Journal of Environmental Management 252 (2019) 109699

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: http://www.elsevier.com/locate/jenvman

Research article

Use of humic substances in froth flotation processes

Lorenzo Reyes-Bozo[a,*], Eduardo Vyhmeister[b], Alex Godoy-Faúndez[c], Pablo Higueras[d], Carlos Fúnez-Guerra[e], Héctor Valdés-González[c], José Luis Salazar[f], Ronaldo Herrera-Urbina[g]

[a] Facultad de Ingeniería, Universidad Autónoma de Chile, Santiago, Chile
[b] Insight Research Centre for Data Analytics, University College Cork, Cork, Ireland
[c] Centro de Investigación en Sustentabilidad y Gestión Estratégica de Recursos, Facultad de Ingeniería, Universidad del Desarrollo, Santiago, Chile
[d] Departamento de Ingeniería Geológica y Minera, Universidad de Castilla-La Mancha, Almadén, Ciudad Real, Spain
[e] Centro Nacional del Hidrógeno, Puertollano, Spain
[f] Departamento de Ingeniería Química, Universidad de Santiago de Chile, Santiago, Chile
[g] Departamento de Ingeniería Química y Metalurgia, Universidad de Sonora, Hermosillo, Mexico

ARTICLE INFO

Keywords:
Froth flotation collectors
Flotation kinetics
Copper and molybdenum concentrates
Recovery
Biosolids as ore collector
Green chemistry

ABSTRACT

Continual growing demand for metals in regular and emerging markets has led to an increasing use of chemicals and reagents in ore processing. This trend force to incur in an increasing use of commodities which inevitable leads to higher operational costs and environmental concern. The chemicals and reagents used in flotation processes especially invoke high costs of handling and disposal due to their hazardous nature, but until now, few studies have been carried out to seek possible alternatives. In order to develop a cheaper and greener processes, these hazardous materials should be replaced by more sustainable products, by-products, or wastes generated by other industries. Biosolids, cheaper and greener than chemical frothers and collectors, have been tested successfully in flotation processes. Studies of removal rates and froth flotation kinetics have been carried out independently, nevertheless a deeper understanding of the tradeoffs involved between the rates and kinetics should be obtained. This work evaluates the use of different collectors (conventional collector (CC), biosolids (and their main components), and mixtures of CC and biosolids main components) in the froth flotation of copper sulfide ores. Tests were carried out in Denver Cells, at fixed collector, frother, and pH levels, in order to estimate metallurgical and kinetic parameters. In rougher flotation tests, biosolids show to be the most efficient non-CCs, achieving Cu recoveries of 64.1%. CC achieved 76.2% Cu recoveries while none of the pure biosolids main components achieved Cu recoveries over 60%. In the kinetics studies, only the partial replacement of CC (by 50% of Humic Acids (HAs) or biosolids) allowed a similar copper recovery once compared with CC (~81% Cu to be obtained with a fast kinetic constant of ~0.88 min^{-1}). For molybdenum, partial replacement of CC produced better recovery and kinetics constants (k of 0.83 min^{-1} and R_∞ of 66.10% for 50% CC - 50% HAs; k of 0.90 min^{-1} and R_∞ of 61.79% for 50% CC - 50% biosolids). Results show that different combinations of biosolids - CC or HAs - CC could achieve optimal flotation conditions. As evaluated, an optimal combinations would allow considerable reductions in energy and chemical consumption.

1. Introduction

The circularization of mineral processing (i.e., replacement of hazardous materials, recycling, and proper final disposal) helps to reduce the carbon intensity of end-products. To this end, it is also desirable to follow a zero-waste management strategy, which involves replacing materials by environmentally-friendlier ones (Burlakovs et al., 2018; Lèbre et al., 2017) and/or reusing wastes into the process. This approach could be implemented in froth flotation, the main process used to concentrate copper sulfide ores, by replacing the chemical reagents (i.e., collectors, frothers, and modifiers). These regents are used to control the particles' superficial wettability and induce floatability over desired mineral selectivity (Herrera-Urbina, 2003). A focus should be given into replace these chemicals since greener materials, such as biosolids (containing humic and fulvic acids), have shown to possess similar properties.

In the froth flotation process, chemical surfactant mixtures tend to describe positive synergistic effects (compared to single collector

---

* Corresponding author.
E-mail address: lorenzo.reyes@uautonoma.cl (L. Reyes-Bozo).

https://doi.org/10.1016/j.jenvman.2019.109699
Received 30 June 2019; Received in revised form 9 September 2019; Accepted 8 October 2019

application), achieving a more stable and stronger froth and an improved reagent distribution over the surface area of the mineral particles (Bradshaw and O'Connor, 2000; Rao, 2004). Indeed, performance and kinetics of froth flotation depend on chemical and/or physical minerals solution selectivity (Ansari and Pawlik, 2007; Ata, 2012; Hadler et al., 2005). Several modes of physicochemical interactions, between collectors and mineral surfaces, are possible when collector mixtures are used. The enhanced performance of mixtures is given by creating different distribution zones with heterogeneous energetically-charged sites on mineral surfaces, leading to improved selectivity, rates, grades, and recoveries (Bradshaw and O'Connor, 2000). A good example of complex chemistry in the flotation process is the porphyry copper (Cu)/molybdenum (Mo) ore froth flotation (Wills, 2006). In its sulfide ores processing shows to be function of collector type, medium pH, and reagent additives, among other operational conditions (e.g., hydrodynamics, cell type, cell configuration, feeding rates, particles size, and pulp density) (Bulatovic, 2007).

Humic and fulvic acids (considered wastes from different industries) contain functional groups that allow them to behave as hydrophilic and hydrophobic compounds. They show to have a negative charge in weakly acidic-to-basic media due to deprotonation (Hizal and Apak, 2006; Stevenson, 1994), which is enhanced or diminished as a function of pH (Apak, 2002; Baek and Yang, 2005). Humic Acids (HAs) can share common binding sites with heavy metals (Tipping et al., 2002) and interact properly with other molecules (including a wide range of minerals) by electrostatic and/or hydrophobic interactions (Fairhurst and Warwick, 1998; Jones and Bryan, 1998; Gamboa and Olea, 2006).

Previous studies carried out by authors (Reyes-Bozo et al., 2011a, 2011b, 2011c, 2014a, 2014b, 2015; Urdiales et al., 2018) reported novel methods to revalorize organic wastes (biosolids and humic substances). These works detail the potential use of biosolids (principally composed by humic substances, sugars, proteins, and nucleic acids) and humic substances as environmentally-friendly froth flotation reagents for the concentration of copper sulfide ores. The use of biosolids and HAs as collector reagent was evaluated through zeta potential measurements, FT-IR analysis and film flotation test (Reyes-Bozo et al., 2011c, 2015). Results showed that biosolids and HAs make the zeta potential of the copper sulfide ore more electronegative. FT-IR studies showed that HAs can physically be adsorb on the main mineralogical species of copper sulfide ore (mainly, chalcopyrite and pyrite) through outer-sphere linkages by hydrogen bonds or van der Waals forces. For the case of biosolids, the presence of phosphorous compounds showed that orthophosphate is chemically adsorbed on the surfaces of main mineralogical species of the copper sulfide ore through inner-sphere linkages. These results implies that biosolids can physically and chemically interact with copper sulfide ores through mechanisms involving inner and outer-sphere linkages. Film flotation tests showed that biosolids and HAs can be used as environmental-friendly collectors in froth flotation processes since they modify the copper sulfide ore hydrophobicity. The ability to form and stabilize foams of biosolids and HAs are evaluated by the Bikerman test (Reyes-Bozo et al., 2011a, 2011b). Both substances showed to have surfactant characteristics and described similar results once compared with industrial frothers (e.g. methyl isobutyl carbinol).

Given the continuous decrease in the Chilean ore Cu grades from 0.74% to 0.65% (Cochilco, 2018), the associations with complex mineralogical species will require increased quantities of chemical reagents (e.g. collectors, frothers and modifiers, representing ~32% of total costs of concentration processes; Cochilco, 2015a) as well as energy and water in froth flotation in order to achieve current and projected productivity (1273.5 million tonnes by 2026). Considering an average rate of 50 g of collector per ton of ore (Reyes-Bozo et al., 2014a, 2014b), a requirement of ~63,675 tonnes of collectors is projected by 2026. This also implies an increase in environmental concerns and impacts on handling and storage (Thomas, 2010). Therefore, the evaluation of novel flotation reagents should consider a positive impact on the production costs, metallurgical performance, energy consumption, and environmental concerns.

The present research focuses into obtain a better insight in the use of biosolids (considered as a less hazardous and more environment-friendly alternative) in the flotation process. The use of biosolids could also allow improvements in the flotation kinetics, energy consumption and, in general, the process sustainability.

The present research focuses on the evaluation (in terms of different froth flotation/extraction efficiency indexes) and, at the same time, the flotation modeling (based on first order kinetic parameters) of Cu and sulfide ores by using different froth flotation collectors (conventional collector (CC), biosolids (and their main components), and mixtures of CC and biosolids main components). The use of fixed dosages of collectors, the calculation of metallurgical indicators (recovery and grades of concentrates) and the estimation of kinetics parameters would enable a better understanding of biosolids and their performance at the froth flotation stage.

2. Materials and methods

2.1. Copper sulfide ore

Copper sulfide ore samples from the southern region of Chile are used in rougher froth flotation and kinetics tests conducted at a laboratory scale. The samples are free of chemical reagents (collectors, frothers, and modifiers) and possess a 50% pass particle size (D_{50}) between 80 and 90 μm. The samples contained minerals such as chalcopyrite (1.80%), covellite (0.11%), molybdenite (0.01%), pyrite (3.30%), and gangue (93.90%). The gangue contained quartz (32.03%), sericite (19.24%), feldspar (13.22%) and plagioclase (10.07%). In terms of metallic assay, the samples had a 0.93% copper (Cu), 0.05% molybdenum (Mo), and 3.80% iron (Fe). The Cu content in the samples is quantified by atomic absorption spectrophotometry with a PerkinElmer Analyst 300 apparatus, while the mineralogical analysis is performed by standard methods according to Gaines et al. (1997). The composition of the samples agrees with previously reported data (Bulatovic, 2007).

2.2. Biosolids and their main components

Biosolids are obtained from a wastewater treatment plant (Essbio, Concepción, Chile) where the biological removal of organic load was performed using activated sludge technology. This biosolid had 66.5% organic matter, a pH of 7.8, and an electrical conductivity of 7.2 mS/cm. As described by Reyes-Bozo et al. (2014b), the total contents of Cu, Mo, Fe and P (in mg/kg) in the biosolid are 280.8, 2.6, 5652.2, and 13,148.3, respectively. The content of humic substances, quantified by a standard method (Sadzawka et al., 2006), are of 10.6% fulvic acid, 2.5% humic acids, and 27.8% humins. α-D-glucose and Bovine Serum Albumin (BSA) from Sigma-Aldrich company are used as sugars and protein representatives contained in the biosolids. Both reagents are technical grade.

Three different types of HAs are evaluated as collector in froth flotation processes. All humic substances are used as representative of HAs present in the biosolids. The first sample of HA is a commercial HA sodium salt (from Sigma-Aldrich company). According to Pandey et al. (1999), this salt has a composition of 44.67% organic carbon, 5.87% hydrogen, 4.88% total nitrogen, 43.9% oxygen, and 0.58% ash with a total acidity of 12.3 moL/kg. The concentrations of the –COOH and phenol (-OH) functional groups are 4.1 and 8.2 moL/kg, respectively (Pandey et al., 1999). The second sample (HA powder I) and third sample (HA powder II) of HAs are from a Chinese provider (Shandong Chuangxin Humic Acid Technology Co. Ltd.). These HAs are sold as mining flotation powders to concentrate copper sulfide ores. Both samples are from leonardite and contain at least 60 wt% of humic substances.

FTIR spectroscopy analysis (pellets of dry KBr analyzed in a Bruker Vector 22 apparatus), shows that all the samples of HAs contained different functional groups. The main groups are carboxylic acids, alcohol, carbonyl, phosphates, sulfates, amides, and sulfides, all of which are capable of interacting with metal species in solution (Baek and Yang, 2005; Reyes-Bozo et al., 2011a).

2.3. Performance and kinetic flotation tests

The use of biosolids and their main components (humic substances, sugars, and protein) as collector of copper sulfide ores is investigated through rougher froth flotation tests conducted in a Denver Cell at laboratory scale. Each test is performed by triplicate. Kinetic evaluations are performed with pure components (HAs, CC, and biosolids) and mixtures with a ratio of 50 wt% (CC - HA or biosolids).

The experimental procedure is established based on a mining company metallurgical laboratory procedure. 0.5 kg of the copper sulfide ore is mixed with 0.3 L of freshwater and is fed to a ball mill. After grinding, CaO solution is added to set the pH at 9.5 and 50 g/t of the collector under evaluation is added. The collectors included industrial chemical reagents (dextrin-101 plus hostaflot-NP107 at ratio 50:50 wt%), HAs, proteins, sugars, or biosolids.

Immediately after collector addition, 1.0 L water is added and a fixed dosage of frothers (methyl isobutyl carbinol, 20 g/t) are added into the Cell. A solid material percentage of 31.0 wt% is maintained. The pulp is stirred at 1200 rpm and the pH readjusted to 9.5 with a CaO solutions. The pulp is further conditioned for 1 min. Immediately after, atmospheric air is introduced into the cell at a rate of 4.0 L/min for 14 min. Table 1 describes a summary of the operational conditions for the performance flotation tests.

The kinetics tests followed the same procedure described above. These tests use 1000 g of copper sulfide ore. The main operational conditions are also described in Table 1. Concentrates are sampled at 1, 3, 6, 10, and 14 min. The cumulative recovery *R(t)* and the instantaneous concentration (grade of Cu in the concentrate) are measured.

2.4. Metallurgical indexes

The collector performances are evaluated through different metallurgical parameters applied to valuable minerals (Cu and Mo). Solids recovered in the froth phase are separated from the liquid by filtration (using Wathmann No. 42 filters). Then, samples are dried at 80 °C for 24 h. The total metal content (mainly Cu, Mo, and iron) of feed, concentrates, and tails are analyzed by atomic absorption spectrophotometry with a PerkinElmer Analyst 300 apparatus.

Table 1
Operating conditions for rougher froth flotation and kinetics tests carried out at laboratory scale.

Parameter	Performance flotation tests	Kinetics flotation tests
Ore mass, dry basis (g)	500 ± 0.01	1000 ± 0.01
Ore density (g/mL)	2.6	2.6
Grind grade (%) −100# Tyler (147 μm)	75.0	75.0
Percentage of solids (w/w)	31.0	31.0
Pulp density (g/mL)	1.21	1.21
Temperature (°C)	20 ± 1	20 ± 1
pH	9.5 ± 0.2	9.5 ± 0.2
Stirring speed (rpm)	1200	1200
Air flow (L/min)	4.0	4.5
Total flotation time (min)	14	1, 3, 6, 10 and 14[a]
Manual paddling frequency (s)	10	10
Nominal capacity of cell (L)	1.5	3.0
Cell rotor type	Impeller	Impeller
Flotation cell material	Stainless steel	Transparent plexiglas
Reposition water	pH 9.5 and 20 g/t MIBC	pH 9.5 and 20 g/t MIBC

[a] Times for sampling of concentrates for kinetics tests.

By using mass balance and the rougher flotation results, the metals (i.e., Cu and Mo) recoveries are obtained as follows (Gupta and Yan, 2006; Wills, 2006):

$$R=\frac{C\cdot c}{F\cdot f}\cdot 100\% \tag{1}$$

where R is the metal recovery; F and C are the mass of the feed and concentrate, respectively; f and c are the feed and concentrate metal assays, respectively. The Enrichment Ratio (*ER*) is calculated as c/f (Gupta and Yan, 2006; Wills, 2006) and the Concentration Ratio (*CR*) is calculated as $(c-T_m)/(f-T_m)$, where T_m is the metal assay in the tail. *ER* tells us the metal content ratio between the concentrate to its feed. *CR* is used to determinate the feed required (in tonnes) to produce one tonne of concentrate.

The separation efficiency index (*SE*) is calculated as described in Eq. (2). R_m is the percentage recovery of the valuable mineral, R_g is the percentage recovery of the gangue into the concentrate, C is the concentrate mass coming from the feed, and m is the percentage of metal content in the valuable mineral. This index attempts to combine recovery and concentrate grade into a single index (Gupta and Yan, 2006; Wills, 2006):

$$SE=R_m-R_g=\frac{100\cdot C\cdot m\cdot(c-f)}{(m-f)\cdot f} \tag{2}$$

2.5. Kinetics parameters estimation

To determine the flotation kinetics rate constant from rougher flotation data we assume that copper sulfide ore flotation follows a first order kinetic (Bulatovic, 2007; Gupta and Yan, 2006). The first order rate equation is expressed in Eq. (3), where *r(t)* is the cumulative recovery after time t, R_∞ is the maximum theoretical flotation recovery, and k is the kinetic rate constant. Eq. (4) shows the expression used to directly evaluate the rate constant.

$$r(t)=R_\infty\cdot(1-\exp(-k\cdot t)) \tag{3}$$

$$k=\left(\frac{1}{t}\right)\cdot\ln\left(\frac{R_\infty}{R_\infty-R(t)}\right) \tag{4}$$

Using the experimental results of Cu and Mo recoveries, the values of k and R_∞ are estimated by least squares minimization between the modelled and the experimental results.

3. Results and discussion

3.1. Performance results of rougher froth flotation tests

Table 2 shows the mass of concentrate recovered after rougher flotation of copper sulfide ore with the different collectors, as well as their Cu, Mo and Fe content (in %), the copper separation efficiency index (*SE*), and the copper enrichment ratio (*ER*). Information on the tails is not reported (estimations can be performed by mass balance). The metal recovery trend, *R*, is shown in Fig. 1.

The calculated Cu concentration ratio (*CR*) for the Conventional Collectors (CC), HA Sigma-Aldrich, HA powder I, HA powder II, BSA, α-D-glucose, and biosolids are 4.44; 5.63; 5.72; 5.63; 4.67; 4.79; and 4.73, respectively. The values clearly establish that large quantities of ore are required to produce 1 ton of Cu concentrate. The CC describes the lower *CR*, while HAs show the highest *CR*. As observed in Table 2 and Fig. 1, the biosolids seems to be the most efficient non-conventional collectors, achieving a recovery of 64.1% Cu while CC achieves 76.2% Cu in the concentrate. These results confirm the existence of a synergetic effect of the regents within the biosolid; none of the biosolids main component achieved values over a 60% Cu in metal recoveries while the recovery produced by the combination of sugars, proteins and humic acids (among others) allows a difference with respect to the CC of

Table 2
Metallic assay of the copper concentrate: concentrate mass, copper separation efficiency index (*SE*), and copper enrichment ratio (*ER*) obtained by rougher froth flotation tests of copper sulfide ore.

Main collector used	Concentrate mass (g)	Copper *SE* Index	Copper *ER* Index	Assay (%)[a]		
				Cu	Mo	Fe
CC	112.6 ± 0.01	55.51	3.41	3.17 ± 0.22	0.11 ± 0.02	7.44 ± 0.81
HA Aldrich	88.8 ± 0.01	33.52	2.85	2.65 ± 0.20	0.10 ± 0.01	4.79 ± 0.13
HA powder I	87.4 ± 0.01	38.77	3.15	2.93 ± 0.09	0.11 ± 0.01	5.11 ± 0.09
HA powder II	88.7 ± 0.01	37.50	3.06	2.85 ± 0.22	0.09 ± 0.01	4.78 ± 0.01
BSA	107.0 ± 0.01	8.77	1.40	1.30 ± 0.07	0.06 ± 0.01	3.91 ± 0.01
α-D-glucose	104.2 ± 0.01	37.78	2.77	2.58 ± 0.25	0.11 ± 0.02	4.70 ± 0.23
Biosolids	105.7 ± 0.01	44.44	3.05	2.84 ± 0.22	0.11 ± 0.01	4.79 ± 0.09

CC: Conventional Collectors; HA: Humic Acid; BSA: Bovine Serum Albumin.
[a] Assay (%) of Cu, Mo and Fe show the average and standard deviation values.

12.1%. Furthermore, the mean standard deviation of the different Cu experiments is estimated as 1.4% therefore, differences higher than 3.6%, for cupper recoveries, can be seen as statistically significant (considering n = 3 and α = 0.05).

Therefore, the total replacement of the collector by biosolids and their main components shows a depressor effect in the Cu concentration.

In regard to the recovery percentage of the non-principal metallic components (Mo or Fe, including gangue), it is observed that HAs describe a lower recovering of the non-principal metal components (mainly Mo). This result imply that HAs could have, qualitatively, a similar number of interactions independent of the metal components. The relatively low recovering percentages could be attributed to a lower capability to form effective froths, a need of higher concentration to form effective metallic-HA interactions, a need of higher concentration of surfactants, and a non-optimal pH.

The use of protein (Bovine Serum Albumin, BSA) shows a lower affinity to the main metallic components (Cu and Mo) and higher affinity to the non-metallic components. Different studies have shown that BSA possess different interactions with Cu(II). At low pH (4.8–5.3), BSA has 3 sites with high affinity to interact with Cu(II) and 16 sites to interact with lower affinity. At pH in the range of 8–10 affinity sites are reduced to only 1 (Monsuka et al., 1993). Given the pH used in the present work, the affinity of BSA with the metallic components is reduced to a point at which the metal-BSA interaction, and therefore its flotation, is considerable low.

D-glucose also describes a higher affinity to the non-principal metallic components once compared with HAs. D-glucose shows a low copper ER index (once compared with the CC).

Based on the previous results (Fig. 1), BSA and D-glucose are not considered for further analysis as pure components.

When considering Mo it is observed that HAs, as pure component collector, shows a relatively low recovery while D-glucose shows a value similar to that of CC (43.3% instead of 46.5%). The biosolid shows Mo recovery values relatively higher than its pure components (44.2%). Since the sugar composition is relatively low in the biosolids (66.5% are organic components with ~2/3 humic components) the highest value of Mo recovery is attributed to synergetic effects between the CC and the biosolids-based collectors. In fact, the mean standard deviation of the different Cu experiments is estimated as 1.07% therefore, differences higher than 2.8%, for cupper recoveries, can be seen as statistically significant (considering n = 3 and α = 0.05).

Pyrite could play a fundamental role when choosing new collectors to concentrate copper sulfide ores. An iron content in the concentrate of about 12% is an expected high limit for industrial Cu rougher froth flotation. Cu concentrates must have enough iron (as FeS) to be autogenously smelted; to achieve a low slag melting temperature. To obtain a final clean Cu concentrate and send this concentrate to the smelter unit, the concentrate must have around 35 wt% Cu, 30 wt% Fe, and 35 wt% S, allowing it to pass the "Net Smelter Return" (NSR; an agreement between concentrator and smelter plants) requirement.

As observed in Table 2, the ratio of Fe to Cu for the flotation with CC is in the order of 2.3, which is considerably higher than the one established in the previous statement (0.86). When this ratio is calculated for the HAs components, each of them shows considerably lower ratios (from 1.68 up to 1.81; i.e. describing a better agreement with the NSR). For the flotation with BSA the Fe to Cu ratio is estimated to be 3.01. This result further supports the elimination of BSA as a pure collector component. D-glucose and the biosolid followed similar trends once compared with the HAs.

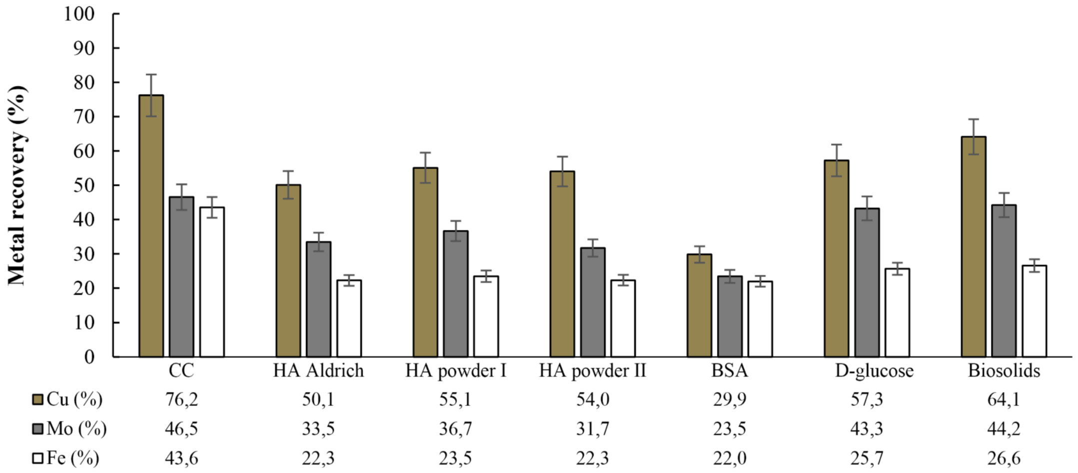

Fig. 1. Copper, Molybdenum and Iron Recovery percentages in the concentrate obtained using different main collectors in froth flotation of copper sulfide ore. Figure show the average values (n = 3) and standard errors.

3.2. Kinetic results

Different kinetic tests are performed in order to obtain a higher insight in the flotation characteristics of biosolids and humic acids (HAs). HAs are selected for the flotation test since, as discussed in the performance evaluations, they behaved as the most suitable replacement for CC. Further evaluation is also conducted via the kinetic studies to test the synergetic effects of CC with alternative collectors.

Fig. 2 shows the cumulative Cu recoveries and the instantaneous Cu grade in the concentrate in function of the different collectors used (and mixtures of them). As observed in the figure, the CC allowed recoveries of up to 81.6% Cu; biosolids and HAs (as pure components) achieved considerably lower recoveries (58.1% and 49.0%, respectively). These results confirm the depressor effect of totally replacing the chemical collector.

The partial replacement of the CC by the alternative collectors allow considerably recovery improvement once compared with the pure collectors. These recoveries are 83.7% and 75.7% for HAs and biosolids partial replacement, respectively. Furthermore, it is observed that instantaneous concentrations are considerably higher for the first minutes of the flotation process when mixtures are used. Regardless of this initial trend, as the times passes, the concentration achieves a values of ~2%, independently of the collector used.

Previous studies performed by Reyes-Bozo et al. (2011a, 2011b, 2011c, 2014a, 2014b, 2015) with similar experimental methods (14 min of flotation) showed that HAs and biosolids achieve recoveries of 35.0% and 18.0%, respectively. There is a discrepancy with this work since different ore mineralogical composition, collector dosage, pH, cell type, and biosolids composition are used. As previously stated, the flotation is function of collector type, medium pH, and additives (Bulatovic, 2007).

Fig. 3 shows the results obtained for Mo. Similar to Cu results, the Mo concentration is approximately the same at the end of the extraction process (14 min), regardless of the collector used.

In terms of the cumulative recoveries, the CC achieved values of 44.3% (after 14 min), while the biosolids and HAs achieved values of 38.1% and 31.6%, respectively. When the CC is mixed with biosolids or humic acids, the values increase to 68.1% and 63.7%, respectively. These results establish a synergetic effect between CC and biomass-based collectors. The synergetic effect of the mixtures is explained by the addition of different functional groups present in humic substances that can interact with mineralogical species (Fairhurst and Warwick, 1998; Jones and Bryan, 1998) by electrostatic and/or hydrophobic interactions (Gamboa and Olea, 2006). The hydrophilic sites present in the humic substances could interact with sulfated (or partially oxidized) mineralogical species, allowing the metal-collector or metal-collectors aggregate to be removed from the froth.

The resulting flotation kinetic parameters are given in Table 3 in function of the metallic component (Cu or Mo) and the collector or mixture of collector used. As observed in Table 3, the kinetic rate constant for Cu flotation, *k,* is relatively similar for pure CC and HAs (0.31 min^{-1} and 0.29 min^{-1}, respectively). This result implies ores treated by HAs would require similar flotation times, once compared with CC, to achieve a limiting or stationary recovery. Regretfully HAs as a pure collector would achieve a recovery that is considerably lower than the CC (R∞ of 48.90% instead of 81.39%). The biosolids achieved higher recoveries but the rate of flotation is lower once compared to CC treatments (i.e. higher volumes, in the continuous process, or higher flotation times, in batch-type processes, would be required to achieve the stationary/stable conditions).

When mixtures of CC and biosolids or HAs are evaluated, the *k* values are considerably higher. This result clearly establishes a synergetic effect that would allow a reduction of the time/volumes required for the flotation process to achieve a specific/stationary recovery. In fact, by considering the mixture of CC-HA, an increase in the order of 2.84 times the flotation rate/speed of the pure CC is observed. This reduction in time requirements would not modify considerably the flotation yield; the maximum theoretical flotation recovery (R_∞) is 81.39% for CC and 80.64% for the CC-HA mixture. In the case of copper froth flotation kinetic parameters, the absolute average percentage error of the model was less than 4.18% (see Table 3). This value was calculated from recoveries measured and estimated by the model.

Considering the Mo results, an increase in the order of 1.46 times the flotation rate of the pure CC is observed when the CC-HA mixture is used. The extraction yield, evaluated by R_∞, also shows a higher value when mixture are used. When the mixture of CC-biosolid is evaluated, an increase in the kinetic rate constant is observed (2.39 and 1.58 times with respect to pure CC for Cu and Mo, respectively), but a reduction of 10.85% in the Cu recovery is obtained (limiting the application of CC-biosolid mixtures). In the case of molybdenum froth flotation kinetic parameters, the absolute average percentage error of the model was less than 2.79% (see Table 3). This value was calculated from recoveries measured and estimated by the model. Independently of this result, further economic and technical evaluations should be performed (that should include energetic, metallic recovering, mixtures concentration, and NSR factors) in order to establish the optimum operational conditions for industrial application.

3.3. Green chemistry in flotation processing: towards sustainable mining

During the 2012–2025 period, the portfolio of new mining projects in Chile is and will continually growth given factors such as growing demand, geological conditions in the country (Cu ore grade), the change of production in the old hydrometallurgical operations, sustainability, etc. In the year 2014, 3.9 million tonnes of Cu by pyrometallurgical processes were produced (~68% of the Chilean total annual Cu production). It is projected that for the year 2026 the production of Cu in concentrate will reach 6.75 million tonnes, reaching around 89% of the total domestic production of Cu (Cochilco, 2015b). It is also projected that in 2026 around 63,675 tonnes of collectors will be used in Cu froth flotation processes.

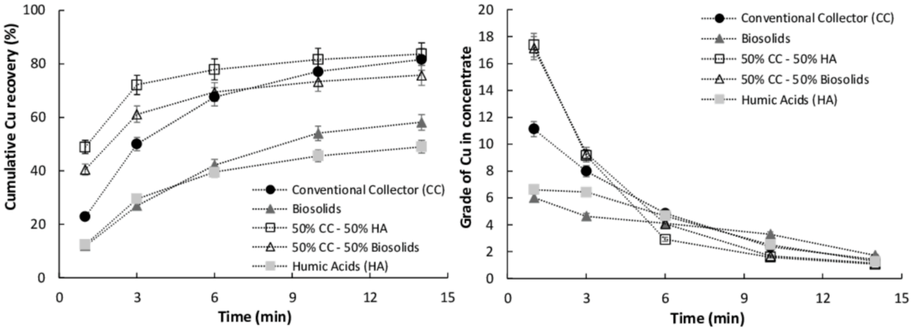

Fig. 2. Cumulative copper recovery and instantaneous grade of copper in the concentrate as function of time for the different collector used in kinetic evaluation. Figures show the average value (n = 3) and standard error is (in general) within the symbols. The dotted lines not necessarily represent linear trends.

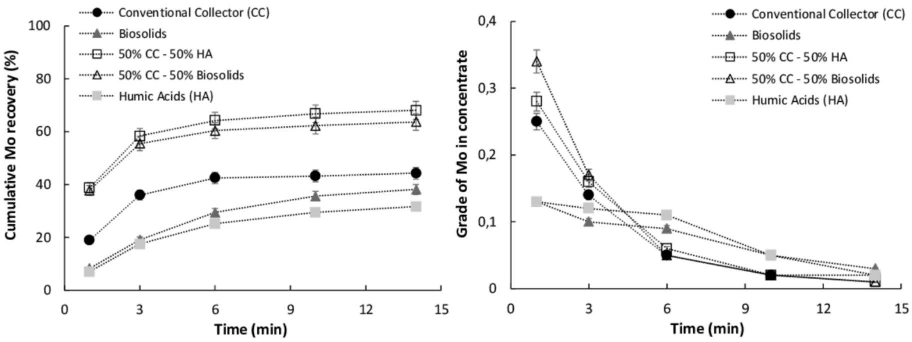

Fig. 3. Cumulative molybdenum recovery and instantaneous grade of molybdenum in the concentrate as function of time for the different collector used in kinetic evaluation. Figures show the average value (n = 3) and standard error is (in general) within the symbols. The dotted lines not necessarily represent linear trends.

Table 3
Flotation kinetic parameters for Cu and Mo.

Collector Used	Copper			Molybdenum		
	k (min^{-1})	R∞ (%)	Absolute average error of the model (%)	k (min^{-1})	R∞ (%)	Absolute average error of the model (%)
CC	0.31	81.39	1.92	0.57	43.89	0.64
Biosolids	0.19	62.75	2.61	0.22	39.92	1.26
50% CC–50% HA	0.88	80.64	3.02	0.83	66.10	2.79
50% CC–50% Biosolids	0.74	72.56	4.18	0.90	61.79	2.50
HA	0.29	48.90	1.79	0.25	32.32	1.27

CC: Conventional Collectors; HA: Humic Acid.

The main collector used in froth flotation processes has a market average cost of 3 USD/kg (Reyes-Bozo et al., 2014a; Yin et al., 2018). As an example, if 125,000 t/day milled copper sulfide ore are processed via froth flotation processes and a 50 g/t of main collector are used in the concentration step, then 6250 kg/day of collector are required and 18,750 USD/day are needed. Considering the use of biosolids (as received from the wastewater treatment plant) to replace 50% of the main collector, the main cost involved in the use of biosolids will be transport (i.e. saves ~9000 USD/day for this scenario).

The use of humic substances as the main collector would incur a final cost of around 2.1 USD/kg. This price was reported by Achurra Cofré (2013), considering the cost structure of a company to transfer technology to the copper mining industry.

When considering the HAs it has to be taken into consideration the sale price, initial sales volume, sales growth, fees, and taxes. In this case, 3125 kg/day of HAs are required and 6563 USD/day are needed. Therefore, the use of mixtures of CC-HA could save around 2800 USD/day.

Using the projected requirement of collector (63,675 tonnes) it can be estimated a total collector cost of ~191 MM USD. The use of the biosolids and humic substances in the froth flotation process could save between 28 and 95 MM USD per year.

From a hazard point of view the replacement of current chemical bye biosolids and humic substances will allow safer operations; the alternatives possess lower environmental and handling concerns than current chemicals (flashpoint, high vaporization rates, residual chemical properties producing unpleasant odor, hazardous materials classification, and potential health effects (Chockalingam et al., 2003; Ralston, 2002; Tan et al., 2005)).

From an energy point of view in 2017 the total fuel and the total electricity consumptions in Cu mining were of 81,851 TJ and 88,066 TJ, respectively. For the concentrating plant the total fuel and total electricity consumptions were around 1149.0 TJ and 49,808.5 TJ (Cochilco, 2018). It is projected an electricity consumption around 142,000 TJ for the year 2025 (with an electricity consumption in the concentrating plant of 87,876 TJ). Since the partial replacement of the CC by organic wastes shows faster kinetic parameters, processing times would be reduced, leading to a reduction in electricity consumption (i.e. operational costs).

4. Conclusions

Biosolids and their main components are evaluated as an alternative to conventional collectors (CC) for the copper sulfide ores concentration processes. CC replacement performance is evaluated by different froth flotation indexes and kinetic parameters. Biosolids (combinations of humic acids, proteins, and sugars) and their main components have shown the capacity to achieve considerable Cu and Mo recovery rates. The highest recovery achieved by the non-conventional collector is of 64.1% for Cu and 44.2% for Mo; relatively close to those achieved by CC (76.2% for Cu and 46.5% for Mo).

The pure main components of biosolids did not achieve higher recoveries, implying a synergetic effect of the biomass components. Humic Acids (HAs) have shown to be one of the principal components that could be used as replacement for CC (based on the indexes obtained).

HAs and biosolids are kinetically tested to totally or partially (50 wt %) replace the CC. The HA - CC mixtures describes the best performance, based on the kinetic parameters and Cu/Mo flotation yields (HA-CC kinetic constant: of 0.88 min^{-1} for Cu and 0.83 min^{-1} for Mo; CC kinetic constant: 0.31 min^{-1} for Cu and 0.57 min^{-1} for Mo).

Further evaluations should be conducted to obtain the optimal mixtures to partially replace CC by the environmentally-sound biosolids or HAs. In addition to environmental benefits, the non-conventional collector could produce a reduction in production costs and, at the same time, an increase of production of byproducts (such as Mo) in the Cu flotation.

Acknowledgment

The authors would like to express the appreciation for the funding that has supported this research. The study was funded by the Chilean CONICYT program through the National Fund for Scientific and Technological Research (FONDECYT), Project No. 11121159. Further support was also received from a grant to Dr. L. Reyes-Bozo from Universidad de Castilla-La Mancha ("Ayudas para estancias de investigadores invitados en la UCLM para el año 2016"); the Science

Foundation Ireland under Grant No. 12/RC/2289 (co-funded by the European Regional Development Fund); and, for Dr. Alex Godoy-Faúndez, CONICYT/FONDAP/15130015.

References

Bradshaw, B.J., O'Connor, C.T., 2000. Bubble-particle adherence: synergistic effect of reagents. In: Wilson, I. (Ed.), Encyclopedia of Separation Science, first ed. Academic Press, pp. 1455–1464.

Achurra Cofré, G., 2013. Creación de una empresa de Base Tecnológica. Bioflotación: Un Spin-off desde la Universidad Católica de Chile hacia la Industria Minera Chilena. Tesis de Magíster. Pontificia Universidad Católica de Chile, Santiago, Chile.

Ansari, A., Pawlik, M., 2007. Floatability of chalcopyrite and molybdenite in the presence of lignosulfonates. Part II. Hallimond tube flotation. Miner. Eng. 20, 609–616. https://doi.org/10.1016/j.mineng.2006.12.008.

Apak, R., 2002. Adsorption of heavy metal ions on soil surfaces and similar substances. In: Encyclopedia of Surface & Colloid Science. Dekker, New York, pp. 385–417.

Ata, S., 2012. Phenomena in the froth phase of flotation – a review. Int. J. Miner. Process. 102–103, 1–12. https://doi.org/10.1016/j.minpro.2011.09.008.

Baek, K., Yang, J.W., 2005. Humic-substance-enhanced ultrafiltration for removal of heavy metals. Separ. Sci. Technol. 40, 699–708. https://doi.org/10.1081/SS-200042665.

Bulatovic, M., 2007. Handbook of Flotation Reagents: Chemistry, Theory and Practice: Volume 1: Flotation of Sulfide Ores, first ed. Elsevier Science, The Netherlands.

Burlakovs, J., Jani, Y., Kriipsalu, M., Vincevica-Gaile, Z., Kaczala, F., Celma, G., Ozola, R., Rozina, L., Rudovica, V., Hogland, M., Viksna, A., Pehme, K.M., Hogland, W., Klavins, M., 2018. On the way to 'zero waste' management: recovery potential of elements, including rare earth elements, from fine fraction of waste. J. Clean. Prod. 186, 81–90. https://doi.org/10.1016/j.jclepro.2018.03.102.

Chockalingam, E., Subramanian, S., Natarajan, K.A., 2003. Studies on biodegradation of organic flotation collectors using *Bacillus polymyxa*. Hydrometallurgy 71, 249–256. https://doi.org/10.1016/S0304-386X(03)00163-4.

Cochilco, Chilean Copper Commission, 2015. Factores clave para el desarrollo de la minería en Chile, Santiago, p. 257.

Cochilco, Chilean Copper Commission, 2015. Inversión en la minería Chilena: Cartera de Proyectos 2015-2024, Santiago, p. 105.

Cochilco, Chilean Copper Commission, 2018. Yearbook: Copper and Other Mineral Statistics 1998-2017. Santiago, p. 168.

Fairhurst, A.J., Warwick, P., 1998. The influence of humic acid on europium-mineral interactions. Colloids Surf., A 145, 229–234. https://doi.org/10.1016/S0927-7757(98)00662-1.

Gaines, V.R., Skinner, W.C., Foord, E.E., Mason, B., Rosenzweig, A., 1997. Dana's New Mineralogy, eighth ed. John Wiley & Sons, Inc.

Gamboa, C., Olea, A.F., 2006. Association of cationic surfactants to humic acid: effect on the surface activity. Colloids Surf., A 278, 241–245. https://doi.org/10.1016/j.colsurfa.2005.12.026.

Gupta, A., Yan, D.S., 2006. Mineral Processing Design and Operation: an Introduction, first ed. Elsevier.

Hadler, K., Aktas, Z., Cilliers, J.J., 2005. The effects of frother and collector distribution on flotation performance. Miner. Eng. 18, 171–177. https://doi.org/10.1016/j.mineng.2004.09.014.

Herrera-Urbina, R., 2003. Recent developments and advances in formulations and applications of chemical reagents used in froth flotation. Min. Proc. Ext. Met. Rev. 24, 139–182. https://doi.org/10.1080/08827500306898.

Hizal, J., Apak, R., 2006. Modeling of copper(II) and lead(II) adsorption on kaolinite-based clay minerals individually and in the presence of humic acid. J. Colloid Interface Sci. 295, 1–13. https://doi.org/10.1016/j.jcis.2005.08.005.

Jones, M.N., Bryan, N.D., 1998. Colloidal properties of humic substances. Adv. Colloid Interface 78, 1–48. https://doi.org/10.1016/S0001-8686(98)00058-X.

Lèbre, E., Corder, G., Golev, A., 2017. The role of the mining industry in a circular economy: a framework for resource management at the mine site level. J. Ind. Ecol. 21 (3), 662–672. https://doi.org/10.1111/jiec.12596.

Monsuka, J., Hegenauer, J., Van Dyke, B.R., Saltman, P., 1993. Intrinsic stoichiometric equilibrium constants for the binding of zinc(II) and copper(II) to the high affinity site of serum albumin. J. Biol. Chem. 268 (29), 21533–21537.

Pandey, A.K., Pandey, S.D., Misra, V., Viswanathan, P.N., 1999. Formation of soluble complexes of metals with humic acid and its environmental significance. Chem. Ecol. 16 (4), 269–282. https://doi.org/10.1080/02757549908037652.

Ralston, I.D., 2002. The process, health, safety and engineering issues related to the storage and use of xanthates. ATD Report No. PRE-2002-003, Mayo de 2002. Anglo American.

Rao, S.R., 2004. Surface Chemistry of Froth Flotation, second ed. Kluwer Academic Plenum Publishers, New York, USA.

Reyes-Bozo, L., Herrera-Urbina, R., Godoy-Faúndez, A., Sáez-Navarrete, C., Herrera, M., Ginocchio, R., 2011. Use of biosolids as froth reagent in flotation process: chemical and physical characterization. Dyn. Rev. Fac. Nac. Minas 78 (167), 66–73.

Reyes-Bozo, L., Herrera-Urbina, R., Sáez-Navarrete, C., Otero, A.F., Godoy-Faúndez, A., Ginocchio, R., 2011. Rougher flotation of copper sulphide ore using biosolids and humic acids. Miner. Eng. 24, 1603–1608. https://doi.org/10.1016/j.mineng.2011.08.014.

Reyes-Bozo, L., Herrera-Urbina, R., Escudey, M., Godoy-Faúndez, A., Sáez-Navarrete, C., Herrera, M., Ginocchio, R., 2011. Role of biosolids on hydrophobic properties of sulfide ores. Int. J. Miner. Process. 100 (3–4), 124–129. https://doi.org/10.1016/j.minpro.2011.05.009.

Reyes-Bozo, L., Godoy-Faúndez, A., Higueras, P., Herrera-Urbina, R., Salazar, J.L., Vyhmeister, E., Valdés-González, H., Antizar-Ladislao, B., 2014. Greening Chilean mining operations through industrial ecology strategies. J. Clean. Prod. 84, 671–679. https://doi.org/10.1016/j.jclepro.2014.03.088.

Reyes-Bozo, L., Higueras, P., Godoy-Faúndez, A., Sobarzo, F., Sáez-Navarrete, C., Vásquez-Bestagno, J., Herrera-Urbina, R., 2014. 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. Miner. Eng. 64, 38–43. https://doi.org/10.1016/j.mineng.2014.04.004.

Reyes-Bozo, L., Escudey, M., Vyhmeister, E., Higueras, P., Godoy-Faúndez, A., Salazar, J. L., Valdés-González, H., Wolf-Sepúlveda, G., Herrera-Urbina, R., 2015. Adsorption of biosolids and their main components on chalcopyrite, molybdenite and pyrite: zeta potential and FTIR spectroscopy studies. Miner. Eng. 78, 128–135. https://doi.org/10.1016/j.mineng.2015.04.021.

Sadzawka, A., Carrasco, M.A., Grez, R., Mora, M.L., Flores, H., Neaman, A., 2006. Métodos de análisis recomendados para los suelos de Chile. Instituto de Investigaciones Agropecuarias (INIA), Santiago, Chile.

Stevenson, F.J., 1994. Humus Chemistry: Genesis, Composition, Reaction. John Wiley & Sons, Inc.

Tan, S.N., Pugh, R.J., Fornasiero, D., Sedev, R., Ralston, J., 2005. Foaming of polypropylene glycols and glycol/MIBC mixtures. Min. Eng. 18, 179–188. https://doi.org/10.1016/j.mineng.2004.08.017.

Thomas, W., 2010. Mining Chemical Handbook. Cytec Industries Inc., USA.

Tipping, E., Rey-Castro, C., Bryan, S.E., Hamilton-Taylor, J., 2002. Al(III) and Fe(III) binding by humic substances in freshwaters and implications for trace metal speciation. Geochem. Cosmochim. Acta 66, 3211–3224. https://doi.org/10.1016/S0016-7037(02)00930-4.

Urdiales, C., Sandoval, M.P., Escudey, M., Pizarro, C., Knicker, H., Reyes-Bozo, L., Antilén, M., 2018. Surfactant properties of humic acids extracted from volcanic soils and their applicability in mineral flotation processes. J. Environ. Manag. 227, 117–123. https://doi.org/10.1016/j.jenvman.2018.08.072.

Wills, B.A., 2006. Mineral Processing Technology: an Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, seventh ed. Elsevier Ltd., Oxford, UK.

Yin, Z., Sun, W., Hu, Y., Zhang, C., Wu, K., 2018. Evaluation of the possibility of copper recovery from tailings by flotation through bench-scale, commissioning, and industrial tests. J. Clean. Prod. 171, 1039–1048. https://doi.org/10.1016/j.jclepro.2017.10.020.