

Article

Flotation of Chalcopyrite and Molybdenite in the Presence of Organics in Water

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Abstract: One of the water constituents that has not been investigated in great detail for potential detrimental effect on mineral flotation is organic matter. This study investigates the effect of natural organic materials contained in water, such as humic, fulvic and tannic acids, on the flotation of copper and molybdenum sulphides in alkaline conditions and in concentrations similar to those found in natural waters. Results show that copper and molybdenum grades decreased with the addition of humic, tannic and fulvic acid in that order, with a larger depression of molybdenite grade and recovery. Adsorption studies using ultraviolet (UV)-visible spectroscopy and X-ray photoelectron spectrometer (XPS) surface analysis confirmed that these organic materials were adsorbed on the minerals surface. Complimentary analyses of froth characteristics, particle size distribution and fine particles entrainment were also conducted to explain the cause of the negative effect of these organic materials on flotation. The flotation results were explained in terms of the decrease in the hydrophobicity of the mineral surfaces due to the adsorption of hydrophilic groups in these organic materials which then prevent bubble-particle adhesion. The larger detrimental effect of humic acid is due to its higher adsorption on the minerals, high molecular weight and carbon content compared with the other organic acids used.

Keywords: organic matter; sulphide minerals; adsorption; flotation

1. Introduction

Organic matter (OM) is a constituent of all types of water and perhaps the most significant impurity in water. Fresh water contains organic matter particulate, or dissolved and generally called humic substances accounting for 40%–90% of the dissolved organic carbon (DOC), divided into two main fractions, humic and fulvic acids [1,2]. Fresh water used in mineral processing and recycled process water contains OM and also carries lingering organic compounds from residual reagents and from the ponds themselves (runoff and sediments). Typical ranges of humic substances concentrations in aquatic systems are 0.03–0.6 mg/L in ground waters, 0.5–4.0 mg/L in rivers and 0.5–40 mg/L in lakes [1]. These organic matters are polyelectrolytes and organic acids with a high molecular weight, presenting many functional groups (carboxylic, hydroxyl, phenolic, aromatic, quinone structures, nitrogen, various aromatic rings and weak aliphatic acids) varying in form and structure depending on environment conditions [3]. They exhibit high surface activity and have dispersant and flocculant properties [4,5]. They were classified for their dispersant, depressant and flocculant properties [4] that can interfere with flotation processes [5–8].

The interaction of OM with sulphide minerals and its effects on their flotation are little understood. Although chalcopyrite recovery and grade are generally high in the flotation of most copper and molybdenum ores, this is not the case for molybdenite, whose flotation is much lower and sensitive to

changes in hydrodynamic and pulp conditions in the flotation cell [9–12]. A few studies have reported the deleterious effect of fulvic and humic acids on molybdenite flotation [13,14]. They showed that organic species in water that originate from reagent and source of water (humic acids, tannins) act as depressants of molybdenite. Hoover [13] presented an approach to the effect of water chemistry on the flotation of molybdenite by emphasizing the presence of cations and colloidal material on molybdenite surface. Indeed, positively charged divalent metal ions such as calcium or magnesium were shown to act as a bridge and promote the adsorption of organic matter on iron hydroxide by the formation of covalent bonds between carboxyl groups in organic matter and the metal hydroxyl at the surface [15]. Various studies [16–18] showed that secondary municipal waste water used in Cu–Mo flotation resulted in lower recovery rates and diminished froth characteristics. They also showed that tertiary treatment of that waste water, foam fractionation (to remove surface-active material of anionic species) and dilution with fresh water were necessary to overcome the problem. The depressive effects of other organics such as lignosulfonate, dextrin, coconut sulphate oil, bacteria and starch on copper and molybdenum minerals flotation have been reported in the literature [11,13,19–22]. These organics have a negative effect on the flotation of other minerals such as pyrochlore [5,23], copper, gold [24], sphalerite and galena [25]. Contrary to numerous results in the literature on the depression of the flotation of sulphide minerals by hydrophilic macromolecules, recent results by Reyes-Bozo and co-authors [26–28] have shown that biosolids, including humic acid, by interacting with sulphide minerals (chalcopyrite and molybdenite) can improve their hydrophobicity, and therefore could be used as an environment-friendly alternative collector and frother in the flotation of sulphide minerals.

Due to the discrepancies in the literature about the effect of these organics on mineral flotation, the present study will compare the effects of the OM, humic, fulvic and tannic acids, in different concentrations in water, on the flotation of copper and molybdenum sulphide minerals in single mineral and in ore experiments. The flotation results will be compared to the extent of OM adsorption and to the species found on the mineral surfaces. Possible mechanisms of OM interaction with the sulphide minerals surface will be discussed.

2. Materials and Methods

2.1. Materials

Single minerals of chalcopyrite and molybdenite were used. Chalcopyrite particles were produced by grinding and sieving pure chalcopyrite (30.1% Cu, 32.1% S, 29.4% Fe from Moonta Bay, Australia) in a ceramic mortar and pestle with a small amount of NaCl (10^{-2} M) solution as background electrolyte. Molybdenite particles were obtained by sieving a high grade ($\text{MoS}_2 > 95\%$) flotation concentrate from a North American mine. The molybdenite particles were cleaned with *n*-propyl bromide >93% (Ensolv) five times to remove the oil collector and washed several times with ethanol. Infrared and XPS analyses revealed no trace of the collector or solvent on the molybdenite surface. Also, a typical South American Cu–Mo sulphide ore (0.7% Cu, 0.66% Cu–S, 0.0103% Mo, and 3.62% Fe) was used with mineralogical composition of quartz 45%, swelling clays 3%, kaolinite 2%, muscovite 34%, plagioclase 2%, turmaline 4%, calcite/dolomite 1%, pyrite 7% and chalcopyrite 2%. A 1.5 kg sample was ground to a D_{80} of 150 μm in a rod mill.

Three different samples of OM were used in the flotation and adsorption experiments: humic acid (HA) sodium salt from Aldrich (commercial grade), tannic acid (TA; standard grade) and fulvic acid (FA) isolated from the Myponga reservoir in South Australia using two non-ionic resins. TA and FA samples were provided by SA-Water, Adelaide. Their molecular weight and carbon content (C) are shown in Table 1. Humic, tannic and fulvic acids are macromolecules mainly composed of aromatic hydrocarbons with phenolic ($\text{pK}_a \sim 8\text{--}9$) and carboxylic ($\text{pK}_a \sim 4$) functional groups in humic and fulvic acids but only phenolic groups in tannic acid [29,30]. In all the experiments, the OM was added before the collector to simulate environmental conditions where OM is already present in the process water.

MilliQ water was used in all experiments. This water was produced by reverse osmosis, two stages of ion exchange and two stages of activated carbon adsorption, with a final filtration through a 0.22 µm filter. This water has a surface tension of 72 mN/m at 25 °C and a pH of 5.6 ± 1 . Sodium hydroxide (NaOH) was used as pH modifier.

Table 1. Molecular weight of organic matter (OM) and their carbon content.

Sample	Humic Acid (HA)	Tannic Acid (TA)	Fulvic Acid (FA)
MW (g/mol)	~2000	1701	500–1000
C (mg/L)	592	510	340

2.2. Flotation Experiments

After grinding, five grams of chalcopyrite in the +38–75 µm size fraction were transferred to a 300 mL Instytut Metali Nieżelaznych (IMN) mechanical flotation machine (IMN, Gliwice, Poland) and the pulp was agitated by an impeller at 2000 rpm and with a gas flow rate of $1.0 \text{ dm}^3 \cdot \text{min}^{-1}$ at pH 9.3 for 2 min before addition of the collector, sodium isopropyl xanthate (SIPX; 7 g/t), and frother, methyl isobutyl carbinol (MIBC; 15 g/t), with conditioning times of 2 and 1 min, respectively, before flotation. For molybdenite, 1 g of +150 µm particles was transferred to the flotation cell and conditioned in water at pH 9.3. Collector (diesel oil; 7 g/t) and frother (MIBC; 15 g/t) were added 2 and 1 min before the start of flotation, respectively. Four concentrates were collected at flotation times of 1, 3, 5 and 8 min (cumulative).

The flotation of the Cu–Mo sulphide ore (1.5 kg) was performed in a 4 L Denver flotation cell (Denver Equipment Co., Charlotte, NC, USA) at a pulp density of 30 wt % solids and an air flow rate of 8 L/min. The pulp was conditioned at pH 10.5 for 2 min with diesel oil (7 g/t) for Mo and isopropyl ethyl thionocarbamate (7 g/t) as primary collector and sodium isopropyl xanthate (2.35 g/t) as secondary collector for Cu before frother addition (alcohol mix of 7 g/t of Mcfroth H-75 and 7 g/t of glycol Dow Froth 1012) and flotation. Concentrates were collected at 2, 6 and 15 min of flotation (cumulative). After 4 min of flotation, 2.35 g/t of the secondary collector was added. All flotation tests were performed in duplicate.

2.3. Particle-Bubble Stability Study

The critical amplitude of vibration for the detachment of a 350–425 µm chalcopyrite or molybdenite particle from a 2 mm bubble in solution was measured using an electro-acoustic technique [31,32]. With this technique, a 2 mm bubble was formed at the end of a capillary tube attached to the membrane of a loudspeaker connected to an audio signal generator. The bubble is contained in a rectangular glass cell (9 cm × 9 cm × 3.5 cm) containing water with 10^{-2} M NaCl in the absence and presence of HA (10 and 20 mg/L) and collector (if required). One particle of chalcopyrite or molybdenite was carefully attached to this bubble and the amplitude of vibration was increased (at a fixed frequency of 50 Hz) until a critical amplitude is reached where the particle detached from the bubble, referred to thereafter as the critical amplitude for detachment. The experiment was repeated ten times for the same particle and for five randomly chosen particles to obtain the average critical amplitude for detachment.

The detachment force of the particle can be calculated using Equation (1) [33]:

$$F_{\text{det,max}} = F_{v,\text{max}} + F_g = m(2\pi f)^2 A + F_g, \quad (1)$$

where $F_{v,\text{max}}$ is the maximum vibration force for the particle, F_g is the particle immersed gravity force calculated by Equation (2), m is the particle mass (kg), A is the measured critical amplitude for detachment (in meter) and f the frequency of vibration (50 Hz).

$$F_g = \frac{4}{3}\pi R_p^3(\rho - \rho_w)g, \quad (2)$$

where ρ_w and ρ are the density of water (1 g/cm^3) and particle (4.19 g/cm^3 for chalcopryrite; 4.75 g/cm^3 for molybdenite), respectively, and R_p is the particle radius ($194 \pm 5 \text{ }\mu\text{m}$, the average of the radius of the 5 particles used, measured by optical microscopy after the experiment). A particle will detach from a bubble if the force of detachment (F_{det}) exceeds the force of attachment (F_{at}) [34].

$$F_{\text{det}} = F_{\text{at}} = \pi\sigma R_p(1 - \cos\theta) \quad (3)$$

where σ is the liquid-gas surface tension (72 mN/m at $25 \text{ }^\circ\text{C}$) and θ is the particle contact angle.

2.4. OM Adsorption Experiments

The UV-visible absorbance of aqueous solutions (10^{-2} M NaCl) containing increasing amounts of OMs was measured with a Cary 5 UV/Vis/NIR spectrometer (Agilent Technologies, Santa Clara, CA, USA) at 277 nm for TA and 330 nm for HA or FA to produce a calibration curve of UV absorbance versus OM concentration. The absorbance was found to increase linearly with OM concentration in the range 0 to 20 mg/L (commonly found in typical natural waters) as is shown in Figure 1. One gram of molybdenite or chalcopryrite ($D_{80} 10 \text{ }\mu\text{m}$) was conditioned in an IMN flotation machine at $\text{pH } 9.3$ with 300 mL of 10^{-2} M NaCl aqueous solutions containing various amounts of OMs (initial concentration, C_{initial} , ranging from 1 to 20 mg/L) for 11 min . A sample of the water was then collected and filtered through a $0.2 \text{ }\mu\text{m}$ Supor membrane. The absorbance of the filtered solution was measured and compared to that in the calibration curve to obtain the concentration of OM non-adsorbed on the minerals (C_{residual}). To remove the contribution of dissolved mineral species in water, a similar experiment was performed with the minerals in the absence of OM and the absorbance of the filtered solution was subtracted from that in the presence of OM. The adsorbed amount of OM, Γ (in milligram of OM per gram of mineral) was determined from the difference between the initial concentration (C_{initial}) and the residual concentration (C_{residual}). All OM adsorption experiments were performed in duplicate.

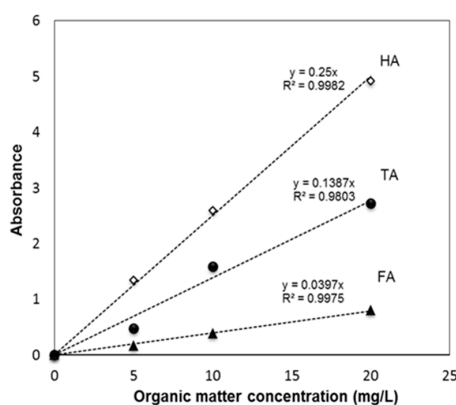


Figure 1. Absorbance versus concentration of humic acid (HA), tannic acid (TA) and fulvic acid (FA) ($\text{NaCl } 10^{-2} \text{ M}$; $\text{pH } 9.3$).

2.5. XRD Analysis

The feed ore and Cu–Mo bulk concentrates were analysed by X-ray diffraction (XRD). The analysis was performed using an Empyrean X-ray diffractometer (PANalytical, Almelo, The Netherlands) with a Cu anode and operated at 40 kV , 30 mA , divergence slit fixed 0.5 , position (2 Theta) from 5° to 100° , wavelength λ of 1.5406 \AA . Analysis of the patterns was performed using the High Score Plus software with PDF-4 (ICDD) database.

2.6. XPS Analysis

A Kratos Axis Ultra X-ray photoelectron spectrometer (XPS) with an Al K α monochromated X-ray source (1486.8 eV) operated at 130 W was used to measure the species present on the mineral surfaces. The samples of chalcopryrite and molybdenite were taken from flotation experiments (with 0 and 20 mg/L HA). They were mounted on a conducting copper tape as slurry, placed on the sample holder and introduced immediately into the forevacuum of the spectrometer. A fixed pass energy of 160 eV was used for the entire survey scan. All measurements were acquired at a take-off angle normal to the surface and were referenced to the C1s peak at 284.4 eV [35]. The XPS spectra were curve fitted using the CasaXPS program (Casa Software Ltd, Teignmouth, UK).

3. Results

3.1. Flotation of Molybdenite and Chalcopryrite in Single Mineral Experiments

Figure 2 shows the recovery of molybdenite and chalcopryrite after 8 min of flotation in the absence and presence of OM with concentrations of 5, 10 and 20 mg/L. Both molybdenite and chalcopryrite recoveries are depressed by these OM in the following order: HA > TA > FA. Increasing the concentration of OM resulted in further depression of molybdenite and chalcopryrite recovery. The recovery of molybdenite was more affected than the recovery of chalcopryrite by the OM addition. In particular, the recovery of molybdenite decreased by 33% after the addition of 20 mg/L TA or FA compared to only 14% for the recovery of chalcopryrite. The different depressions of flotation obtained by these OM may be related to their different levels of adsorption on the minerals.

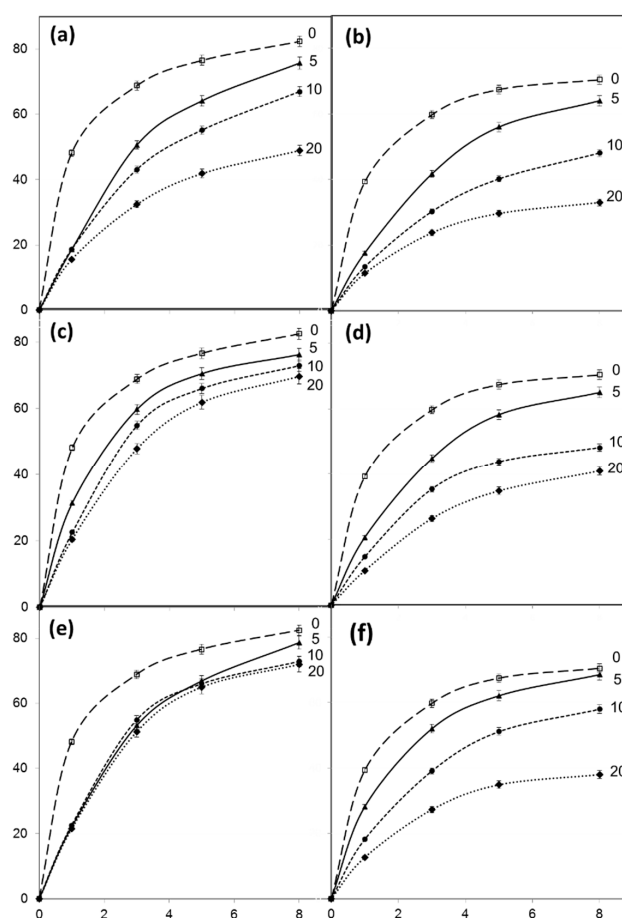


Figure 2. Cumulative recoveries as a function of flotation time and organic matter concentration (mg/L) for chalcopryrite with HA (a); TA (c); and FA (e) and for molybdenite with HA (b); TA (d) and FA (f) (pH = 9.3).

3.2. Effect of Organic Materials on the Flotation of Copper and Molybdenum in a Sulphide Cu–Mo Ore

The effects of OM (at a concentration of 20 mg/L) on the flotation of the Cerro Verde ore are presented in Figure 3. The final copper recovery was not affected by OM addition but the molybdenum recoveries were depressed only by HA or TA addition, from 75% to 36% for HA and to 59% for TA, despite mass recoveries increasing. The trends of larger depression of molybdenum recovery than copper recovery by these OMs and the larger depression by humic acid observed in the flotation of the sulphide ore are in agreement with the results obtained in the single mineral study.

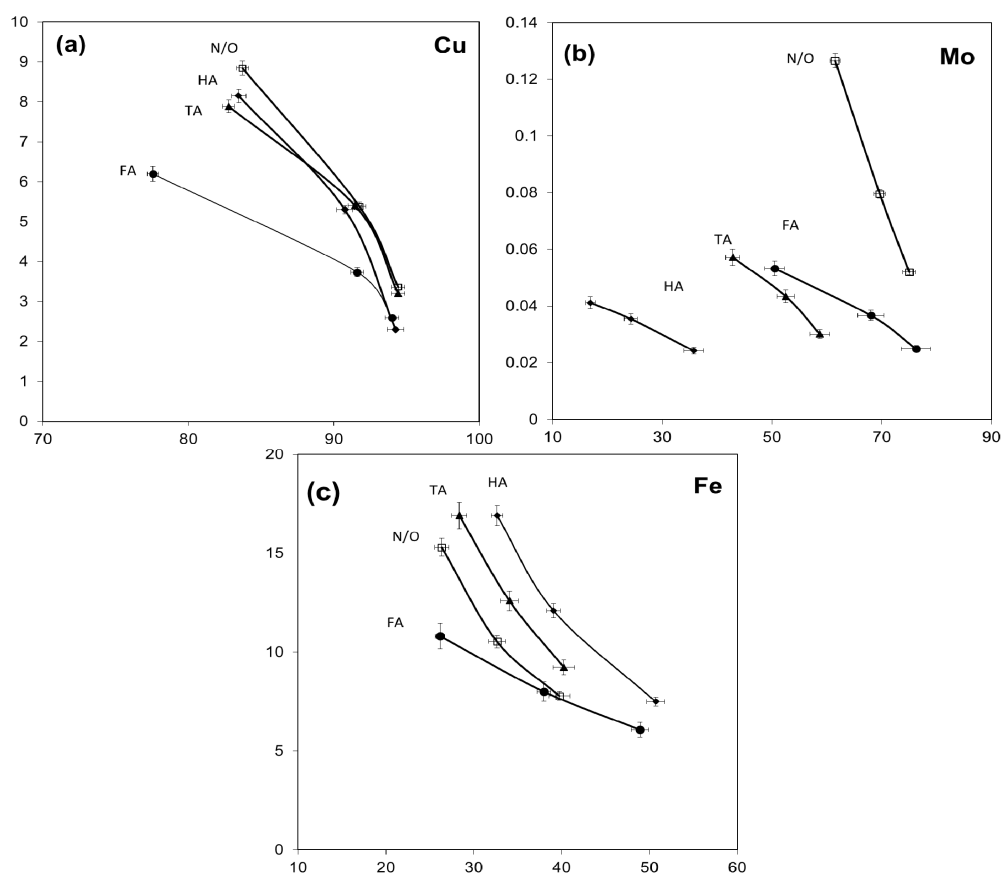


Figure 3. Grades versus recoveries of Cu (a); Mo (b); and Fe (c) in the bulk Cu–Mo flotation concentrate without (N/O) and with the addition of 20 mg/L of organic matter at pH 10.5.

Moreover, the final iron recovery increased with OM addition, except with tannic acid. The increase in iron recovery is certainly not associated with an increased recovery of the copper-iron sulphide minerals such as chalcopyrite (as copper recovery remains constant) but rather to an increased recovery of the iron gangue minerals such as kornelite and pyrite, as seen in Table 2 after XRD analysis of the feed and concentrates.

Table 2. Mass balance of Cu–Mo bulk concentrates without (N/O) and with 20 mg/L of humic or fulvic acid (from X-ray diffraction (XRD) analysis).

OM	% Recovery				
	Chalcopyrite	Quartz	Kaolin	Kornelite	Pyrite
N/O	74	23	77	52	10
HA	64	28	99	78	20
FA	63	27	83	66	17

Grades of copper and particularly molybdenum decreased with OM addition. This decrease in Cu and Mo grades is mainly related to the increased recovery of the gangue minerals, kornelite, pyrite, quartz and kaolin (Table 2).

Changes in the froth characteristics were observed in the presence of OM. An abundant but unstable froth (small bubbles) was obtained, particularly with HA and FA. This led to an increase in total mass recoveries (>5%) in the presence of OMs in the order HA \approx FA > TA. This increase in frothing may contribute to unselective flotation of gangue minerals. Also, the addition of OM increased water recovery in the concentrates by approximately 10%, which results in a higher entrainment of fine gangue mineral particles including pyrite. Indeed, particle size distribution analysis shows that after HA or FA addition, the amount of fine particles (<5 μ m) increased in the concentrates from 14% to 22%. The increase in frothing and fine particles entrainment observed after addition of OM may be one explanation for the different effects of OM on sulphide minerals flotation reported in the literature.

The quantitative chemical composition (by XRD analysis) of the bulk Cu–Mo concentrates for the -38 and $+38$ μ m fractions is shown in Figure 4. The results confirm the decrease of chalcopyrite flotation and the increase of pyrite flotation after the addition of HA and FA. The -38 μ m fraction of the concentrate has a higher percentage of quartz and kornelite and less kaolin with HA and FA addition, while the $+38$ μ m fraction has a higher percentage of kaolin and kornelite and less quartz than in the concentrate without HA and FA.

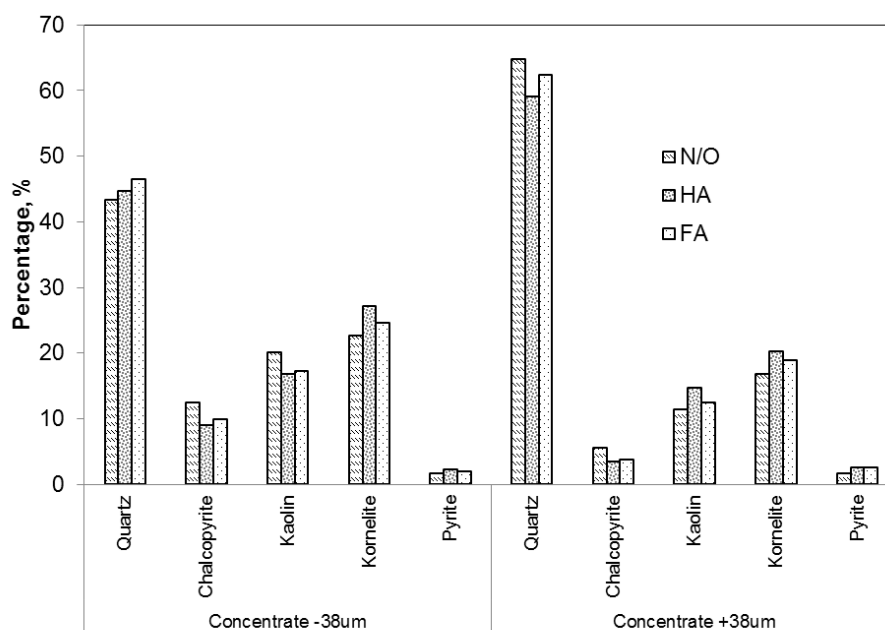


Figure 4. XRD analysis of species present in the bulk Cu–Mo concentrates without (N/O) and with 20 mg/L of humic acid (HA) or fulvic acid (FA).

3.3. Adsorption of Organic Materials on Molybdenite and Chalcopyrite

From the change in the UV-visible absorbance of the OMs in solution after contact with chalcopyrite and molybdenite and the calibration curves in Figure 1, it was possible to calculate the concentration of OM adsorbed on these minerals. Results in Figure 5 indicate that the OMs do adsorb on the sulphide minerals, which validates the interpretation for the depression of mineral flotation observed in Figure 2. Furthermore, HA adsorption on the two minerals is the highest and FA the lowest, which is in agreement with the trend of depression of mineral flotation by the OMs in Figure 2.

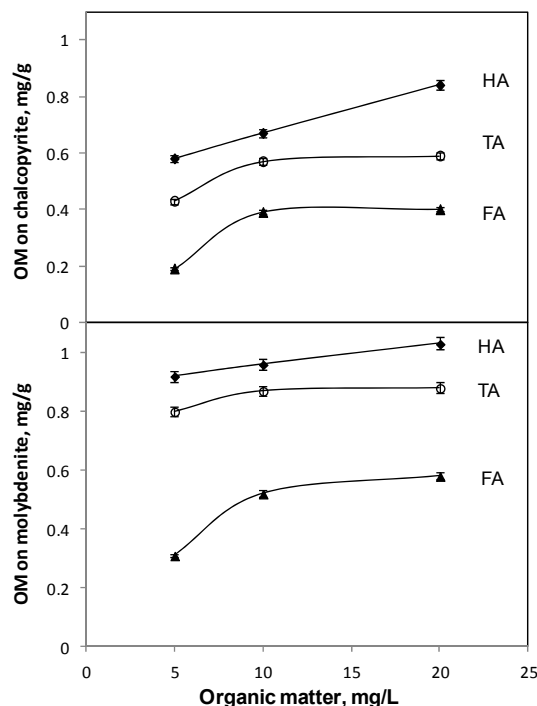


Figure 5. Concentration of OM adsorbed on (top) chalcopyrite; and (bottom) molybdenite (NaCl 10^{-2} M, pH 9.3).

The major change observed in the XPS survey spectrum (not shown) is the presence of a small N1s peak at approximately 400 eV [35] observed after humic acid addition, which is clear evidence that humic acid has indeed adsorbed on chalcopyrite and molybdenite. The proportions (at.%) of elements (C, O, Cu, Mo, Fe, S, N) on the surface of chalcopyrite and molybdenite particles collected just after eight min of flotation without and with addition of humic acid are shown in Table 3. Very small changes in the proportions of the elements were observed after humic acid addition, except for the N species increasing from zero to two percent on chalcopyrite and to eight percent on molybdenite. The high resolution C1s, O1s, Cu2p, Mo3d, Fe2p and S2p XPS spectra of chalcopyrite and molybdenite were deconvoluted into individual components [36]. The high resolution spectra and the results of the spectral deconvolution were almost identical before and after humic acid addition (not shown), which indicates that the interaction between humic acid and the mineral surface is not chemical in nature.

Table 3. Proportion (at.%) of the elements measured by X-ray photoelectron spectrometer (XPS) on the chalcopyrite and molybdenite surface without and with 20 mg/L humic acid (HA).

Mineral	Condition	C	O	Cu	Mo	Fe	S	N
Chalcopyrite	No HA	42	25	7	-	4	22	0
	With HA	43	23	7	-	4	21	2
Molybdenite	No HA	28	22	-	21	-	29	0
	With HA	29	17	-	18	-	27	8

3.4. Critical Amplitude, Detachment Force and Contact Angle

The hydrophobicity of a surface is usually evaluated by its contact angle. For particles, the measurement of their contact angle is difficult [37–41] and has some limitations. Usually, it requires the particles to be dried before measurement of the rate of wetting of their surface with a wetting and non-wetting liquid. Although the drying process is gentle, it may change the surface chemistry and therefore affect the final results, especially in the case of sulphide minerals, which are prone

to oxidation. Particle surface hydrophobicity can also be estimated through the measurement of particle-bubble detachment force using an electro-acoustic technique or atomic force microscopy [31]. With the electro-acoustic technique, the critical amplitude of vibration of a particle-bubble aggregate required to detach the particle from the bubble (at constant frequency) is measured. This critical amplitude for detachment reflects the strength of adhesion between particle and bubble and therefore should be proportional to particle hydrophobicity. This technique preserves the chemistry of the particle surface as the preparation/conditioning of the particles is the same as that in flotation. Recent results have shown that the critical amplitude for detachment of particles increases with their contact angles [42,43] and the technique is more sensitive for contact angles higher than 40°. Results in Table 4 show that the critical amplitude for detachment of the chalcopyrite particles increases from 0.56 to 1.16 mm with addition of 2 g/t SIPX collector but remains constant after addition of 10 or 20 g/t HA (1.15 and 1.16 mm, respectively). For the molybdenite particles, the effect of HA addition is more pronounced with the critical amplitude for detachment decreasing from 3.48 mm without HA to 2.02 and 1.02 mm with addition of 10 and 20 g/t HA, respectively. Table 4 also shows the corresponding values of the force of detachment and contact angle calculated with Equations (1) to (3). The results of these particle detachment experiments have shown that in the presence of HA the contact angle of the molybdenite particles and therefore the strength of adhesion between a molybdenite particle and a bubble are reduced, which explains the decrease in molybdenite recovery. For the chalcopyrite particles, HA had no effect on their detachment from the bubble and did not depress Cu recovery in the ore flotation experiment (Figure 3) but HA decreased chalcopyrite recovery in the single mineral flotation experiment (Figure 2). Different experimental conditions exist in these experiments that could explain the different results obtained for chalcopyrite: for example, competition in the adsorption of reagents on the surface of the various minerals present in the ore may occur; one particle is present at a time in the particle detachment experiment compared to multi-particles in the flotation experiments; also, the particles size and level of turbulence were different in these experiments.

Table 4. Critical amplitude of vibration (50 Hz) for the detachment of chalcopyrite and molybdenite particles, force of detachment and particle contact angle (NaCl 10^{-2} M, pH = 9.3) with 10 and 20 mg/L HA concentration.

Collector/OM g/t	Chalcopyrite			Molybdenite		
	Amplitude, mm \pm 0.02 mm	$F_{\text{detachment}}$ (N)	Contact Angle	Amplitude, mm \pm 0.02 mm	$F_{\text{detachment}}$ (N)	Contact Angle
SIPX, 0	0.56	8.17×10^{-6}	36	3.48	5.12×10^{-5}	99
SIPX, 2	1.16	1.59×10^{-5}	50	-	-	-
SIPX, 2; HA, 10	1.16	1.59×10^{-5}	50	-	-	-
SIPX, 2; HA, 20	1.15	1.58×10^{-5}	50	-	-	-
HA, 10	-	-	-	2.02	3.02×10^{-5}	72
HA, 20	-	-	-	1.02	1.58×10^{-5}	50

4. Discussion

The results of chalcopyrite and molybdenite flotation (Figure 2) and OM adsorption (Figure 5 and XPS study) on these two minerals indicate that, first, OM adsorption is the cause of the depression of mineral flotation in agreement with similar observations that the adsorption of hydrophilic macromolecules such as humic acid [14], lignosulfonate [11], guar gum [44] or polyacrylamides [45] on sulphide minerals results in the depression of the flotation of these minerals. More importantly, the results of critical amplitude of vibration for particle detachment (Table 4) clearly indicate that the strength of adhesion between the molybdenite particles and bubbles (and molybdenite hydrophobicity) is decreased after HA addition. Secondly, the results point to the importance of the molecular weight of these OM as the trend observed for OM adsorption and mineral depression (HA > TA > FA) is the same as the trend of their molecular weight (Table 1). This is in agreement with literature results showing that higher molecular weight polymers adsorb more than lower molecular weight ones because of their lower solubility in water and higher number of functional groups to anchor on mineral

sites [11,46,47]. Indeed, OM with a high molecular weight and a high number of functional groups have been shown to exhibit higher affinities for mineral surfaces [48–51] containing many non-identical binding sites [52,53]. Thirdly, the results confirm previous observations that molybdenite flotation is more affected by the presence of hydrophilic polymers than chalcopyrite, especially with TA and FA, which have little effect on chalcopyrite flotation (for example [11]).

The adsorption mechanism for these OM is not an electrostatic interaction as both minerals and OM are negatively charged in basic pH conditions [2,54,55] and therefore these OM should be electrostatically repelled from the mineral surfaces [56]. Chemical interaction between the carboxyl groups of the organic materials and copper, molybdenum or iron mineral sites is possible [57], although tannic acid does not have any carboxyl groups but does adsorb and depress mineral flotation. However, it has been postulated that chemical interactions between the hydroxyl groups of polysaccharide (e.g., guar gum) with the metal hydroxyl groups at the mineral surface (e.g., chalcopyrite) may also occur in addition to hydrogen bonding [58,59]. A similar observation has been made for the interaction of biosolids with chalcopyrite, molybdenite and pyrite, although a weaker interaction such as hydrogen bonding or van der Waals force was proposed for the interaction of humic acid with these sulphide minerals [27,60]. The higher adsorption of HA than TA on the minerals surface may also be attributed to the presence of carboxyl groups on HA which are absent on TA and may chemically interact with mineral sites. Therefore, in the present study hydrogen bonding between the hydroxyl groups of organic materials and the mineral surface is likely to be the main adsorption mechanism [4,61] because hydroxyl groups are the common species in the three organic materials and no evidence of chemical interaction has been observed using XPS surface analysis.

Moreover, adsorption of these OM on the sulphide mineral surface may also prevent collector adsorption [4] and therefore also contributes to the depression of these sulphide minerals. Indeed, Ansari and Pawlik [62] reported that the adsorption of lignosulfonates is accompanied by desorption of the physically adsorbed xanthate while Rath and co-workers [59] suggested that the collector xanthate is consumed by (interacts with) guar gum and therefore it can no longer increase the surface hydrophobicity of chalcopyrite.

5. Conclusions

Poor quality process water can significantly impact on the performance of mineral beneficiation processes. These waters may contain a high amount of organic matter such as humic, fulvic and tannic acids. In this study, the effect of these three organic matters on the flotation of two sulphide minerals, chalcopyrite and molybdenite, in single mineral and ore experiments was investigated. The flotation recoveries of molybdenite and chalcopyrite were depressed in the presence of these organic matters, with humic acid being the stronger depressant followed by tannic acid and fulvic acid. These flotation results are well explained by the amount of organic matters adsorbed on the two minerals with more adsorption of humic acid than tannic acid and fulvic acid. These acids, which contain a large number of carboxyl and phenolic groups (only phenolic groups in tannic acid) adsorb on the mineral surface, forming a hydrophilic barrier for collector adsorption and bubble attachment, which results in reduced mineral flotation. With its higher molecular weight, humic acid can form more hydrogen bonding between its hydroxyl groups and those on the mineral surface than the other two organic matters. Furthermore, these organic matters also have a negative effect on the froth stability, which results in a higher entrainment of fine gangue mineral particles in the ore and therefore a decrease in the chalcopyrite and molybdenite grades.

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