

Article

Investigation of Copper Recovery from a New Copper Deposit (Nussir) in Northern-Norway: Thionocarbamates and Xanthate-Thionocarbamate Blend as Collectors

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Abstract: Norway has newly seen an upsurge of interest in exploiting its mineral deposits influenced by fresh Government focus and survey support for previously under-prospected areas. One of the major areas of interest is a huge copper deposit, operated by Nussir ASA, located in the Repparfjord tectonic window in the Caledonides of west Finnmark. The latest mineral resource estimation is from July 2014, which states that Nussir consists of 5.8 million tonnes of indicated resources and 60.2 million tonnes of inferred resources, giving 66 million tonnes of copper ore. This paper represents the first study on processing characteristics of this ore to date. Our parallel studies using xanthates and dithiophosphates as collectors for Nussir ore flotation examined the grade and recovery of copper, silver, gold, and platinum group (PGM) minerals. Therefore, in this subsequent study, a chelating agent *n*-Butoxycarbonyl-*O*-*n*-butyl thionocarbamate (BBT) is used as a collector and it was found that the recovery and grades of the economically interesting minerals are improved at as low as 2×10^{-5} M collector concentration. Zeta potential, Hallimond flotation and adsorption studies were initially performed in order to assess the selective interaction of BBT and its blend with SIBX (Sodium Isobutyl xanthate) on the three copper minerals of the ore. The bench scale flotation experiments were performed using mixtures of xanthate and thionocarbamate collectors of the Nussir ore and both the resulting copper recovery and grade employing these collector mixtures is observed to be 2–8% superior to the use of a single collector system. Additionally, the current study revealed that the metallurgical results are strongly influenced by the ratio of the collectors in the mixture and particularly the sequence of the collector addition.

Keywords: chalcopyrite; chalcocite; bornite; zeta potential; adsorption; collector-mineral interaction; flotation

1. Introduction

There is a growing demand for copper and it is projected that current copper demands will exceed production by 2050 [1]. Primary copper sulphide ore reserves are declining while the new ore deposits are chiefly complex in nature and are primarily of a low copper grade. Consequently, more selective collectors are being used in the froth flotation process for high recovery of the existing resources. As mentioned in the earlier work [2,3], a new Nussir copper mine located in northern Norway is planning to begin its production in the near future. The copper minerals (chalcopyrite, chalcocite and bornite) are uniformly distributed in all size ranges in the ore sample under study. Silver, gold and PGM (Platinum group minerals) are also closely associated with these copper sulphides, although in minor amounts.

These precious metals are recovered by metallurgical processing. Flotation is performed to successfully separate copper sulphides from other gangue minerals in the ore, prior to metallurgical

processes. In flotation experiments, collector selection is a crucial parameter for high recovery and grade of all the economically interesting minerals. Copper sulphides are generally floated with thiol collectors at high pH value since pyrite can be depressed in this region. Pyrite or other iron sulphides are usually gangue sulphide minerals present in most of the copper sulphide ores. However, in the Nussir deposit, iron sulphides are not present and therefore beneficiation of this ore would be feasible in the natural pH (pH 8) region. It has been reported that thionocarbamates are more selective and are more stable in acidic/neutral solutions than xanthates and dithiophosphates, which makes it possible to use them as acid/neutral-circuit collectors. The reason is that the thionocarbamates are chelating agents. However, the selectivity of these collectors is hugely influenced by the pKa value of the collector as it represents the tendency of the donor atom to donate electrons to the metal atom, or acceptor. The pKa value for butyl thionocarbamate $\approx 8/9$ and it was thus selected as a candidate flotation collector for the Nussir ore [4].

Previous works have studied the flotation characteristics and zeta potential values of copper sulphides in the presence of thionocarbamates have been studied [4–7]. Ackerman et al. [8] indicated that at a pH 8.5, the recovery of chalcocite and chalcopyrite was high (ca. 90%), while recovery for bornite was low. The adsorption of thionocarbamates on Cu-minerals are presented in several studies and primarily all the studies report that the mode of adsorption is chemisorption on Cu-sites through Sulphur(S) [6,9,10]. The collecting ability of thionocarbamate is directly influenced by the electron density of the reactive centre (sulphur atom) such that it is enhanced when the electron density of the reactive centre is raised by the electron-donating group. The other possible heteroatoms in thionocarbamate are oxygen(O) and nitrogen(N); thionocarbamates can form a six-membered ring complex with copper ions through their carbonyl oxygen, nitrogen and thiol sulphur atoms. Bogdanov et al. [9] stated that both the S and N of the collector formed a bond with the Cu atom. Alternatively, Glembotskii [10] stated that in the dialkyl thionocarbamates, both the electron density on the hetero atom, and its steric accessibility, decreased in the order $S > O > N$. Additionally, if the chemisorption of the collector to Cu on the surface of Cu-sulphides involves a heteroatom in addition to the S, it would be the O rather than the N. Ackerman et al. [11] employed *O*-isopropyl-*N*-ethyl thionocarbamate (IPETC) as a collector and showed that, while the S was the most reactive atom in a thionocarbamate molecule, the N must be available for chelate ring formation. Therefore, N would be the heteroatom other than S, involved in the interaction instead of O.

Leppinen et al. [6] performed in-situ Fourier transform infrared spectroscopy (FTIR) studies and found that, except at very low pH, adsorption of IPETC thionocarbamate on chalcocite was higher than on chalcopyrite. They showed that below pH 6, IPETC adsorbed on chalcocite through the S only, but above pH 6, adsorption was through both S and O. A completely different perspective was presented by Yoon and Basilio [12]. They proposed that thionocarbamates adsorb on sulphide minerals via a dissolution–precipitation mechanism, which results in a metal thiol compound being formed on the mineral surface. Later, Woods and Hope [13] and Woods et al. [14] provided evidence for chemisorption of thionocarbamate on Cu metal through the S on surface Cu atoms. Buckley et al. [15] performed a detailed study of the interaction of IPETC with copper sulphides. These authors claim that merely 30% collector is chemisorbed on bornite, whereas 70% of the surface had been adsorbed by the protonated IPETC on bornite in acidic pH. Overall, there is a common opinion that pH is the most important factor responsible for the difference in adsorption behaviour of thionocarbamate on copper sulphides. Therefore, pH is considered as the major parameter in the current study.

Previously, several researchers demonstrated that collector mixtures were better reagents for the flotation of valuable minerals than the single collector systems [16–21]. The rate of flotation is reported to be higher with collector blends as compared to the single collector system [16,22–24]. Plaskin et al., [22].; Lotter and Bradshaw, [16] also observed other advantages, such as improvement in coarse particle recovery and middlings recovery. Additionally, the total collector dosage of the mixed collector was lower than the single collector concentration in several studies [20,23]. Bagci et al. [25] and Critchley and Riaz [18] studied the sequence of collector addition and proposed that the adsorption

is improved by the addition of weaker but more selective collectors (dithiophosphate) before the less selective collector (SIBX). In general, thionocarbamates are known as the most selective collector for sulphide flotation and are reported to have the highest collector strength of all the thiol collectors.

In the process of developing a flowsheet for Cu-recovery, thionocarbamate and its blend with xanthate are examined as candidates for flotation collector to beneficiate the ore. Xanthate and dithiophosphate were employed as collectors for Nussir copper ore in our previous studies and high copper recovery (95%) and grade (24%) were observed but at the expense of high dosage of collector [2,3]. In the current study, the flotation behaviour of copper minerals from Nussir ore samples is investigated in the presence of a thionocarbamate collector with prior analysis of collector influence on pure minerals. The adsorption of BBT collector on the valuable copper minerals and the gangue minerals (carbonates and silicates) of the ore was initially determined with zeta potential, Hallimond tube flotation and quantitative and qualitative adsorption studies. An attempt is made to explain the adsorption mechanism by FTIR spectral studies. Since the Nussir ore is free from iron impurities, successful collector selection would be of benefit to future copper deposits of a similar mineral constitution. Based on the literature, the mixture of xanthate and thionocarbamate collectors in different proportions are studied in this paper to find the best reagent scheme for Nussir ore flotation. This collector blend is capable of reducing production costs and potentially providing an increase in efficiency in terms of copper recovery and grade. The information from this study will then contribute and assist the detailed flowsheet development being performed in parallel in collaboration with SGS minerals and Woodgrove, Canada. In the current study mixtures of BBT and SIBX are also examined as collectors for the flotation of copper minerals from the Nussir ore sample. Additionally, the sequence of collector addition was initially evaluated with quantitative adsorption studies and further substantiated with bench-scale flotation results.

2. Materials and Methods

Ore samples were obtained from two different parts (panels) of the Nussir mine in Norway, Nussir North East (N-NE) and Nussir Old west (N-OW). The material was crushed and ground using a jaw crusher with a 3 mm opening and subsequently, a ball mill with steel media. The material was further screened to $-105\ \mu\text{m}$ size fraction. The chemical composition of the feed ore and products were analysed with a BRUKER S8 Tiger 4 kW X-ray spectrometer (XRF) (Bruker, Billerica, MA, USA), while the mineralogical composition was analysed with a BRUKER D8 Advance X-ray diffraction (XRD) and quantified with the Rietveld method (Table 1).

The chalcocite, chalcopyrite and bornite pure minerals were purchased from a vendor, and these samples were obtained from Cornwall (England), Falun (Sweden) and Virgen (Austria), respectively, in the form of small centimetre size rock pieces. To prepare the copper sulphide materials for the various experiments, the material was milled in a ball mill using 660 g of stainless-steel balls ($\varnothing 1.8\ \text{mm}$), followed by sieving to retrieve the $-150 + 45\ \mu\text{m}$ size fraction for single mineral Hallimond tube flotation tests. Samples for zeta potential and adsorption experiments of the $-10\ \mu\text{m}$ size fractions were prepared by grinding a portion of the $-45\ \mu\text{m}$ material in a Fritsch P6 Pulverizette planetary mono mill at 300 rpm followed by ultrasound assisted wet screening with a $10\ \mu\text{m}$ screen.

The *n*-butoxycarbonyl-*O*-*n* butyl thionocarbamate (BBT) used in these experiments was supplied by the Solvay Cytec group. The molecular weight of this collector was 264 g mol/L, as specified by the manufacturer. Methyl isobutyl carbinol (MIBC) was employed as the frother. The pH was adjusted with dilute solutions of reagent grade milli Q water with HCl and NaOH. Deionized water was used in all the Hallimond flotation tests and for the zeta potential experiments. Additionally, a standard quartz suspension was used for calibrating the zeta potential instrument. Copper nitrate was employed to prepare the Cu-thionocarbamate precipitates respectively for reference spectra in Fourier transform infrared spectroscopy (FTIR) analysis. The Brunauer–Emmett–Teller (BET) surface area of the $-10\ \mu\text{m}$ size chalcopyrite, chalcocite and bornite samples were 0.88, 1.11 and 1.31 m^2/g respectively.

2.1. Zeta Potential Measurements

The zeta-potential measurements on chalcopyrite, chalcocite and bornite were performed using a DT-310 from Quantachrome/Dispersion Technologies, (the DT-310 instrument being based on electroacoustic technology). A 2 g mineral was added to the desired amounts of solution, magnetically stirred for 5 min, after the pH was adjusted using HCl or NaOH. Pulp pH was recorded while measuring the zeta-potential of samples. To assess the accuracy of zeta-potential measurements, the experiments were performed for three independent suspensions. The average value was reported and the measurement errors were found to be within ± 5 mV.

2.2. Hallimond Flotation Tests

Single mineral flotation tests were performed using a Hallimond cell of 100 mL volume. A 2 g portion of the mineral sample was conditioned in a predetermined concentration/pH of reagent solution for 5 min and the suspension was transferred to the flotation cell. The flotation was conducted for 1 min at an air flow rate of 8 mL/min. When the tests were performed with mixed collectors, the mineral was conditioned in a solution containing both the reagents at a specified concentration ratio.

2.3. Adsorption Studies

The UV absorbance spectrum of the collector(s) in solution was measured with a UV-2401PC spectrometer (Shimadzu, Kyoto, Japan). A calibration curve was established using 50 mL thionocarbamate solutions of differing concentrations, ranging from 1×10^{-8} to 8×10^{-3} M at 253 nm wavelength. The adsorption studies were performed with a 2 g of mineral sample ($-10 \mu\text{m}$) conditioned in a series of conical flasks at a desired concentration of BBT. The equilibration time of 30 min was maintained. The supernatant was filtered and analysed by a UV-visible spectrometer, making necessary dilutions. The adsorption of BBT on metal surfaces was calculated from the difference in the concentration of initial and residual BBT in the solution.

The adsorption experiments on the three copper sulphides were also performed using a mixture of SIBX and BBT as collectors. The adsorption experiments were performed at pH 8 and the procedure for solution preparation is in parallel with the single collector system.

2.4. FTIR Measurements

Fourier Transform Infrared spectra of the collectors in solution was measured with a Bruker Vertex 80v Infrared spectrometer at a resolution of 4 cm^{-1} using 200 scans with a narrow band liquid nitrogen cooled MCT detector. The mineral was used as a reference while recording the spectra of mineral samples treated with reagent. Additionally, the spectra of the minerals, reagent and Cu-thionocarbamate precipitates were recorded for reference. The experimental procedure with powdered samples was as follows: The mineral samples of 2 g each were suspended in a 50 mL solution of the desired reagent concentration and specified pH. The equilibration time of 30 min was maintained. The solution was filtered and the solids were dried under inert conditions to be used in the experiments.

2.5. Bench Scale Flotation

The bench scale flotation experiments were performed by adding 200 g of the $-105 \mu\text{m}$ ore sample to an aqueous solution in a 1 L mechanical flotation cell. The suspension was initially conditioned with HCl/NaOH to adjust pH for 5 min in the cell before addition of collector and frother. Following this initial stirring phase, the BBT and MIBC were added to the suspension and the conditioning continued for 5 and 2 min, respectively. During flotation, the impeller speed and air flow were fixed at 1200 rpm and 3.0 L/min, respectively. A flotation time of 5 min was used.

3. Results

Nussir ore contains chiefly chalcopyrite, chalcocite and bornite copper minerals with minor quantities of gold, silver and platinum group minerals (PGM). The mineral and elemental distribution of the ore is shown in Table 1. Pure mineral interaction with BBT collector is assessed by zeta potential, Hallimond flotation and adsorption studies.

Table 1. Quantitative analysis of the ore sample using: XRF and XRD analysis.

	N-NE	N-OW	N-NE	N-OW		N-NE	N-OW	Cp	Cc	Bn
Element	Wt. %	Element	g/t	Minerals	Wt. %					
Al	4.9	Cd	<2	Chalcopyrite	0.02	3.5	92	3.2	2.1	
Ca	11	Bi	<20	Chalcocite	2.1	0.01	1.02	93.2	2.9	
Fe	1.8	Pt	<20	Bornite	8.5	9.2	0.61	1.2	90.9	
K	2.1	Au	1.06	Calcite	40.5	9.0	1.78	1.9	3.1	
Mg	1.2	Ag	18	Dolomite	12.3	20.9	2.10	0.2	0.1	
Mn	0.27	Sb	<10	Quartz	12.3	29.8	0.8	0.08	-	
Na	1.1	Se	<30	Microline	-	5.8	-	-	-	
S	5.42									
Cu	6.87									

Nussir North East (N-NE) and Nussir Old west (N-OW); cp-chalcopyrite, cc-chalcocite, bn-bornite.

3.1. Zeta Potential Studies

Figure 1 presents the zeta-potential values of copper sulphides untreated and treated with BBT as a function of pH. It is evident from the results that the iso-electric point (IEP) of chalcopyrite and chalcocite was at a of pH 4 and 4.3, respectively. The IEP of bornite is at two pH values 2.8 and 6; the surface of all the three copper sulphides was mainly negatively charged over the pH range of 5–12. Zhao et al. [26], Kelebek and Smith [27] and Fullston et al. [28] reported similar IEP values for these minerals. The differences occur based on oxidation of sulphide surfaces. After interacting with 4×10^{-5} M BBT, the zeta potential values of all the three copper sulphides decreased dramatically, thus indicating adsorption of BBT on the copper sulphides. Cu-minerals are negatively charged in aqueous solution; the adsorption of anionic (negative heads) collectors indicates that the mode of adsorption is chemisorption on the metal sites (Cu-sites), which was later substantiated by the FTIR spectral studies. The decrease in zeta potential values of the copper sulphides conditioned with BBT was far more negative than those conditioned with SIBX. The comparison is produced with respect to our parallel study [2,3].

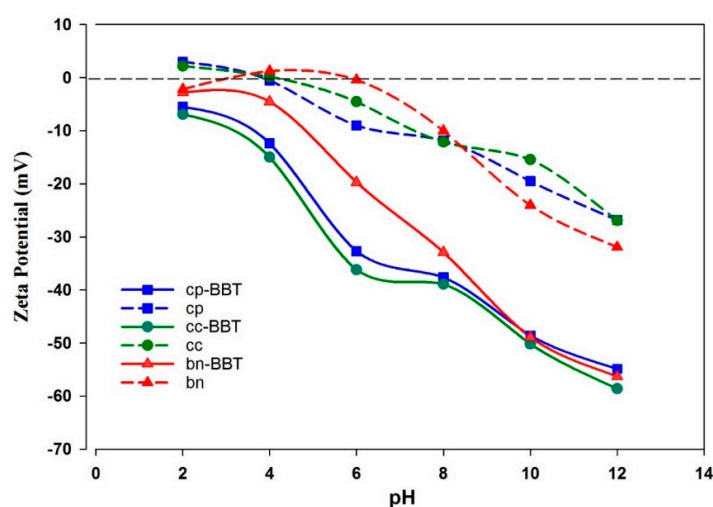


Figure 1. Zeta potential of copper minerals in *n*-Butoxycarbonyl-*O*-*n*-butyl thionocarbamate (BBT) and an aqueous solution as a function of pH at collector concentration 4×10^{-5} M. cp-chalcopyrite, cc-chalcocite, bn-bornite.

Chalcocite showed a maximum decrease in zeta potential values among the three copper minerals, which is understandably due to the absence of Fe in the lattice and thus being prone to less oxidation. At the same time, the decrease in zeta potential values of chalcopyrite and bornite after addition of the collector is also significant.

The zeta potential results in Figures 2 and 3 show a synergistic action between BBT and SIBX in the collector blend. It is found that the zeta potentials of copper sulphides are more negative in the presence of BBT-SIBX blend as compared to the single collector systems. Figure 2 indicates far less influence of SIBX and BBT mixture on quartz and calcite in the neutral pH region. Previously, studies have shown the absence of (or less) interaction of thiol collectors with carbonate and silicate minerals [29]. The 1:1 blend of the collectors adsorbs on calcite in the acidic pH region, which corresponds to meagre electrostatic adsorption. In Figure 3, zeta potential values of all the three collector blends are more negative than the individual collector systems. Thus, it indicates adsorption of both the collectors on all the three copper mineral surfaces. Another observation is the copper sulphides conditioned with the collector mixture with a higher proportion of BBT showed relatively more negative zeta potential than those conditioned with higher amounts of SIBX. The probability of dithiolate formation with xanthate molecule is higher [4]. When BBT is present in higher quantities in the mixture, it occupies first on the surface sites. Subsequently, neutral and strongly hydrophobic xanthate dimers are attached through van der Waal's bonding with the hydrocarbon chains of the previously adsorbed BBT. Thus, the adsorption of xanthate and thionocarbamate together forms a strong and stable structure enhancing a balance of better distributed and more strongly held chemisorbed species and more hydrophobic neutral physiosorbed dithiolates. Alternatively, when xanthates are present in higher quantities, it occupies first on the surface active sites, leaving less room for BBT to adsorb. Due to high selectivity of the BBT collector, it refrains to adsorb on the xanthate adsorbed sites [14,25].

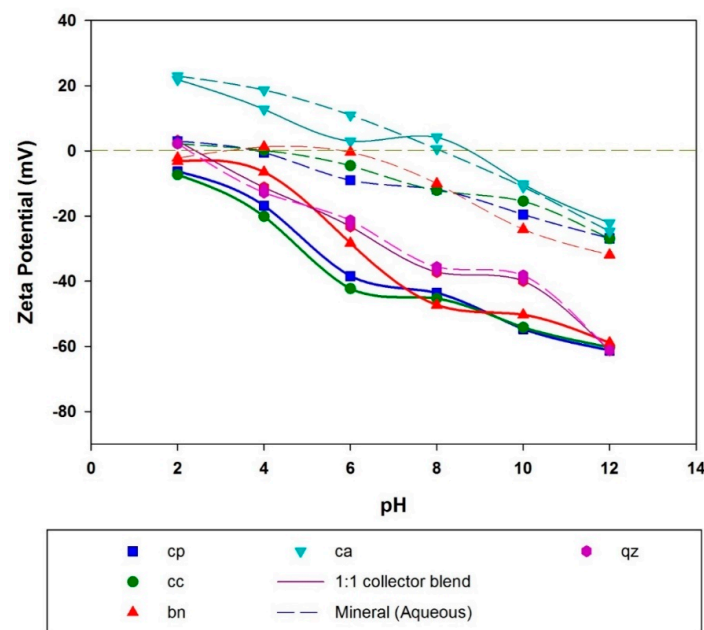


Figure 2. Zeta potentials of copper and gangue minerals in a mixed collector system (1:1 ratio of Sodium Isobutyl xanthate: *n*-Butoxycarbonyl-*O*-*n*-butyl thionocarbamate(SIBX:BBT), both added simultaneously) as a function of pH. cp-chalcopyrite, cc-chalcocite, bn-bornite.

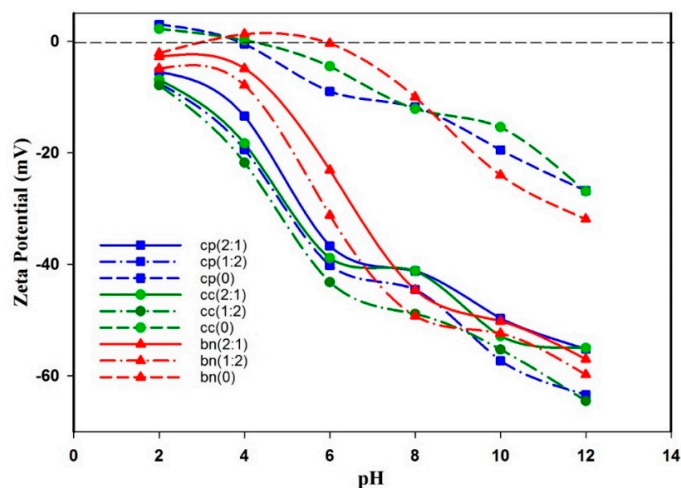


Figure 3. Zeta potentials of chalcopyrite, chalcocite and bornite in a mixed collector (SIBX:BBT) system as a function of pH. cp-chalcopyrite, cc-chalcocite, bn-bornite.

3.2. Hallimond Flotation Results

The flotation response of the three copper minerals was assessed by the Hallimond flotation experiments and the results are shown in Figure 4. Chalcocite and bornite indicate a highest recovery at pH 6–8 and chalcopyrite shows maximum floatability at pH 8. Similar results were observed by Fairthorne [4]. Although, in this study, the recoveries of the copper minerals are constantly high at all pH values above pH 4. The pKa value of this collector is 8–10 [4]; thus, the best results are observed at pH 8. Fairthorne [4] stated that above the pKa value of thionocarbamates, a repulsive interaction occurs between the collector and sulphide mineral surface. The decrease in copper mineral recoveries in the alkaline pH region could be explained with either the solubility product of the collector or metal hydroxide formation [4,30]. The zeta potential values of the three copper sulphides also decrease significantly in the neutral pH zone (pH 6–8); thus, the flotation results corroborate with the zeta potential outcomes. In the acidic pH region (<pH 4) physio sorption of the protonated collector is also favoured along with chemisorption [15], which leads to moderate recoveries of copper minerals. The flotation results of calcite and quartz are minimal at all pH values. Flotation responses of gangue minerals (calcite and quartz) are negligible at this collector concentration indicating less or no interaction with BBT collector.

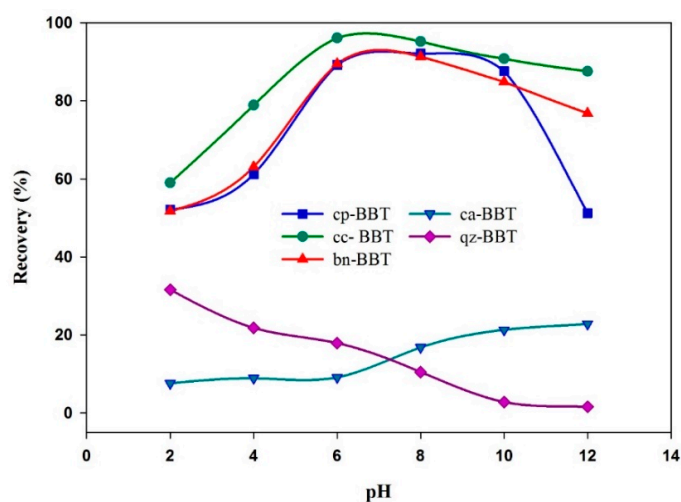


Figure 4. Hallimond flotation recovery as a function of pH at collector concentration 4×10^{-5} M. cp-chalcopyrite, cc-chalcocite, bn-bornite, ca-calcite, qz-quartz.

Mixtures of xanthate and thionocarbamate are employed as collectors and the results are presented as a function of the pH in Figure 5. Chalcocite shows maximum recovery out of the three copper sulphides examined. The recoveries, in general, are 5–17% higher when the collector mixtures were used as compared to single collector systems. The results depicting the recoveries of copper minerals are maximum when the proportion of thionocarbamate is greater in the collector mixture. These results are in agreement with the zeta potential results; zeta potential results also indicated a significant decrease when the proportion of thionocarbamate was greater in the collector mixture. As explained in Section 3.1, the adsorption of xanthate and thionocarbamate together forms a strong and stable structure enhancing a balance of better distributed and more strongly held chemisorbed species and hydrophobic neutral physiosorbed dithiolates [25]. The recoveries follow a similar trend for all the three copper minerals; increasing until pH 8 followed by a decrease at pH 12. Overall, floatability of chalcocite is 2% to 20% higher than that of the other two copper minerals for all the combinations of collector mixtures at pH 8. The improvements in the SIBX:BBT mixture are understandably due to synergistic adsorption of both collectors.

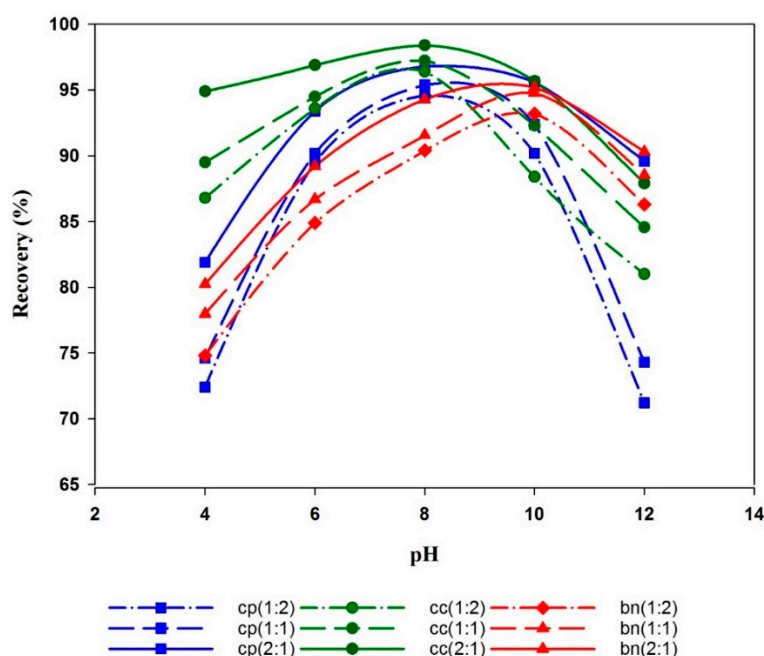


Figure 5. Hallimond flotation recovery of copper sulphides in presence of collector blend (SIBX:BBT) as a function of pH at collector concentration 3×10^{-5} M. cp-chalcopyrite, cc-chalcocite, bn-bornite.

Figure 6 shows the recoveries of calcite and quartz in the presence of mixtures of xanthates and thionocarbamates as a function of pH. In general, the recoveries of these gangue minerals are less than 15%. At acidic pH, the recovery of both calcite and quartz is high, specifically in the presence of SIBX:BBT (1:1 and 2:1) blend. This increase in recovery of calcite will be attributed to electrostatic adsorption of both the collectors in coordination with the zeta potential results. The recovery of both the gangue minerals is low at pH 8. Thus, it can be noted that selective flotation of copper sulphides from these gangue minerals can be achieved at natural pH of the ore (pH 8).

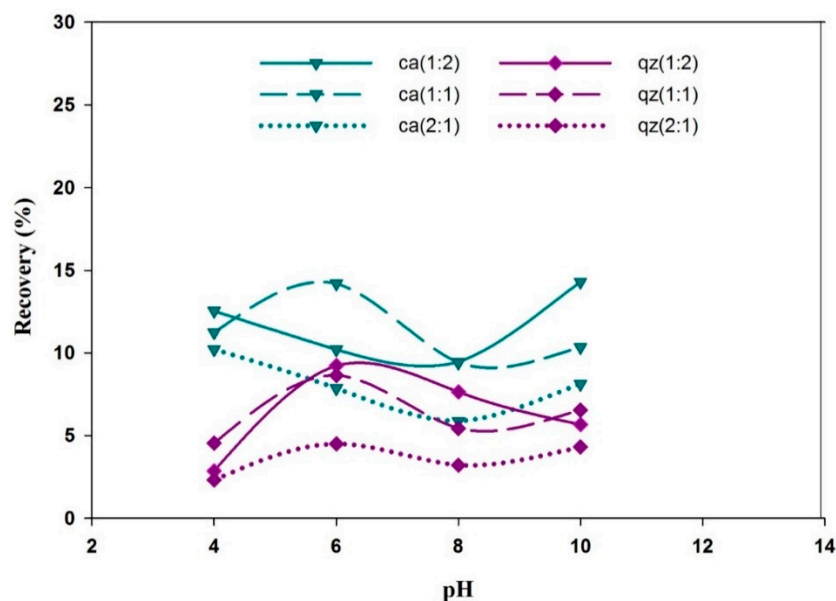


Figure 6. Hallimond flotation recovery of gangue minerals in presence of collector blend as a function of pH at collector concentration 3×10^{-5} M. ca-calcite, qz-quartz.

3.3. Adsorption Studies

Adsorption of BBT on the copper sulphide surfaces has been investigated by the solution depletion method using UV-Visible spectroscopy. The high intensity characteristic peak of BBT was observed at 253 nm. Feeble peaks at 213, 238, 271 and 303 nm were present which indicates distinct species of the collector as in agreement with Fairthorne [4]. Earlier, Finkelstein and Goold [31] reported low adsorption of thionocarbamate on sulphide minerals and the fraction of a theoretical monolayer adsorbed from solution at pH 8 was 0.16 θ for chalcocite, 0.11 θ for chalcopyrite and 0.04 θ for bornite.

The adsorption isotherms of BBT on chalcopyrite, chalcocite and bornite at pH 8 are shown in Figure 7a. This figure shows that the adsorption of BBT on copper sulphides begins at a lower equilibrium concentration and continuously increases with increasing concentration. Considering the cross sectional area of the BBT molecule as 42 Å² [4], one complete monolayer coverage is theoretically calculated as at 3.9 μmol/m². The adsorption densities of chalcocite (2.2 μmol/m²) and bornite (2.16 μmol/m²) increase and attain a plateau value at and above collector concentration 1.8×10^{-5} M and 1.76×10^{-5} M respectively. The chalcopyrite isotherm initially increases and levels off at equilibrium concentration 4.2×10^{-5} M corresponding to 1.7 μmol/m². Earlier several researchers indicated that multilayer coverage of thionocarbamate collector forms on chalcopyrite and chalcocite [5,15,32,33]. The authors showed that a monolayer is formed, followed by the physically adsorbed collector (anionic or protonated) on the top of monolayer, leading to multilayers of thionocarbamate. The current study suggests that the thionocarbamate adsorbs on the chalcopyrite surface by forming a clear monolayer followed by an increase in adsorption density, which can be further explained with the FTIR studies.

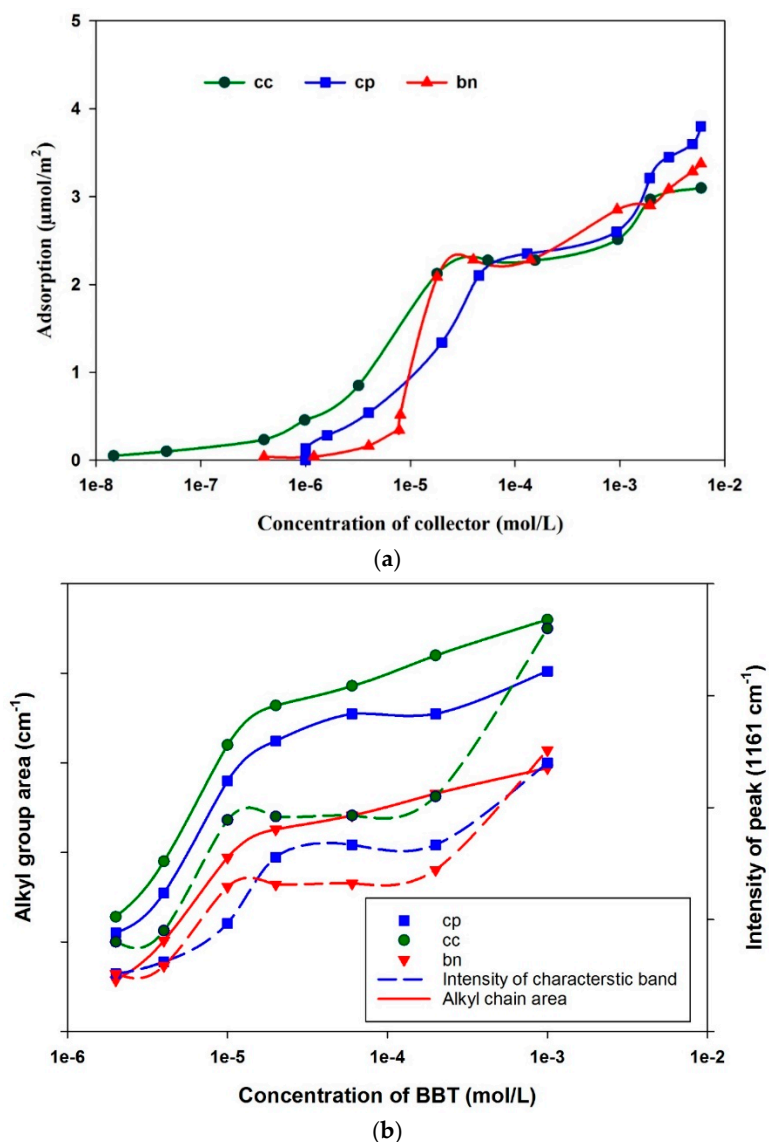


Figure 7. (a) Adsorption of thionocarbamate on the copper sulphide surface at pH 8; (b) Intensities of characteristic BBT band and area under alkyl chain bands for chalcopyrite, chalcocite and bornite (FTIR studies). cp-chalcopyrite, cc-chalcocite, bn-bornite, ca-calcite, qz-quartz.

Figure 7b shows the area under alkyl chain region between $2600\text{--}2900 \text{ cm}^{-1}$ (the spectra are presented later in the Section 3.4) for all the three copper minerals with respect to the initial BBT concentration. The area under the alkyl chain bands is measured with the facility available within the spectral manipulation feature. The adsorption begins at a low concentration of collector for all the three copper minerals chalcopyrite, chalcocite and bornite. These results are in agreement with the quantitative adsorption results in Figure 7a. The area under the alkyl chain values for chalcopyrite, chalcocite and bornite is approximately constant above the collector concentration of $4 \times 10^{-5} \text{ M}$, $2 \times 10^{-5} \text{ M}$ and $2 \times 10^{-5} \text{ M}$, respectively. The same figure also depicts the intensities of the characteristic functional group band of BBT as a function of the collector concentration. The intensities of BBT absorbance bands at 1160 cm^{-1} for chalcocite and bornite are nearly constant above $2 \times 10^{-5} \text{ M}$. The intensity of the characteristic BBT band for chalcopyrite at 1160 cm^{-1} is approximately constant above $4 \times 10^{-5} \text{ M}$ in accordance with the quantitative adsorption results. The sudden increase in area under alkyl chain or intensities of functional group band at higher concentration ($1 \times 10^{-3} \text{ M}$) after a distinct plateau could be attributed to physically adsorbed collector layers on the top of the chemisorbed monolayer.

The adsorption mechanism of mixtures of the collectors was also investigated in different ratios of SIBX and BBT by using the same solution depletion method at pH 8 (Figures 8–10). The characteristic peaks at 301 nm, 228 nm and 253 nm of both SIBX and BBT are present in the spectra, indicating adsorption of both the reagents. The distinct dixanthogen band was noticed. The total equilibrium concentration of the collectors in the mixture is 3×10^{-5} M for all the experiments. Figures 8–10 show the role of the sequence of the collector addition on the adsorption densities. All the three figures show an increase in adsorption densities while collector mixtures are employed. It is known that the surface of sulphide minerals consists of various sites that have different surface activity and the strong collector adsorbs on the stronger active sites while the residual weak sites are available for the less selective collector in the mixture. When a mixture of selective and non-selective (reactive) collectors is added to a suspension, each collector adsorbs on the most suitable site. Therefore, the amount of collector adsorbed on the mineral surface increased [25,34].

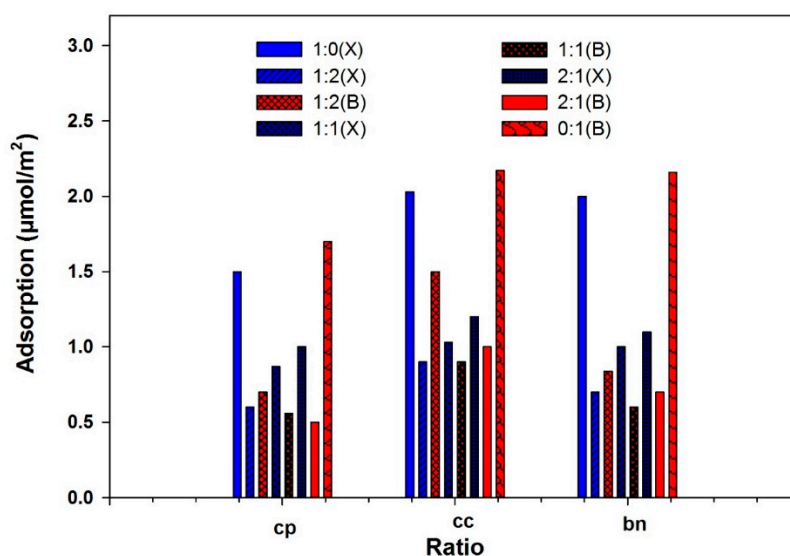


Figure 8. Adsorption of collectors from the mixtures of SIBX(X) and BBT(B) at pH 8.2 and total concentration 3×10^{-5} M (SIBX was added first). cp-chalcocopyrite, cc-chalcocite, bn-bornite.

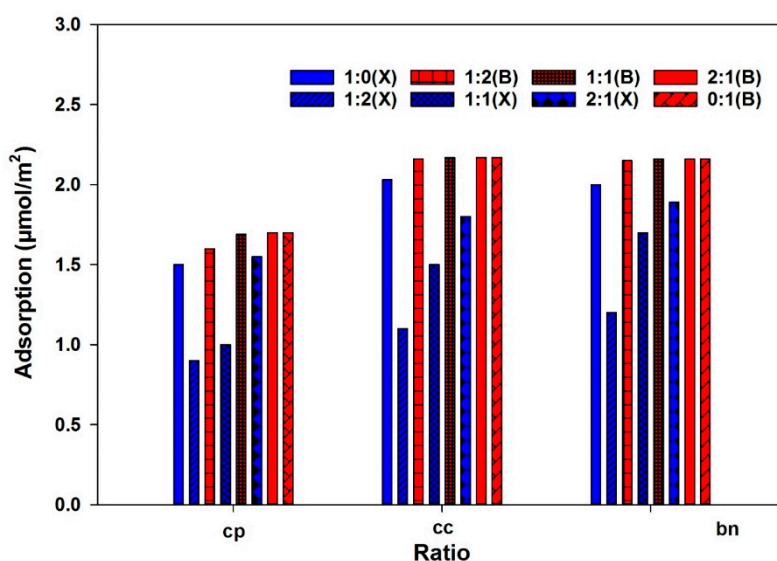


Figure 9. Adsorption of collectors from the mixtures of SIBX(X) and BBT(B) at pH 8.2 and total concentration 3×10^{-5} M (BBT was added first); cp-chalcocopyrite, cc-chalcocite, bn-bornite.

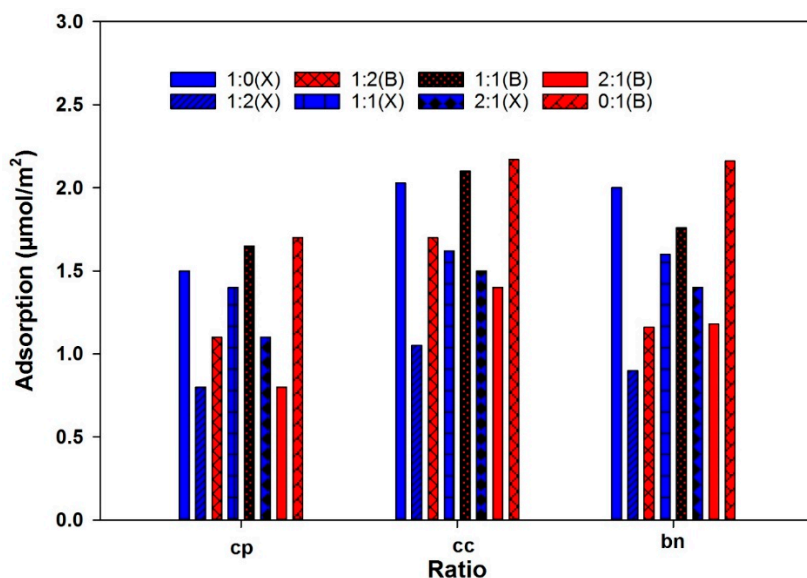


Figure 10. Adsorption of collectors from the mixtures of SIBX(X) and BBT(B) at pH 8.2 and total concentration 3×10^{-5} M (SIBX and BBT were added simultaneously). cp-chalcopyrite, cc-chalcocite, bn-bornite.

Figure 8 shows the amount of collector adsorbed on chalcopyrite, chalcocite and bornite when SIBX was added first in the suspension. In the case of 2:1 and 1:1 ratios of SIBX: BBT blends, a higher proportion of SIBX was adsorbed on chalcopyrite and bornite than BBT. However, in the 1:2 suite, where the concentration of BBT is higher than SIBX, a far small difference between adsorbed SIBX and BBT is noticed for these minerals. It is known that xanthates are more reactive than thionocarbamates, whereas the latter is a more selective collector at this pH [16]. In this case, when SIBX was added prior to BBT, it acquired almost all the active sites, leaving less room for the BBT molecules to adsorb. Addition of SIBX prior to BBT simply masked further adsorption of BBT on the copper sulphides. BBT being a more selective collector failed to adsorb further on the SIBX adsorbed sites. For chalcocite, the adsorption of SIBX and BBT differed less for the collector blends, 2:1 and 1:1, while a significant difference in adsorption densities is noted for the reagent suite 1:2. The reason is varying oxidation states of the three minerals.

Figure 9 shows the adsorption results when BBT is added prior to SIBX. In this case, the adsorption of BBT on chalcopyrite, chalcocite and bornite is higher for the 1:2 SIBX and BBT blend. In spite of high SIBX concentration in 2:1 and 1:1 collector suites (compared to 1:2), the adsorption of SIBX was lower than the BBT molecules for chalcopyrite and bornite. Thus, chalcopyrite, chalcocite and bornite conditioned with any of the collector blends, exhibit less coverage of xanthate than thionocarbamate, although the proportion of xanthate is higher than BBT in the collector blend. This is due to the adsorption of BBT on higher energy sites, which was added prior to SIBX. While, BBT was added first, being a more selective collector, it occupied the higher active (or less oxidized) sites. The xanthate molecules being more reactive adsorb on the remaining sites and its dithiolate successively physiosorbed forming a condense stable structure [25].

Figure 10 shows the results when SIBX and BBT were added together. The adsorption of the collectors was influenced by the relative ratio of the collectors used in the mixtures. It is clearly observed that the adsorption amount of BBT on chalcocite is significantly higher for the 1:2 and 1:1 collector suite. In fact, for the collector blends 2:1, where the concentration of SIBX is higher than BBT, the adsorption densities are comparable. In the case of chalcopyrite and bornite, the adsorption densities of SIBX were lower than BBT for 1:2 and 1:1 collector suits. However, in the terminal collector suite, the adsorption densities of SIBX are higher than BBT. For the collector ratio 1:1, the amount of BBT adsorbed is higher than SIBX for all the three copper minerals showing high selectivity of BBT.

Thus, the overall results clearly indicate that differences in behaviour of the sequence of collector addition are a crucial factor for the adsorption of these thiol collectors on copper sulphides.

Overall, best results were observed while BBT was added prior to SIBX; the stronger collector BBT preferentially adsorbs on the active Cu-sulphide mineral surface and xanthate (a relatively less-selective collector) adsorbs on the remaining sites, thus improving the surface coverage and further enhancing the floatability. Thus, the cumulative adsorption of both the collectors is maximum while BBT is added first to the suspension. Previous studies [7,25] have explained that the formation of dithiolates is more prevalent for xanthates as compared to thionocarbamates. Thus, when BBT is added prior to the solution, it occupies the higher energy sites and xanthates adsorb on the remaining sites. Additionally, the dixanthogen is physisorbed to form a more stable structure. However, the synergistic adsorption on chalcocite surface is maximum; which is most likely due to the absence of iron in its structure.

3.4. FTIR Studies

FTIR spectra of BBT, SIBX and Cu (BBT)₂ precipitate is shown in Figure 11 and a summary of the peaks is presented in Table 2. In the collector spectrum, the band at 1501 cm⁻¹ indicates mixed vibrations from C–N stretching and N–H deformation vibrations. Additionally, the bands at 1391 cm⁻¹ are designated to C–N stretching, N–H deformation and C–H deformation. The strong peak at 1032 cm⁻¹ is attributed to C–N, C=S and C–H vibrations [35,36]. The peak at 1161 cm⁻¹ most likely due to combinations of C=(O)–O and C(=S)–N group vibrations. The band at 1221–1241 cm⁻¹ corresponds to C–O stretching vibrations and the broad band at 1710–1761 cm⁻¹ refers to C=O band. In the copper precipitate spectrum, the strong peak is shifted from 1032 cm⁻¹ to 1065 cm⁻¹, which is attributed to C–N, C=S and C–H vibrations. The C–O and C=O stretching vibration shifts by approximately 12 cm⁻¹ and 34 cm⁻¹ respectively in agreement with previous infrared studies indicating precipitate [5,7].

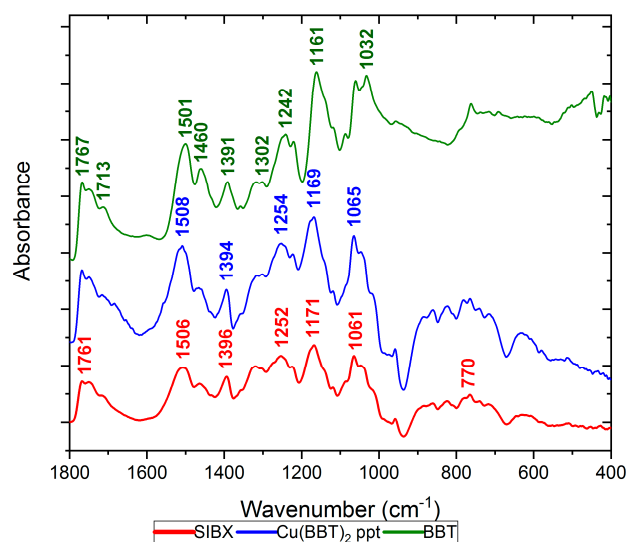


Figure 11. DRIFT spectra of xanthate, thionocarbamate and copper thionocarbamate precipitates.

The spectra of chalcopyrite, chalcocite and bornite conditioned with BBT (4×10^{-5} M) are presented in Figures 12–14, respectively. The chalcopyrite conditioned with BBT spectra shows peaks at 1032 and 1061 cm⁻¹. Involving the contribution from C–N, C=S and C–H vibrations similar to the collector spectrum with minor shifts indicating chemisorption. Another peak indicated at 1169 cm⁻¹ refers to C=(O)–O and C(=S)–N group vibrations. At pH 4, the bands are more similar to the BBT bands and the adsorption of the collectors is highest at this pH value as the intensities of the bands are the maximum of all the pH values tested in the current study. However, the intensities of the bands decrease gradually between pH 4 and 11; the peak intensities are considerably lower at pH 11. Thus,

the adsorption of BBT on chalcopyrite decreases continuously with increasing pH and these results are in agreement with Glembotskii [37] and Leppinen et al. [6].

The spectrum of chalcocite conditioned with BBT at pH 4 shows bands at 1034, 1169, 1254 and 1508 cm^{-1} , which are the same bands depicted in the BBT spectrum, with minor shifts indicating chemisorption. In this spectrum, peak at 1169 cm^{-1} relates to the combinations of C=(O)-O and C(=S)-N group vibrations. The spectrum of chalcocite conditioned with BBT at pH 6 shows strong peaks at 1034, 1163 and 1392 cm^{-1} that corresponds to the same collector spectrum; however, the intensities of peaks are higher at pH 6 than pH 4. Similar peaks are observed for chalcocite conditioned with BBT at pH 8, with lower intensity than pH 6. Thus, the adsorption increases until pH 6 and further decreases, which is also reflected by the flotation response.

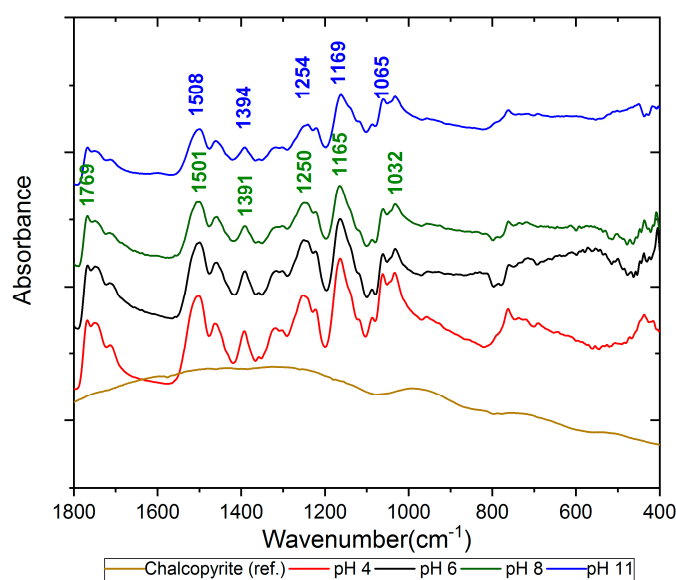


Figure 12. DRIFT spectra of thionocarbamate adsorption on chalcopyrite with increasing pH.

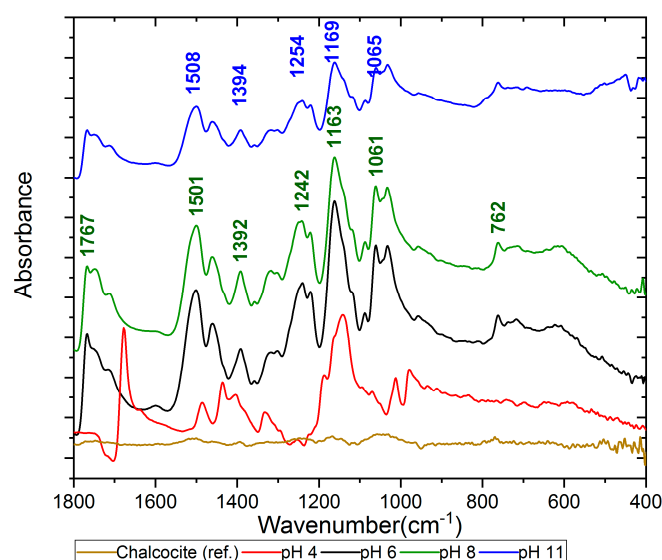


Figure 13. DRIFT spectra of thionocarbamate adsorption on chalcocite with increasing pH.

The bornite conditioned with BBT spectrum shows bands at 1047 and 1242 cm^{-1} which corresponds to C-N vibrations and C-O vibration respectively. The band at 1171 corresponds to combinations of C=(O)-O and C(=S)-N group vibrations. Additionally, the peak at 1508 cm^{-1} refers to mixed vibrations from C-N stretching and N-H deformation. Minor shifts are noticed, which

indicates chemisorption. The peaks of bornite conditioned with BBT, like other copper sulphides at pH 11 has lower intensities than acidic and neutral pH values, indicating a decrease in adsorption with respect to pH [7,38].

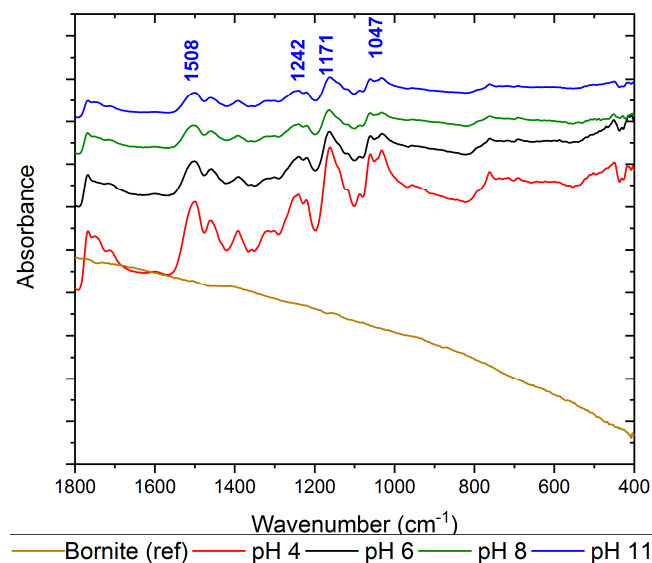


Figure 14. DRIFT spectra of thionocarbamate adsorption on bornite with increasing pH.

Figure 15 presents the spectra of the three copper minerals conditioned with BBT and the SIBX blend in the ratio 1:1 at pH 8. The chalcopyrite, chalcocite and bornite spectra show peaks at 1032, and 1161 cm^{-1} indicating C–N vibrations and combinations of C(=O)–O and C(=S)–N group vibrations respectively. The characteristic peaks of both SIBX and BBT are present on the spectrum indicating adsorption of both the collectors. However, in chalcopyrite and bornite, the characteristic peaks of BBT are more pronounced than SIBX, indicating higher adsorption of BBT. It can also be asserted that BBT, being a more selective collector adsorbs on the active sites and masks the co-adsorbed SIBX bands. This result is in agreement with the quantitative adsorption studies. The mode of adsorption in the case of the collector blend has been a topic of discussion over many years. According to our investigations, SIBX and BBT are both adsorbed on chalcopyrite, chalcocite and bornite, whereas the intensities of peaks are higher for chalcocite. The results are in agreement with the quantitative adsorption studies.

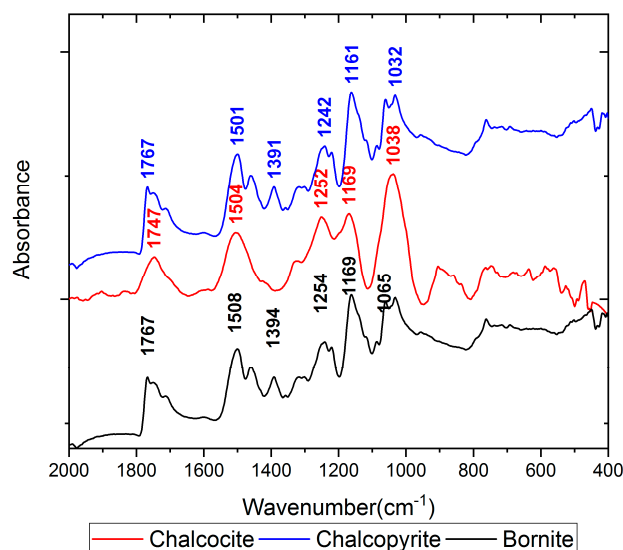


Figure 15. DRIFT spectra of thionocarbamate and xanthate collector blend (1:1) adsorption on copper sulphides at pH 8 and the total concentration of collector 3×10^{-5} M.

Table 2. Summary of Fourier transform infrared (FTIR) bands of thionocarbamate, Cu-thionocarbamate precipitate, xanthate.

Spectrum Name	Bands (cm ⁻¹)	Significance	Reference
Thionocarbamate (BBT)	1032	C–N, C=S, C–H	[5,35]
	1161	C=(–O)–O, C=(–S)–N	[35,36]
	1221–1242,1391	C–O	[35,36]
	1561	C–N	
	1710–1761	C=O	[5,35]
Xanthate (SIBX)	1061	C=S	[35,36]
	1396	C=S	[5,35]
	1171	C–O–C	[35,36]
	1252	C–N	[35,36]
	1506	C–N	[35]
Cu-Thionocarbamate precipitate	1065	C–N, C=S, C–H	[35]
	1169	C=(–O)–O, C=(–S)–N	[35]
	1254	C–O	
	1394	C–O,C–H	[5,35,36]

3.5. Bench Scale Flotation

The bench scale flotation experiments were performed using BBT as a collector in the pH range 4 to 10 and the results are presented in Table 3. The results show high recoveries of Cu, Au and Ag, for all pH values. In the acidic pH region, the copper grade and recovery are 19.4% and 89.5 % respectively. A 7% increase in both the Cu-grade and recovery was observed at natural pH (8). Additionally, in the alkaline pH region, the copper grade and recovery significantly decrease to 19.7% and 84.1% respectively. According to the zeta potential and Hallimond flotation results, thionocarbamate collectors performed best in the pH region 6–8. Additionally, the adsorption of BBT on all the three Cu-minerals was at a maximum in pH range 6–8. The natural ore flotation results are consistent with the pure mineral flotation and adsorption studies (FTIR). The recovery of Cu, Ag and Au was below 75% using xanthate collector [2] at this collector dosage. In the current study, it is noted that the recovery of these valuable metals is significantly increased with thionocarbamates due to high selectivity. According to the current mineralogical analyses, these precious minerals are present with the base copper ore, but a thorough analysis is required for a better insight into their situation within the copper ore's mineralogical assemblage.

Table 3. Grade and Recovery results with respect to varying pH at collector concentration 4×10^{-5} M.

Product	pH	Grade			Recovery (%)		
		Cu (%)	Au,Ag (g/t)		Cu	Au	Ag
Tot_Conc	4	19.4	3.6	416	89.5	99.4	87.3
		Tail	0.02	0.001	0.1	9.1	0.21
Tot_conc	6	22.2	3.4	397	94.4	98.8	93.6
		Tail	0.02	0.001	0.1	5.6	0.2
Tot_conc	8	26.8	3.8	437	96.4	98.4	91.2
		Tail	0.01	0.001	0.1	3.4	0.2
Tot_conc	12	19.7	3.6	414	84.1	94.0	87.9
		Tail	0.02	0.002	0.2	14.3	5.20

Table 4 depicts the results of copper ore flotation with respect to the sequence of the collector addition in the presence of xanthate and thionocarbamate collector mixture in the ratio 1:1. The results showed overall higher recoveries and grades as compared to a single reagent system. Although not

shown in this communication, the mixture of xanthate and thionocarbamate collector with a higher proportion of BBT displayed best metallurgical results for all valuable minerals of the Nussir ore.

Table 4. Grade and Recovery in presence of a mixture of SIBX and BBT (1:1) at total collector concentration 3×10^{-5} M and natural pH with respect to the sequence of the collector addition.

Product	Grade Cu (%); Au,Ag (g/t)			Recovery (%)		
	Cu	Au	Ag	Cu	Au	Ag
Conc #	25.8	3.8	391	96.2	97.2	97.4
Tail	0.01	0.001	0.1	3.5	2.0	2.4
Conc *	26.6	4	401	97.1	98.48	98.49
Tail	0.01	0.001	0.1	2.7	1.2	1.5
Conc +	27.1	4.03	413	97.8	99.20	98.9
Tail	0.01	0.001	0.08	0.98	0.3	0.4

Collector added first: # SIBX; * together; + BBT.

Lowest recovery and grades were observed when xanthates were added prior to thionocarbamate in the flotation cell. The results improved when both the collectors were added together. However, the Cu-recovery specifically is increased when BBT was added first in the flotation cell. An increase of approximately 1.3% in the cumulative grade and 1.6% increase in cumulative recovery was observed when BBT was added prior to SIBX in the suspension. In Section 3.3, the highest adsorption densities were observed when thionocarbamates were added prior to xanthate. Thus, the bench scale flotation results are in agreement with the pure mineral adsorption studies.

4. Conclusions

In the current study, the role of thionocarbamates as a collector for Nussir copper ore has been discussed relative to xanthate and dithiophosphate. The adsorption mechanisms of BBT on copper sulphide and gangue minerals were studied by quantitative adsorption studies, zeta-potential and FTIR measurements, which showed that the adsorption of BBT on copper sulphides is by chemisorption.

The zeta potential studies using BBT as a collector showed an increase in negative potentials of copper minerals due to chemical adsorption of BBT on the surface. However, the variations in zeta potential values of gangue minerals after addition of collector are insignificant. The results of using mixtures of BBT and SIBX collectors, clearly stipulate that the zeta potential values are far more negative as compared to single collector systems, indicating adsorption of both the collectors. However, it has generally been observed that copper sulphides conditioned with BBT show more negative zeta potential values as compared to those conditioned with other thiol collectors (xanthate and dithiophosphate).

Single mineral flotation results using BBT as a collector indicate that the recoveries are consistently high irrespective of the variation in pH. Thus, due to high selectivity and low solubilities of thionocarbamates, the recoveries are independent of pH. Moreover, the flotation response of gangue minerals (calcite and quartz) are low at all pH values. Based on data from the pure mineral studies, it can be stated that the copper sulphides can be floated in the natural pH region, where the collector concentration was 4×10^{-5} M. Xanthate and thionocarbamate blends were employed as collectors in different proportions. It was noted that the recovery with collector mixtures was always higher than single collector systems. Chalcocite showed the highest recoveries irrespective of the proportion of SIBX or BBT in the collector blend due to the absence of iron in the lattice.

The quantitative and qualitative adsorption studies revealed that the interaction of thionocarbamate and copper sulphides was a chemical reaction. It was also indicated that in mixed collector systems, the sequence of collector addition is held responsible for the proportion of collector entities from the component of the collector blend adsorbed on the copper mineral surface. Infrared

adsorption results obtained with chalcopyrite, chalcocite and bornite indicate chemisorption of BBT on the surface via S, O and N. In all the three cases, the adsorption was higher at a neutral pH. Spectra of copper sulphides conditioned with mixed collector (1:1) show both the xanthate and thionocarbamate characteristic bands on the three copper minerals. However, strong peaks of both SIBX and BBT are observed on the chalcopyrite and bornite spectra, whereas strong bands of BBT are observed on the chalcocite spectrum.

Bench scale flotation of the Nussir ore sample with BBT as a collector showed that at a natural pH and collector concentration of 4×10^{-5} M, a cumulative concentrate grade of 26.8% copper with a recovery of 96.4% is obtained. Flotation of all three economically interesting minerals was improved using BBT as a collector (as compared to xanthate and dithiophosphate from our previous studies). Thus, the bench scale flotation results are consistent with pure mineral studies. Bench scale flotation with a mixed collector scheme showed synergistic action of both the collectors which resulted in the highest grade and recovery of the economically interesting minerals; specifically, the grade is improved for the entire range of collector mixture. The sequence of collector addition is one important factor for improving metallurgical results; the valuable mineral recoveries are increased when BBT was added first in the flotation cell. In summary, the economically interesting minerals in the Nussir deposit could be better floated in the order of thionocarbamates > dithiophosphate > xanthate; additionally, either DBD or BBT mixed with SIBX improve product grade and recovery of copper.

Author Contributions: P.D. carried out the experimental part, interpreted the data and wrote the manuscript. M.T. edited the manuscript and made the necessary English corrections and also contributed in final formatting. H.R.K. also contributed in interpretation of data and reviewed the manuscript. H.R.K. also provided resources, project administration, reviewed and edited the manuscript.

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

Abbreviations

PGM	Platinum group minerals
BBT	<i>n</i> -Butoxycarbonyl- <i>O</i> - <i>n</i> -butyl thionocarbamate
SIBX	Sodium isobutyl xanthate
FTIR	Fourier Transform Infra red
θ	monolayer
IPETC	<i>O</i> -isopropyl- <i>N</i> -ethyl thionocarbamate
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
MIBC	Methyl Isobutyl Carbinol
DBD	Dissecondary butyl dithiophosphate
cp	Chalcopyrite
cc	Chalcocite
bn	Bornite
ca	calcite
qz	quartz

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