chemical reagents are nowadays required to concentrate copper sulphide ores by flotation. These chemicals include

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collectors, depressants, activators, modifiers and frothers, used in order to separate valuable copper-containing minerals from gangue minerals. Their properties allow the control of the wettability of solid surfaces, the electrochemistry of the solution, the dispersion and aggregation of solid particles, and also the generation of foam stability (Hadler et al., 2005; Herrera-Urbina, 2003). On the other hand, many of these chemicals are expensive, and some have been classified as hazardous materials because they may affect both the environment and health of humans, flora and fauna if improperly managed and disposed (Ralston, 2002; Thomas, 2010). Since copper production has been increasing lately as a driving economical force to achieve development, the copper mining sector is in a tipping point to achieve equilibrium between development and sustainable production, thus avoiding increasing levels of pollutant discharges towards the environment. Therefore, the mining industry needs new environment-friendly reagents for froth flotation and to use new strategies and concepts derived from industrial ecology, cleaner production, green chemistry and sustainable engineering.

A new and novel way of biosolids revalorization is described in the literature (Reyes-Bozo et al. 2011a, b, c), where the potential use of biosolids and humic substances - both environmentfriendly compounds - as froth flotation reagents for the concentration of copper sulphide ores has been documented. The typical chemical composition of stabilized biosolids is highly diverse and varies according to geographic region, population consumption habits, degree of industrialization of cities, and the type of process applied by the wastewater treatment plant (Peppas et al., 2000). Despite this, as cited in specialized literature (Baham and Sposito, 1982; Eskicioglu et al., 2006; Parnaudeau and Dignac, 2007; Ras et al., 2008; Reyes-Bozo et al., 2011a) the main components of biosolids could be polysaccharides (sugars), proteins (aminoacids) and to a lesser extent humic substances (fulvic and humic acids), and nucleic acids. The main functional groups present in humic acids are carboxylic acids, alcohol, carbonyl, phosphates, sulphates, amides and sulphides, all of which are capable of interacting with metal species in solution (Baek and Yang, 2005).

In Chile, final disposal of biosolids is limited to landfills and monofills (SISS, 2010); however, under local regulation it is feasible to use biosolids in mining operations (Minsegpres, 2009). This option is considered to be the final disposal. Therefore, the use of biosolids in phytostabilization of tailings and the new use disclosed in our manuscript (use of biosolids in froth flotation processes) are feasible in Chile.

According to statistics and forecasting from Superintendencia de Servicios Sanitarios (Chilean Superintendency of Sanitary Services), biosolids generators are mainly located in the central and southern regions of Chile (SISS, 2010). In the central zone of Chile (Metropolitan Region and regions V and VIII), which is the most significant producer, 220,000 tonnes/year are produced. Then, biosolids will be inevitably generated and these wastes will be disposed in a safe way.

The aim of this research was to evaluate the possibility of using solid wastes generated in wastewater treatment plants as new environment-friendly froth flotation agents. In particular, biosolids and their main components were tested in modified Hallimond tubes as feasible collectors for chalcopyrite, pyrite and molybdenite as well as the use of humic acids as main collector for the flotation of copper sulphide ores.

# 2. Materials and methods

## 2.1. Chalcopyrite, pyrite, and molybdenite samples

Chalcopyrite and pyrite samples were obtained from División Los Bronces (Anglo American, Chile), while molybdenite sample was supplied by Molymet (Santiago, Chile). Samples of chalcopyrite and pyrite were ground in an IKA MF 10 Basic Microfine Grinder apparatus. They were then sieved for 6 min on a Rotap (W.S. Tyler Model Number RX-29-10) to obtain  $125-150 \,\mu m$  ( $-100 + 120 \,msh$ ) size fractions for microflotation tests in a modified Hallimond tube.

Mineralogical analyzes of these samples indicates that the chalcopyrite sample contains 65.4% chalcopyrite, 13.4% pyrite, 9.9% magnetite, and 10.2% nonmetallic gangue minerals. The purity of the pyrite sample was found to be 95.8%, with minor contents of chalcopyrite (0.5%) ad nonmetallic gangue (3.2%). The purity of the molybdenite sample was found to be 98.7%, with minor contents of chalcopyrite (0.6%) and nonmetallic gangue (0.7%). Elemental chemical analyzes were also performed for each of these mineral samples. A portion of the sample was digested via microwave by using the Rock High Sulfide Method: once digestion was completed it was centrifuged and sent to an atomic absorption spectrometer (ICP-MS, Perkin Elmer ELAN 6100) for analysis. A nitrous-oxide/ acetylene flame was used as the oxidant for quantification of molybdenum. Dumas combustion method was used to quantify sulphur contents. The elemental chemical composition of the chalcopyrite, molybdenite and pyrite samples is given in Table 1.

### 2.2. Biosolid sample

Biosolids used in this study were obtained from a wastewater treatment plant (Essbio, Concepción, Chile). The biological removal of organic load was performed by using activated sludge technology. The samples were previously ground using mortars, homogenized and sieved to a fraction smaller than 1 mm. Biosolids samples were physically and chemically analyzed in certified laboratories (Análisis Ambientales and Laboratorio de Suelos y Análisis Foliar, PUCV). Biosolids, whose aqueous suspensions (1:2.5 solid:water ratio) have a pH of 7.8 and an electrical conductivity of 7.2 mS/cm, were found to contain 66.5% organic matter. The total content (in mg/kg) of Cu, Fe, Mo and P was 280.8; 5652.2; 2.6 and 13148.3, respectively. All metal content were determined by atomic absorption spectrophotometry with a Perkin Elmer Analyst 300 apparatus. The content of humic substances, quantified by standard method (Sadzawka et al., 2006), was 10.6% fulvic acid, 2.5% humic acids and 27.8% humins.

#### 2.3. Microflotation tests in a modified Hallimond tube

Assessment of the collecting ability of biosolids and their main components was performed with a modified Hallimond tube. A commercial salt of humic acid (Aldrich) was used as representative of humic substances present in biosolids. According to Pandey et al. (1999), this humic acid has a characteristic composition of 44.67% organic carbon, 5.87% hydrogen, 4.88% total nitrogen, 43.9%

Table 1	
Elemental chemical composition of chalcopyrite, pyrite and molybdenite s	amples.

Sample	Chemical composition (%)	Value
Chalcopyrite	Total copper	21.5
	Total iron	30.2
	Total sulphur	26.2
	Total molybdenum	0.01
Pyrite	Total copper	0.2
	Total iron	46.8
	Total sulphur	47.5
	Total molybdenum	0.01
Molybdenite	Total copper	0.2
	Total iron	0.6
	Total sulphur	61.4
	Total molybdenum	37.7

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