

Article

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

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Abstract: The Norwegian mining industry is currently showing increasing interest in the production of metals. Recent research has demonstrated promising results identifying the high potential of the Nussir deposit for the production of copper and other valuable minerals. Mineralogical characterization for Nussir ore samples and their flotation concentrates was performed with optical microscopy and Zeiss automated mineralogy (Mineralogic) where the fine copper sulphide middlings were not completely recovered with a traditional sodium isobutyl xanthate (SIBX) collector. In the current study, dithiophosphate and a mixture of xanthate and dithiophosphate collectors' interaction on copper and other gangue mineral components of the ore sample were investigated with zeta potential, quantitative adsorption, FTIR studies and Hallimond tube flotation. All the results for single mineral experiments confirmed the feasibility of selective copper sulphide flotation by dissecondary butyl dithiophosphate (DBD) as collector. The blend of xanthate and dithiophosphate was chemically adsorbed as individual entities on the surface of the copper minerals via competitive adsorption. A systematic study with DBD and a mixed collector (SIBX and DBD) system was conducted on the coarse grind ($-105\ \mu\text{m}$) of the Nussir ore sample, and the results showed a synergistic interaction between the two reagents. The beneficiated copper concentrate using this mixture of collectors is indeed of improved copper grade and recovery. The highest copper recovery in bench scale flotation was 95.3% with a concentrate grade of 19.4% Cu for DBD collector, whereas mixtures of dithiophosphate and xanthate collectors in the ratio of 3:1 resulted in the highest copper grade (24.7%) and recovery (96.3%).

Keywords: Nussir ore; chalcopyrite; chalcocite; bornite; calcite; quartz; zeta potential; hallimond flotation; bench scale flotation

1. Introduction

Nussir ASA, located in the Kvalsund area of Finnmark, is exploring the Nussir and Ulveryggen deposits, and production is anticipated to begin in the near future. With a metal endowment totalling ca. 6% copper, Nussir is one of the largest deposits in Norway. Nussir copper ore is comprised within a relatively simple deposit with very high-grade copper minerals, and the presence of other iron sulphide impurities are negligible in the ore. 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 ore contains approximately from 0.5% to 6% copper, which varies significantly based on geographical location. The copper mineralogy mainly consists of chalcopyrite, chalcocite and bornite [1], and the ore has very little inclusion of iron

sulphides. The deposit also contains some traces of economically interesting elements such as silver, gold and platinum group elements (PGE). The traditional method for processing copper sulphide ores is by flotation, which is both economical and suitable as per the environmental standards. The most important factor in flotation of sulphides is the choice of reagents for optimum flotation. A priori, the advanced mineralogy and surface properties of these minerals in this ore deposit are necessary for a judicious choice of the collector for flotation to recover valuable minerals.

Automated mineralogical characterization using energy-dispersive scanning electron microscopy (SEM–EDS) is gaining significance in mineral processing operations because of its ability to collect statistically valid quantitative data on mineral distributions, liberation and associations. This data adds precise information on particulates that have traditionally been characterized by bulk mineralogical and chemical methods and optical microscopy. Dhar et al. [2] found that the percentage of liberation of Cu sulphides is approximately 80% for the Nussir ore sample at $-105\ \mu\text{m}$. This study shows that a major part of the copper is present in middlings, which were difficult to recover using the traditional xanthate collector.

Earlier, in the development of ore processing flotation, xanthates were almost always employed as collectors for flotation performed on metal sulphides. Due to the high selectivity of dithiophosphates, these collectors were also employed for selective copper sulphide flotation, and a few studies explained the interaction of dithiophosphates with pure copper minerals [3–7]. The mechanism of copper mineral flotation with dithiophosphates is believed to be the chemical adsorption of the dithiophosphate collector by the formation of cuprous dithiophosphate in neutral and slightly alkaline conditions. Recently, Zhong et al. [8] indicated that the recovery of pure chalcopyrite was high in the presence of dithiophosphate even at natural pH 8 (of the ore) and further showed optimum flotation results of bench scale flotation of a copper ore at the same pH. In the current study, the adsorption and interaction mechanism of disecundary butyl dithiophosphate (DBD) was investigated using pure minerals and bench scale flotation tests which were performed on Nussir ore samples as a function of pH and collector concentration. Additionally, the response of the DBD collector towards chalcopyrite, chalcocite and bornite has been presented and compared with xanthate as a collector.

In the past, Glembotskii [9] demonstrated that when a weaker collector is added to a stronger collector, the mixture results in an increase in recovery as compared to the individual strong collector system. Later, Bradshaw et al. [10,11] and Lotter and Bradshaw [12] reviewed the use of various mixtures of collectors in sulphide flotation where the selectivity and, thereby, the recovery and grade increase depending on the proportions of constituents of the collector blend. Additionally, the same authors indicated that the recoveries of middlings could be increased with the usage of mixtures of collectors in optimum ratios. A synergistic interaction of the collectors results in a greater adsorption, which increases the hydrophobicity of the desired mineral.

The synergism of the collectors in blends is generally explained with bench scale flotation or microflotation studies; only a few studies were performed on the basis of adsorption results. In 1980, Wakamatsu et al. [13] reported the co-adsorption of collectors at low concentrations and the competitive adsorption at high concentrations of ethyl xanthates (EX) and dibutyl dithiophosphate (DBDTP) collectors in the region of pH 6–7 for galena. Adsorption studies were performed with the solution depletion/abstraction method, and they stated that the adsorption of xanthates increased and DBDTP decreased for the equimolar mixtures of both the collectors at higher collector concentrations. Alternatively, Corin et al. [14] found no evidence of a synergistic effect between diethyl dithiophosphate (DEDTP) and isobutyl xanthate (IBX) for a platinum group ore. The authors reported that the dithiophosphate led to the stabilization of the froth phase and did not contribute to enhancing the hydrophobicity of the mineral surface. However, McFadzean et al. [15,16] showed that a significant increase in pure mineral flotation was observed in the presence of DEDTP and IBX collector mixtures for galena. They clarified that the improvement in the flotation performance relies on the sequence of collector addition. Additionally, the same authors, in 2013, observed synergism in the batch flotation of pyrite with a mixture of IBX and DEDTP.

Woods [7] studied xanthates and dithiocarbamate mixtures and explained that the chemisorbed collector species were more evenly distributed on the mineral surface than physisorbed species. A mixture may result in a balance of better distributed, more strongly held chemisorbed species and more hydrophobic neutral physisorbed dithiolates, and this could result in the formation of a multilayer surface product that is more strongly attached to the mineral surface. Bagci et al. [17] and Critchley and Riaz [18] proposed that the adsorption is improved by the addition of a weaker but more selective collector (dithiophosphate) before the less selective collector (SIBX).

This paper represents the first study on processing characteristics of the Nussir ore to date. In the process of developing a flowsheet for Cu-recovery, dithiophosphate and its blend with xanthate are examined as candidates for the flotation collector to beneficiate the ore. Since the Nussir ore is free from iron impurities, a successful collector selection would be of benefit to future copper deposits of similar mineral constitution. Based on the literature, the mixture of xanthate and dithiophosphate collectors in different proportions is 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 mining and Woodgrove, Canada. Prior to this, the adsorption of both the individual collectors in the collector mixture (SIBX-DBD) on copper sulphide minerals were evaluated using adsorption studies. To our knowledge, no studies have been reported explaining the nature and quantity of adsorption of dithiophosphates and xanthates on copper sulphides. An attempt has been made to demonstrate the mixed dithiophosphate and xanthate adsorption on the copper minerals with quantitative and qualitative adsorption studies together with zeta potential, pure mineral and bench scale flotation studies.

2. Materials and Methods

Pure mineral rock specimens of chalcopyrite (>92% grade), chalcocite (>93% grade) and bornite (>91% grade) were purchased commercially. The samples were obtained from Sweden, England and Austria respectively. Pure crystalline calcite and quartz samples used in these experiments were obtained from Norway. The sample preparation procedure for zeta potential measurements, FTIR studies, adsorption studies and Hallimond flotation tests was a three-fold process: (i) crushing using a jaw crusher with 3 mm discharge-opening, (ii) milling using a ball mill followed by sieving to collect the size range from -150 to $+45$ μm to be used in the Hallimond flotation (iii) for the zeta potential, adsorption studies and FTIR experiments. A portion of the -45 μm sample was further milled in a Fritsch Pulverisette 6 (Idar-Oberstein, Germany) planetary mono mill and wet screened to -10 μm . Precautions were taken during the whole milling and sieving process until the initial conditioning phase for the Hallimond flotation or zeta potential experiments to ensure that surface oxidation did not affect the results.

The Nussir ore (Figure 1) material was collected from two different parts (panels) of the mine, Nussir North East (N-NE) and Nussir Old West (N-OW). For bench scale flotation tests, the samples were thoroughly mixed, crushed and milled to -105 μm (coarse grind).

Cytec Solvay group supplied the reagents used in these experiments. The molecular weight of DBD used in the preparation of collector solutions was 264 $\text{g}\cdot\text{mol}^{-1}$, (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 of HCl and NaOH. Deionized water was used in all the studies with a pure mineral system, whereas tap water was used for the bench scale flotation tests. Additionally, a standard quartz suspension was used for calibrating the zeta potential instrument. Copper nitrate was employed to prepare the Cu-precipitates with a DBD collector for FTIR analysis. The Brunauer–Emmett–Teller (BET) surface areas for the -10 μm size fraction of chalcopyrite, chalcocite and bornite were 0.98 , 1.31 and 1.01 $\text{m}^2\cdot\text{g}^{-1}$ respectively.



Figure 1. (a) The Nussir drill hole specimen: Veinlets of chalcocite and bornite on a carbonate structure; (b) the crushed ore sample received from Nussir ASA.

2.1. Zeiss Mineralogical Mining Method

All samples were initially examined by optical microscopy. Subsequent automated mineralogy analyses were performed with the Zeiss Mineralogical Mining System at the Department of Matériaux et Environnement, Université de Liège, Belgium.

The Zeiss Mineralogical Mining System is a new generation of Automated Mineralogy systems designed to provide information on the modal mineralogy (by area % and wt %), morphology of analysed grains/particles, mineral liberation, locking characteristics, mineral association, chemical assay and element department. Data acquisition by the Mineralogical was performed using a Zeiss Sigma 300 field emission gun equipped with two Bruker EDX detectors (XFlash®630 SDD energy dispersive spectrometer). The operating conditions used for the data acquisition were a 20 kV acceleration voltage, a current of 20 nA, a 8.5 mm working distance and a “full mapping” analytical mode. Analyses were conducted on selected representative areas of the whole specimen with a mapping step size of 3 µm and from 0.025 to 0.03 seconds of dwelling time.

For the microscopic observations, approximately 1 g of representative sample was embedded in a mixture made with 0.4 g of PRINTEX®carbon black powder, 15 mL of epoxy resin and 2 mL of hardener to obtain blocks of 3 cm diameter. The addition of carbon black avoids the grain settlement by density into resin and allows a good spatial dispersion of particles [19].

2.2. Zeta Potential Measurements

The zeta potential measurements were performed using a DT-300 system instrument from Quantachrome/Dispersion Technologies, which works on the electroacoustic techniques principle. The chalcopyrite, chalcocite, bornite, quartz and calcite samples were first analysed in the particle size analyser to obtain the mean particle diameter. A 2 g sample of pure mineral was transferred into a 100 mL beaker containing 50 mL solution of a desired pH and concentration of DBD. Conditioning was performed in the following order before recording the titration experiments in the pH range from 2 to 12: (i) a pH adjustment for 5 min and (ii) collector addition for 5 min. During titration, the pH was adjusted using 1 M HCl and 1 M NaOH. The conductivity and pH of the suspension were monitored continuously during the measurement, and the ambient temperature was maintained at 22 ± 0.5 °C. All experiments were performed in triplicate, and an average result was reported.

2.3. Adsorption Measurements

Adsorption experiments of DBD and mixed DBD-SIBX collectors on copper sulphide surfaces were performed with a UV-2401PC (Shimadzu, Kyoto, Japan) spectrometer. A calibration curve was established using the UV-spectra taken for 50 mL of different aqueous DBD solutions (from 1×10^{-7} to 2×10^{-3} M). The pH of the solution was adjusted to approximately 8.2 with 1 M HCl and 1 M NaOH. To these collector solutions, 2 g of -10 µm each of chalcopyrite, chalcocite and bornite was added and stirred for 30 min. The suspensions were further filtered, and the supernatant solutions were

characterised in a UV-Visible spectrometer (with required dilution). The amount of dithiophosphate adsorbed was calculated from the difference between initial and residual concentration of the solutions.

Another set of experiments were performed using mixtures of dithiophosphate and xanthate collectors in 1:1 ratio under similar conditions. The characteristic peaks of SIBX and DBD were used for the estimation of the amount of dithiophosphate and xanthate adsorbed.

2.4. FTIR Measurements

Mineral samples conditioned with the desired collector(s) concentration and specified pH from the quantitative adsorption studies were dried and analysed with a Bruker Vertex 80v Infrared spectrometer. A typical FTIR spectrum was an average of 200 scans measured at a 4 cm^{-1} resolution with a narrow band liquid nitrogen cooled MCT detector. The pure mineral powder was used as a reference while recording the spectra of the reagent-treated mineral samples. The spectra of copper sulphides conditioned with 1:1 xanthate and dithiophosphate were also analysed by an infrared spectrometer. Additionally, the spectra of the minerals, reagent and Cu-dithiophosphate precipitates were noted for reference. The atmospheric water was always subtracted from the sample spectrum. The area under the alkyl chain bands and the intensities of functional group bands were measured with the facility available within spectral manipulation.

2.5. Hallimond Tube Flotation Experiments

The Hallimond flotation tests were conducted with 2 g from -150 to $+50\ \mu\text{m}$ size chalcopyrite, chalcocite, bornite, calcite and quartz samples in a 100 mL Hallimond tube flotation cell. The first step was to adjust the desired pH level using HCl and NaOH. Afterwards, the collector and frother were added and conditioning was performed for 5 and 2 min respectively in a 100 mL standard volumetric flask. The sample was conditioned with a magnetic stirrer for the respective time and subsequently transferred to the Hallimond flotation cell. Air was supplied at the rate of $8\text{ ml}\cdot\text{min}^{-1}$, and flotation time was 1 min. The floated and tailing fractions were collected separately, dried and weighed. The flotation cell was thoroughly washed using ethanol and subsequently rinsed with deionized water after each experiment. All experiments were performed in triplicate, and an average result was reported.

2.6. Bench Scale Flotation Tests

The bench scale flotation experiments were performed with 200 g ($-105\ \mu\text{m}$ size fraction) of ore, wet ground with tap water in a steel mill with a 1 kg grinding medium followed by flotation in a Maelgwyn bench scale flotation cell of 1 L capacity. The following reagents were added in sequence: a pH regulator, collectors and a frother, the dosages of which varied from one experiment to another. The impeller speed and airflow rate were fixed at 1200 rpm and $3\text{ L}\cdot\text{min}^{-1}$, respectively. The flotation was performed in two stages, where the total flotation time was 4 min. The resulting purified copper sulphide concentrates were filtered, dried and chemically analysed with a Bruker AXS S8 Tiger Wavelength Dispersive XRF.

3. Results

3.1. Mineralogy

The ore consists primarily of chalcopyrite, chalcocite and bornite with a minimal amount of covellite. A SEM image is presented in Figure 2, which represents all the copper sulphides in the ore. The presence of economically valuable precious metal minerals in low quantities was also noted. Mineralogical characterisation revealed that the copper minerals from the panel N-NE are dominated by bornite and chalcocite with a small amount of chalcopyrite, while the N-OW composite is rich in bornite and chalcopyrite with small amounts of chalcocite. In our previous investigations, the flotation experiments performed with xanthate as a collector showed that the maximum grade and recovery were 14% and 91% Cu, respectively [20].

Before and after the bench scale flotation of the ore with xanthate, the feed and float materials analyzed with Mineralogic revealed that a significant quantity of copper sulphides in the feed material are associated with other copper sulphides, silicate and carbonate minerals. The middlings percentage in both the samples for the $-105\ \mu\text{m}$ range is approximately 10%–17%. Although the ore is relatively simple, with little or no intrusion of iron sulphides, the silicate and carbonate gangue minerals are finely disseminated within the matrix of ore samples. The overall distribution of the various associations of copper sulphides before and after flotation with xanthate and dithiophosphate and these two collectors in the blend (1:1) is presented in Figure 3.

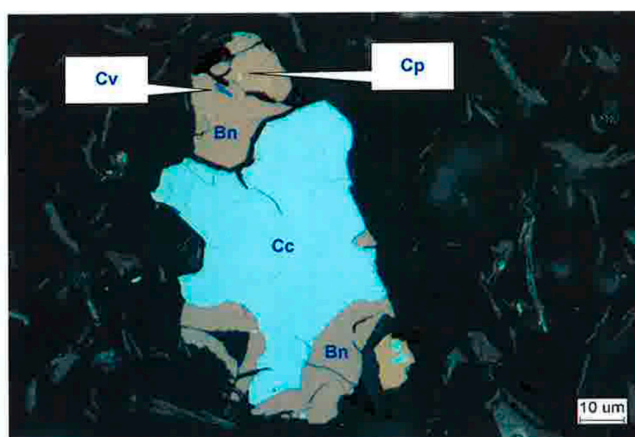


Figure 2. A photomicrograph of the copper sulphides present in the ore. Cc—chalcocite; Bn—bornite; Cp—chalcopyrite; Cv—covellite.

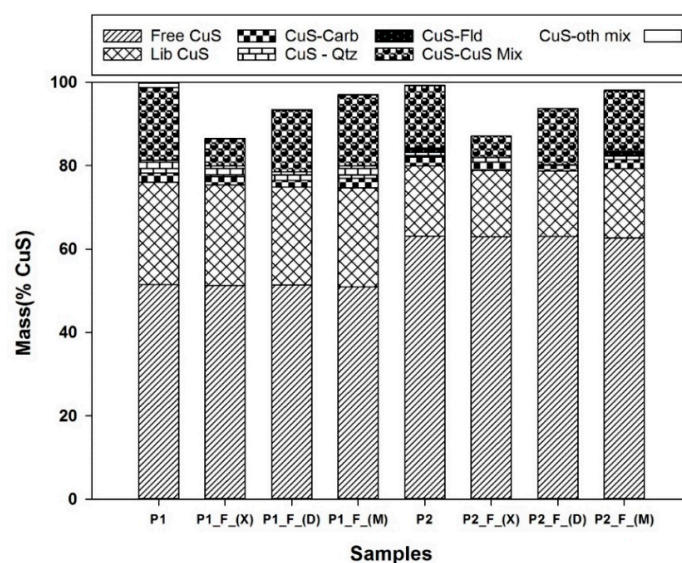


Figure 3. The distribution of various associations of copper sulphides in the Old West (N-OW; P1) and Nussir North East (N-NE; P2) samples at collector concentration 3×10^{-5} M and pH 8.2. P1 and P2—Feed; F—Flotation product; X—sodium isobutyl xanthate (SIBX); D—dissecondary butyl dithiophosphate (DBD); M—SIBX:DBD = 1:1 ratio (Liberated: >80% liberation; Free: Fully liberated; and Middling: <80% liberation).

The liberated copper sulphides were clearly floated when using SIBX as a collector, while a significant amount of middlings did not float with xanthate at collector concentration 3×10^{-5} M. It is noticeable that the flotation of copper sulphide–carbonate/silicate blends (CuS-carb/CuS-Qtz) is equally efficient as the copper sulphide–copper sulphide (CuS–CuS) blends in the presence of xanthate collectors. Apparently, at the same collector dosage, a considerable amount (ca. 8%–10%) of

copper sulphide middlings (specifically CuS–CuS blends) were able to float with a DBD collector; less flotation of CuS-carb/CuS-Qtz is observed. Moreover, a substantial amount of associated mixed copper sulphide particles were floated, together with CuS-carb/CuS-Qtz blend minerals in the presence of the mixture of SIBX and DBD collector. The results are in agreement with the previous findings that SIBX is a stronger (more reactive) collector and that DBD is more selective towards copper sulphides [10]. Earlier, a few researchers [11] also observed improvement in coarse particle recovery and middlings recovery with collector mixtures on Cu/Pt ores. Therefore, dithiophosphate and dithiophosphate-xanthate blends were studied as collectors, and an extensive investigation has been made to assess the interaction of these collectors with the pure copper sulphide minerals. Detailed bench scale flotation results as a function of pH and collector concentration are presented later in the flotation section.

3.2. Zeta Potential Studies

The zeta potential values of chalcopyrite, chalcocite, bornite, calcite and quartz were measured as a function of pH in aqueous solution, and the results are presented in Figure 4. The isoelectric points (IEPs) of chalcopyrite and chalcocite are located at pH 4 and 4.3 respectively. The IEPs of bornite are at two pH values, 2.8 and 6. Zhao et al. [21], Kelebek and Smith [22], and Fullston et al. [23] reported similar results. The IEP of gangue minerals, calcite and quartz, are at pH 8.2 and 2.1. These values are in agreement with previously reported results by Somasundaran [24]. In Figures 4 and 5, the zeta potential values decrease with increasing pH values in the presence and absence of the collector. There is a shift towards negative zeta potential values after the addition of the anionic DBD collector, which signifies the adsorption of the reagent on the copper sulphide surface and the mode of adsorption is chemisorption on Cu-sites, which is later shown by the FTIR studies. It is evident that the zeta potential values of copper sulphides also decreased with the subsequent addition of SIBX [2]. However, the copper sulphides conditioned with DBD show more negative potentials (in the pH range 4–9) as compared to those conditioned with SIBX. Overall, it is observed that the zeta potential values of copper sulphides decrease significantly in the acidic and neutral pH region, whereas in alkaline pH, there is a minimal decrease in zeta potential values.

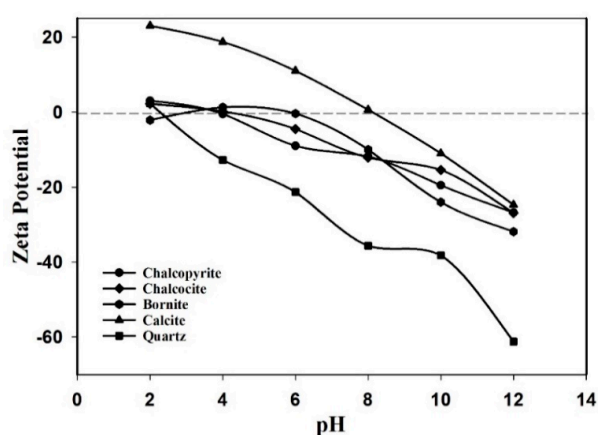


Figure 4. The zeta potential of copper minerals and gangue minerals in aqueous solution.

The zeta potential values of copper sulphides conditioned with mixtures of the collector (total collector concentration: 3×10^{-5} M) are shown in Figure 6. A major shift towards negative values in the zeta potentials of copper sulphides is observed in the pH range 6–10. It is noted that when the fraction of DBD is greater in the reagent mixture, the values of zeta potential are more negative. This is consistent with the single collector systems, where values of zeta potential were more negative for copper sulphides conditioned with DBD as compared to SIBX [2]. In addition, the negative potentials of copper sulphides are higher in the mixed reagent system compared to a single reagent system,

indicating an adsorption of both the collectors on the surface of the copper minerals. It is also noted that the behaviour of different copper sulphides is largely dependent on the composition of the reagents employed in the experiments. Less variation in zeta potential values in the presence of different compositions of DBD-SIBX mixtures is observed as compared to bornite and chalcocopyrite (Cu–Fe sulphides). The presence of different active sites of Cu and Fe would be achieved due to the different degrees of their oxidation sites. The flotation behaviour of these copper sulphide minerals in the presence of DBD and collector blends is further examined with Hallimond tube flotation experiments.

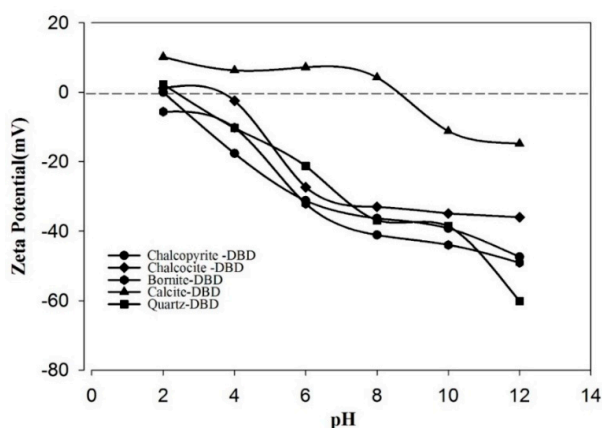


Figure 5. The zeta potentials of minerals as a function of pH at DBD concentration 5×10^{-5} M.

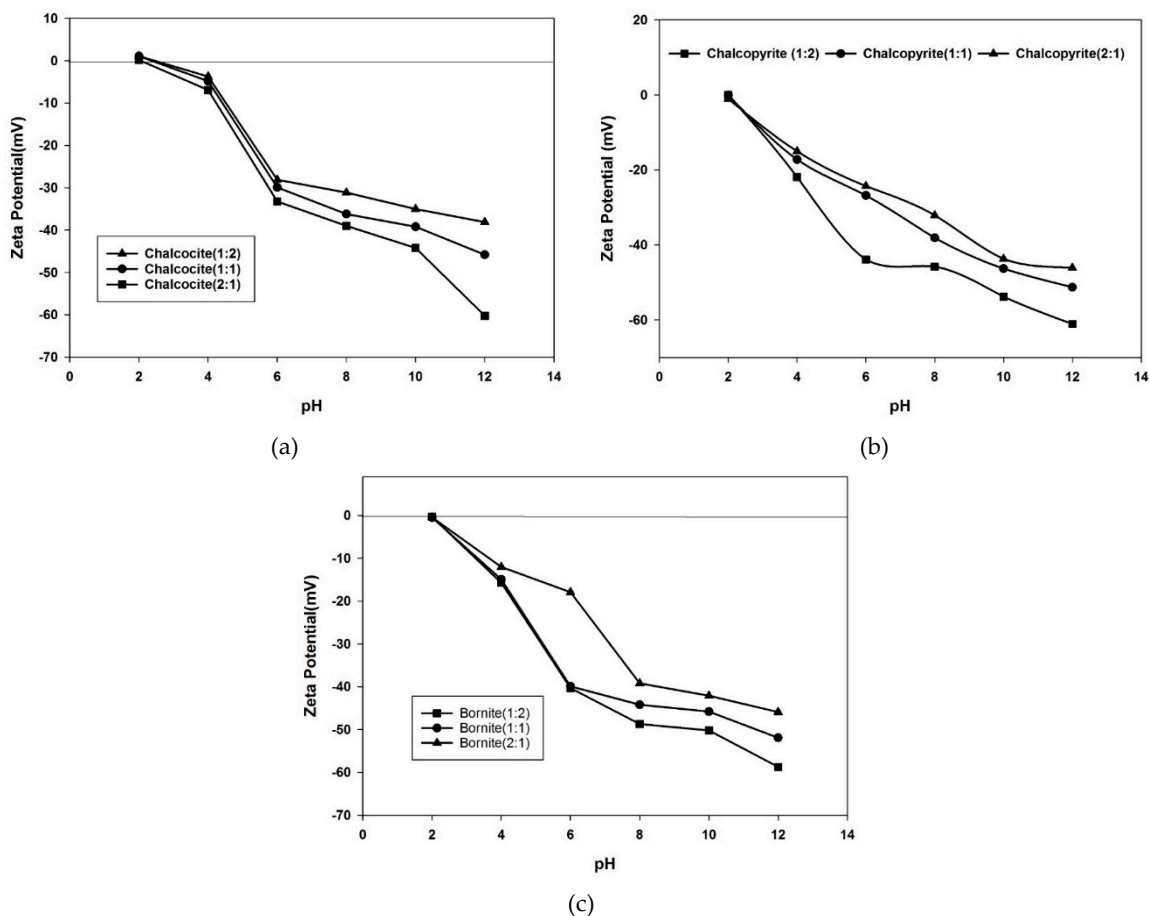


Figure 6. The zeta potentials of (a) chalcocopyrite, (b) chalcocite, and (c) bornite as a function of pH in presence of collector mixture (SIBX:DBD).

3.3. Hallimond Flotation Studies

The floatability of chalcopyrite, chalcocite, bornite, calcite and quartz in the presence of DBD is investigated as a function of pH (Figure 7). In this figure, the highest recoveries for all the three sulphides were observed for $\text{pH} \approx 6$, while the recoveries are also considerably high at $\text{pH} 8-9$. At acidic pH values, the recoveries of chalcocite, chalcopyrite and bornite are low, while the recoveries are consistently more than 70% above $\text{pH} 5$. However, the recovery of copper sulphides, specifically chalcopyrite, is relatively less at $\text{pH} 12$. It is known that the copper-iron sulphides are oxidised more in alkaline solutions as compared to acidic or neutral solutions. In fact, the precipitation of metal species as hydroxides is predominantly prevalent in alkaline pH values. Therefore, recovery decreased in alkaline pH solutions and is due to the heavy surface coating hydrophilic metal hydroxides [5,25]. The high recovery of copper sulphides signifies a high selectivity of DBD in a wide pH range ($\text{pH} 4-11$).

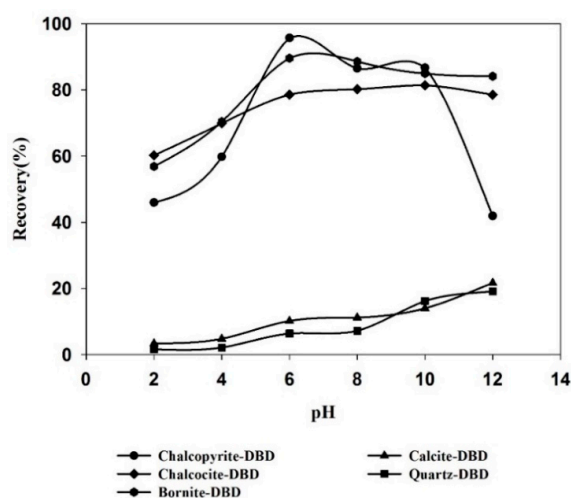


Figure 7. The Hallimond flotation recovery as a function of pH at collector concentration 5×10^{-5} M.

Figure 8 depicts the recovery of pure mineral flotation as a function of collector concentration at a natural pH. The results are very similar to our earlier findings on flotation of copper sulphides with SIBX as the collector. However, it is noticeable that a lesser amount of DBD is required as compared to SIBX for a higher flotation of copper sulphides. Chalcopyrite and bornite show a sudden rise in recovery at collector concentration 1×10^{-5} M, whereas chalcocite shows a steady increase in recovery. In general, the flotation response of chalcopyrite and bornite is slightly higher than chalcocite. These results are consistent with the zeta potential results. The recovery of calcite and quartz also increases to 20%–30% at a high collector concentration: ca. 1×10^{-4} M. All the comparisons with xanthate are performed based on our earlier investigation [20].

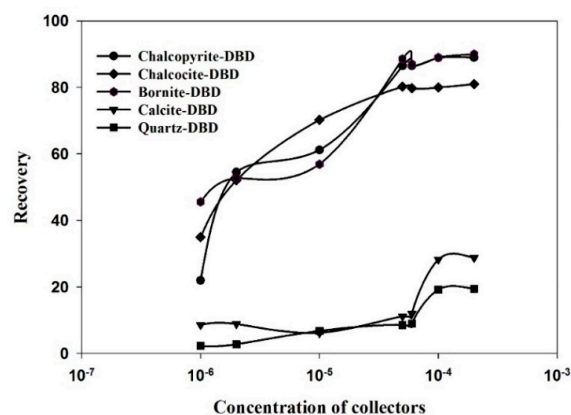


Figure 8. Hallimond flotation recovery as a function of collector concentration at a natural pH.

The floatability studies of pure minerals with collector mixtures at a natural pH and total collector concentration 3×10^{-5} M is shown in Figure 9. The recoveries of pure chalcopyrite and bornite minerals have two maxima, at pH 6 and 9, when SIBX:DBD is 1:2. However, when SIBX:DBD = 1:2, the recovery of chalcocite showed a maximum recovery at pH 8/9. These results are in agreement with the outcomes of individual reagent systems, where chalcocite indicated higher recoveries at pH 8, whereas chalcopyrite and bornite indicated a maximum recovery at pH 6. The recoveries of calcite and quartz are significantly lower for all the three different ratios. In general, it is observed that the synergistic action of both the reagents results in better recoveries than an individual collector scheme for all the single pure minerals. The major advantage of using collector mixtures is the total concentration of collectors required for flotation of copper sulphides is relatively lower than the single collector system. The improvements in the SIBX:DBD mixture are understandably due to a simple case of competitive adsorption (explained later in Section 3.4 adsorption studies) where DBD adsorbs on the higher active sites followed by the adsorption of the more reactive xanthate collectors on the remaining low activity sites.

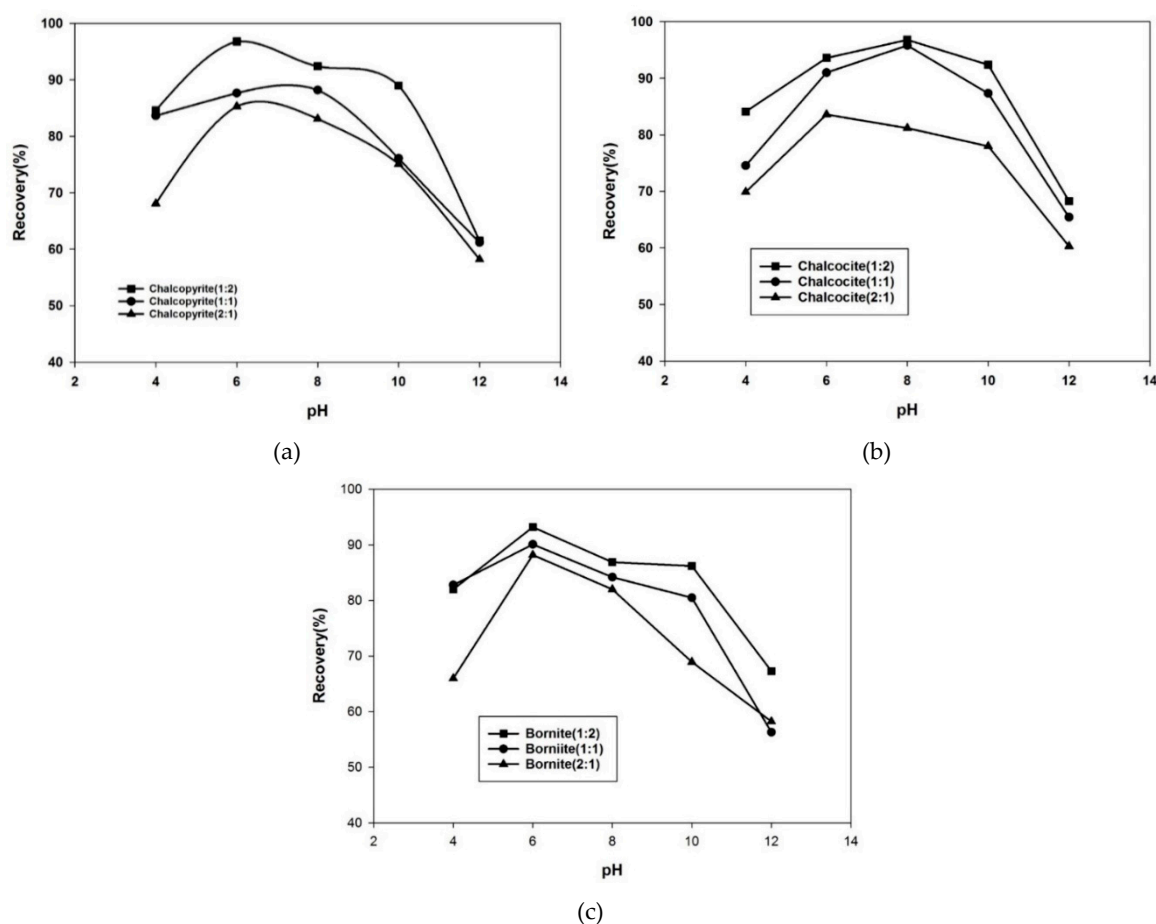


Figure 9. The Hallimond flotation recovery of (a) chalcopyrite, (b) chalcocite, and (c) bornite in the presence of a collector blend as a function of pH at collector concentration 3×10^{-5} M.

3.4. Adsorption Studies

The adsorption of DBD from aqueous solution onto copper minerals has been studied by the solution depletion method using a UV-Visible spectrometer. The high intensity characteristic peak of DBD was observed at 226 nm [25]. The adsorption mechanism of a mixture of the collectors was also investigated at a 1:1 ratio of SIBX and DBD by using the same spectroscopy method at pH 8. The characteristic peaks at 301 nm and 226 nm of SIBX and DBD respectively were present in the spectra, allowing the adsorption of individual collectors from the mixture. A feeble dixanthogen peak was

observed in the spectra (only at high concentrations), but the dimer of dithiophosphates was not present in the UV spectra because this dithiophosphate dimer has far lower solubility, $5 \times 10^{-7} \text{ mol}\cdot\text{dm}^{-3}$, as compared to dixanthogen ($1.25 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ [6]).

The adsorption isotherms of DBD on chalcopyrite, chalcocite and bornite at pH 8 are shown in Figure 10. This figure shows that the adsorption of DBD on chalcopyrite and bornite begins at a lower equilibrium concentration while the onset of adsorption for chalcocite is found to be $9.2 \times 10^{-6} \text{ M}$. Initially, when a copper sulphide is introduced to the reagent solution, the mineral surface is hydrated due to the faster diffusion of water molecules compared to bulk ligand molecules (Raju and Forsling [26]). Further, the chemical adsorption of DBD on the Cu^{2+} sites of copper minerals occurs which is also observed from the FTIR spectra, resulting in a hydrophobic surface. Considering the cross-sectional area of a DBD molecule as 35.4 \AA^2 (as calculated by Matsuoka and Ichikoku [27]), a monolayer is anticipated to form at an adsorption density of $4.6 \text{ }\mu\text{mol}\cdot\text{m}^{-2}$. In Figure 11, the isotherm of chalcopyrite attains the plateau value at $3.6 \text{ }\mu\text{mol}\cdot\text{m}^{-2}$, thus indicating a 0.8 monolayer. Previously, Petrus et al. [28] observed less than a monolayer coverage of dithiophosphate on chalcopyrite at an equilibrium concentration $1.54 \times 10^{-5} \text{ M}$. Our findings are in accordance with these studies, indicating less than a monolayer adsorption on the chalcopyrite surface followed by a sudden increase in adsorption density above concentration $1.87 \times 10^{-4} \text{ M}$. The increase after a plateau region can be attributed to precipitate formation in the bulk of solution, or another assertion can be multilayers of surface product are adsorbed on the chemisorbed monolayer [7,17,25]. The chalcocite-xanthate adsorption isotherm indicates a marginal increase in adsorption density, followed by a steep rise in the slope which corresponds to the onset of adsorption due to the accumulation of the collector at equilibrium concentration $9.2 \times 10^{-6} \text{ M}$. These results show a less than monolayer coverage of DBD on bornite where the adsorption density is merely $3.2 \text{ }\mu\text{mol}\cdot\text{m}^{-2}$. The bornite isotherm also depicts less than monolayer coverage, and the isotherm levels off at $2.8 \text{ }\mu\text{mol}\cdot\text{m}^{-2}$. In addition, the chalcocite and bornite isotherms also indicate an increasing adsorption density at a high concentration of DBD ($\approx 1 \times 10^{-3} \text{ M}$) corresponding to an increase in adsorption in the form of $\text{Cu}(\text{DBD})+(\text{DBD})_2$ species of collector on the chemisorbed layer [4,10].

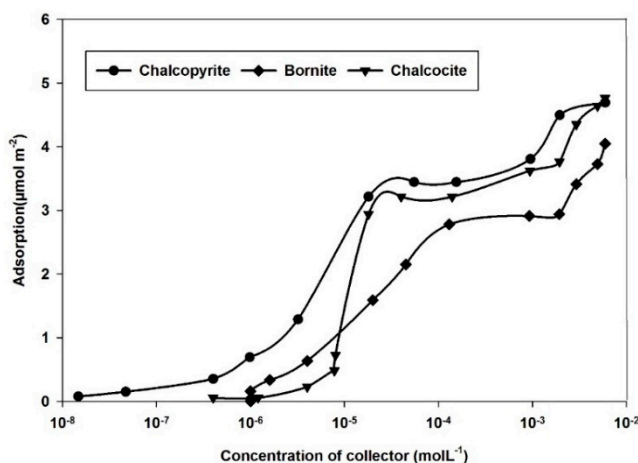


Figure 10. The adsorption of dithiophosphate on the copper sulphide surface at pH 8.

Figure 11 shows the area under the alkyl chain region between $2600\text{--}2900 \text{ cm}^{-1}$ (the spectra are presented later in Section 3.5 FTIR) for all the three copper minerals with respect to DBD concentration. The area under the alkyl chain bands was measured with the facility available within the spectral manipulation feature. Adsorption begins at low concentration of collector for chalcopyrite and bornite, while the onset of adsorption for chalcocite was observed at $1 \times 10^{-5} \text{ M}$. These results are in agreement with the quantitative adsorption results. The area under the alkyl chain values for chalcopyrite, bornite and chalcocite is approximately constant above collector concentration of $2 \times 10^{-5} \text{ M}$, $8 \times 10^{-5} \text{ M}$ and $2 \times 10^{-5} \text{ M}$ respectively. The same figure also depicts the intensities of the characteristic functional

group band of DBD as a function of collector concentration. The intensities of DBD absorbance bands at 964 and 953 cm^{-1} for chalcopyrite and chalcocite respectively are nearly constant above 2×10^{-5} M. The intensity of the characteristic DBD band for bornite at 949 cm^{-1} is approximately constant above 1×10^{-4} M in accordance with the quantitative adsorption results. Although not shown in this communication, the FTIR spectra recorded at higher concentrations clearly showed the presence of randomly oriented collector species on the top of chemisorbed layers.

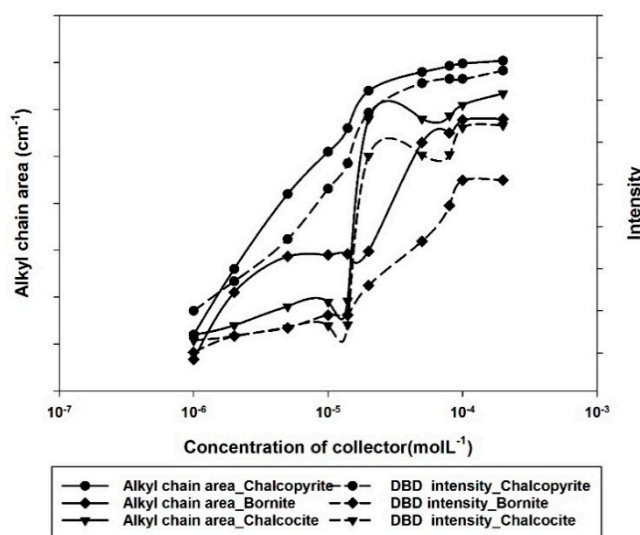


Figure 11. The intensities of the characteristic DBD band and the area under the alkyl chain bands for chalcopyrite, chalcocite and bornite.

Figures 12 and 13 shows the adsorption isotherms of SIBX and DBD on copper minerals in the presence of both these collectors' mixture (1:1) at pH 8. In general, both the collectors in the mixture are adsorbed on all the three copper minerals. However, the differences in the functional groups of SIBX and DBD influence the chemical reactions between the collector and mineral surface. The independent isotherms of SIBX and DBD depicts less than a monolayer coverage (θ) of the individual reagent on chalcopyrite. The adsorption corresponds precisely to 0.24θ of SIBX and 0.6θ of DBD on chalcopyrite. Similarly, based on the two plots, the proportion of DBD adsorbed on chalcocite is more than SIBX, and both reagents show less than a monolayer coverage. In the case of both chalcopyrite and chalcocite, the onset of adsorption for DBD is at a relatively lower concentration than SIBX, indicating competitive adsorption of the collectors. Alternatively, for bornite, the commencement of adsorption of SIBX is at a comparatively lower concentration than DBD. However, the quantity of adsorption of both the collectors is comparable above the equivalent concentration 5.2×10^{-5} M. The stability of the resulting species at the surface is also dependent on the differences in the proportions of reagents in the collector blend, which is not covered in this study. Bagci et al. [17] indicated that dithiophosphinates are more selective to copper sulphides as compared to xanthates, based on the electronegativities of the functional groups. In this study, DBD preferentially adsorbs on chalcopyrite and chalcocite in accordance with Bagci et al. [17]. However, the preferential adsorption of SIBX on bornite is probably due to the presence of Fe in the lattice, which could be a result of different oxidation sites. Previously, Ackerman et al. [29] also reported a decrease in the floatability of bornite in the alkaline pH region, whereas the flotation response of chalcopyrite and chalcocite was high. Therefore, the decrease in adsorption density may lead to a decrease in floatability; similarly, in our pure mineral flotation results, a small decrease in flotation response of bornite is observed. Unlike Wakamatsu et al. [13], our study shows the co-adsorption of collectors at high concentrations; xanthates being more reactive shows a greater adsorption than DBD.

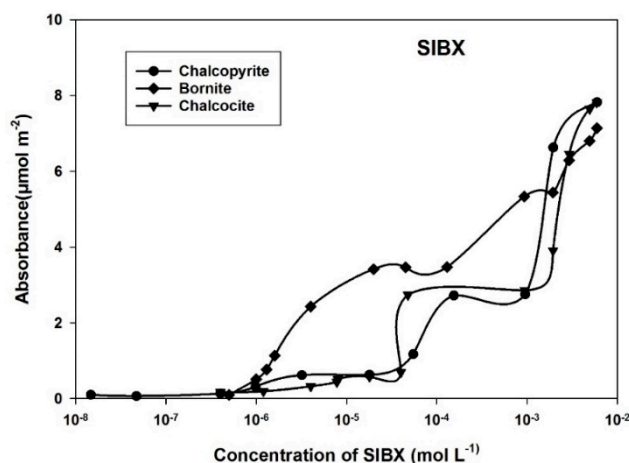


Figure 12. The adsorption of xanthate from a mixture of xanthate and dithiophosphate on the copper sulphide surface at pH 8.

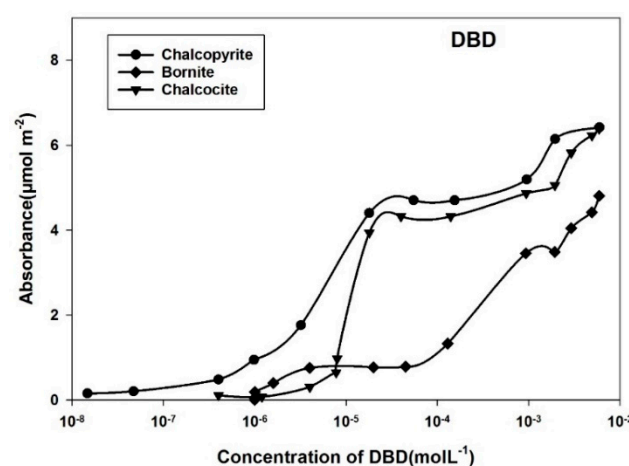


Figure 13. The adsorption of dithiophosphate from a mixture of xanthate and dithiophosphate on the copper sulphide surface at pH 8.

Figure 14 shows the intensities of characteristic SIBX and DBD bands for all the three copper minerals in the presence of mixtures of both the collectors. The intensities of the distinctive DBD peak at 985 cm^{-1} are more than the SIBX peak at 1065 cm^{-1} for chalcopyrite. In the case of chalcocite, the intensities of the characteristic DBD peak at 895 cm^{-1} are greater than the SIBX peak at 1192 cm^{-1} . For bornite, the SIBX peak at 1206 cm^{-1} is of a higher intensity than that of the DBD peak at 745 cm^{-1} . These results corroborate the quantitative adsorption studies shown in Figures 11 and 12. SIBX preferentially adsorbed on bornite and the quantity of adsorption are comparable to DBD. The area under the alkyl chain for both the collectors is represented in Figure 15, and the results show that the areas under the alkyl chain for all the three copper minerals are approximately constant above cumulative concentration $1 \times 10^{-5}\text{ M}$. Future works within this study will investigate the various proportions of collectors in the blend.

In general, the surfaces of the copper sulphides comprise various degrees of surface-active sites. It is understood that when the collector mixture is introduced in the mineral solution, the selective collector first adsorbs on the strong active sites [7]. The less selective collector there will adsorb on the residual weak sites. The different molecular structures of the functional groups of xanthates and dithiophosphates influences the reactions between the collector and mineral surface and, thus, the stability of the species at the surface. Donor atoms are crucial in the interaction between collectors and the mineral surface. Collectors having highly electronegative donor atoms possess a higher affinity for adsorption and are considered as less selective collectors. Thus, the selectivity of the collectors can be

explained with their respective electro negativities. Nagraj [30] stated that the electronegativities (EN) of O and C atom in xanthate molecules are higher than the P atoms in the structure of dithiophosphates; thus, the selectivity of DBD is higher than SIBX.

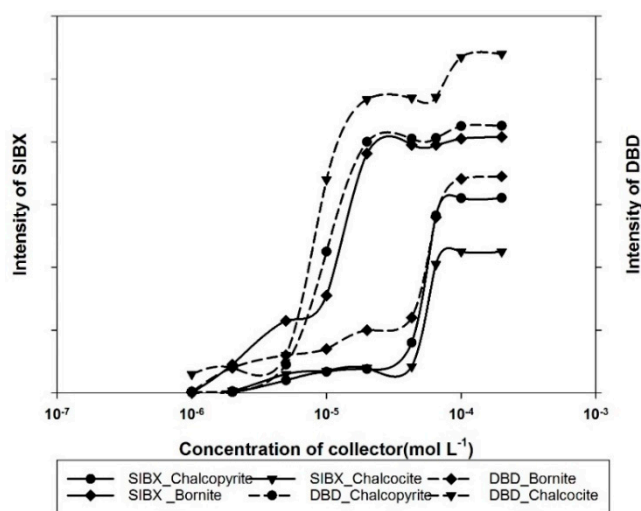


Figure 14. The intensities of characteristic SIBX and DBD bands for chalcopyrite, chalcocite and bornite.

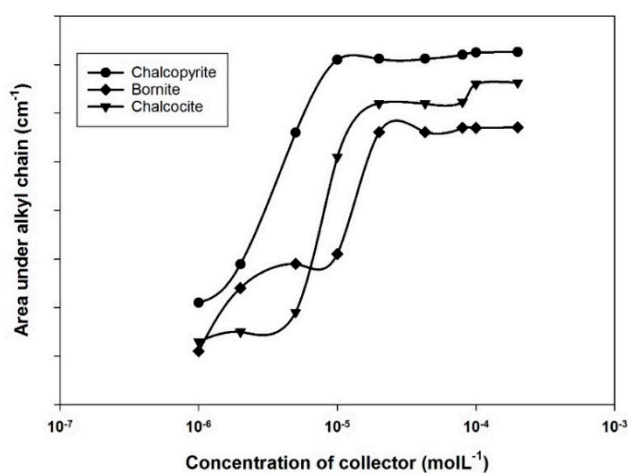


Figure 15. The area under the alkyl chain bands for chalcopyrite, chalcocite and bornite in the presence of SIBX and DBD blend (1:1).

Our adsorption study demonstrates that DBD is adsorbed first on the chalcopyrite and chalcocite surfaces followed by SIBX on the weak sites. A similar competitive adsorption is observed for bornite, where SIBX adsorbs first and, subsequently, DBD adsorbs, which is due to the different degrees of oxidation.

3.5. FTIR Studies

The DRIFT spectra of pure copper sulphide minerals, SIBX, DBD and the Cu-precipitate (CuDBD + Cu(DBD)₂) as reference spectra are shown in Figure 16. The dithiophosphate and copper-dithiophosphate precipitate spectra indicated a band structure especially below 980 cm⁻¹ (in the region 500–970 cm⁻¹). The vibrational bands between 510–575 cm⁻¹ represent P–S stretching bands and between 630–830 cm⁻¹ correspond to P–O–C symmetric stretching vibrations [31–33]. The bands between 900 and 1100 cm⁻¹ are attributed to P–O–C asymmetric stretching vibration [32,33]. In the collector spectrum, the bands at 735, 787, 828 and 860 cm⁻¹ represent P–O–C symmetric stretching. The bands at 531 and 614 cm⁻¹ indicate P–S stretching and P=S stretching modes respectively;

these peaks are attributed to the PS_2 group of DBD. The broad peak at 984 cm^{-1} signifies P–O–C asymmetric stretching vibration. The copper precipitate spectrum indicates characteristic peaks at 523 cm^{-1} and 642 cm^{-1} which correspond to P–S stretching and P=S stretching modes respectively. Additionally, this spectrum shows a peculiar sharp peak at 970 cm^{-1} which refers to P–O–C asymmetric stretching vibration.

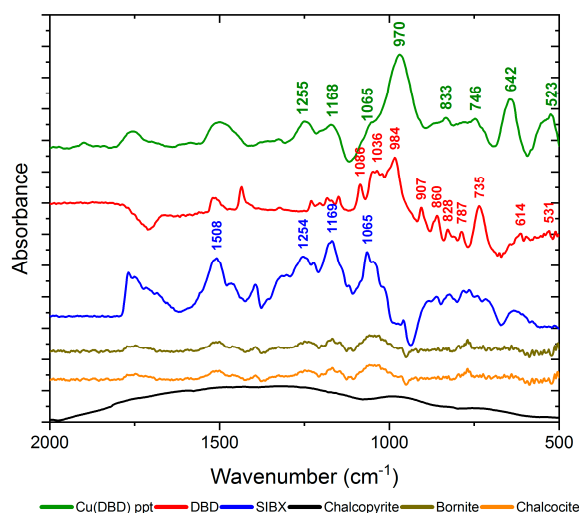


Figure 16. The DRIFT spectra of xanthate, dithiophosphate and copper dithiophosphate precipitates.

Figures 17–19 represent the FTIR spectra of chalcopyrite, bornite and chalcocite conditioned with various concentrations of DBD. After the interaction with DBD, the characteristic peaks for pure chalcopyrite become weak and the characteristic peak (984 cm^{-1}) of DBD becomes evident. The spectra of chalcopyrite in Figure 17 reveals the presence of a peak at 964 cm^{-1} at and above a $1 \times 10^{-5}\text{ M}$ concentration, which corresponds to the asymmetric P–O–C stretching of DBD. The bands at 777 cm^{-1} and 531 cm^{-1} refer to P–O–C symmetric stretching and P–S stretching vibrations. The shift in P–O–C and P–S vibrations indicate the chemical adsorption of the collector on Cu-sites of chalcopyrite.

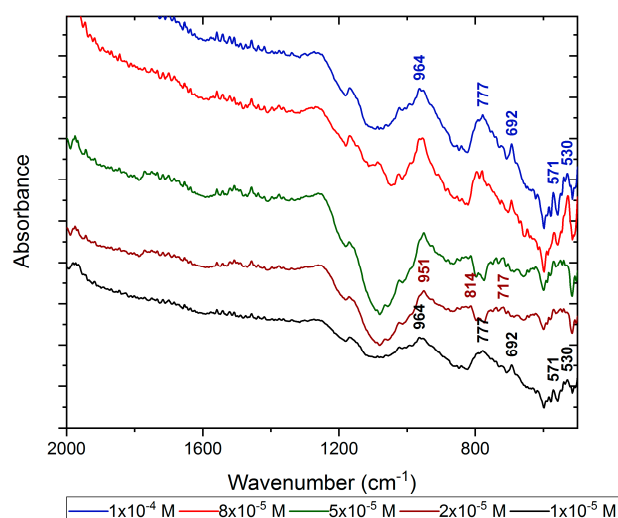


Figure 17. The DRIFT spectra of dithiophosphate adsorption on chalcopyrite with increasing collector concentration.

Similarly, the spectra of bornite and chalcocite conditioned with various concentrations of DBD are shown in Figures 18 and 19. For bornite, a shift is observed in the P–O–C symmetric and asymmetric stretching vibrations of DBD to 814 and 949 cm^{-1} respectively. The peak at 623 cm^{-1} which is related

to P=S stretching vibrations is observed at and above a 8×10^{-5} M concentration of the collector, indicating the chemisorption of the collector on Cu sites. In the case of chalcocite, 953 and 685 cm^{-1} peaks can be noted, which correspond to P–O–C stretching, and the band below 600 cm^{-1} refers to P=S stretching vibration (dithiolate formation). The shift in P–O–C stretching and P=S stretching vibration is related to the chemisorption of DBD on the chalcocite surface. All the changes suggested that the S and O atoms in the functional group of DBD might have taken part in the reaction with these ions.

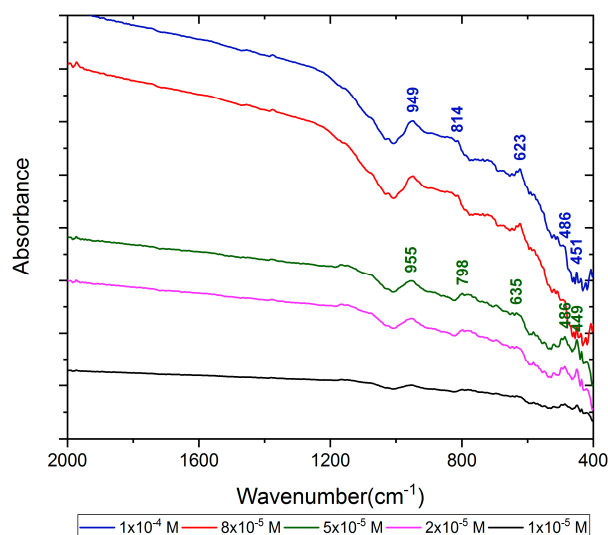


Figure 18. The DRIFT spectra of dithiophosphate adsorption on bornite with increasing collector concentration.

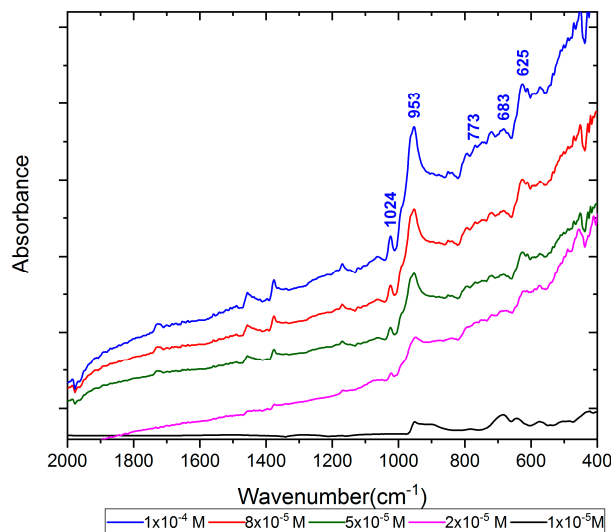


Figure 19. The DRIFT spectra of dithiophosphate adsorption on chalcocite with increasing collector concentration.

Figure 20 depicts the spectra of adsorption of a mixed xanthate and dithiophosphate collector (1:1) at pH 8 on the three copper minerals. The characteristic xanthate bands are between 900 and 1300 cm^{-1} , and the dithiophosphate bands are between 600 and 1000 cm^{-1} . This indicates adsorption of both the collectors on all the three copper mineral surfaces. However, the spectrum of chalcopyrite shows two strong peaks at 883 and 985 cm^{-1} , characterising P–O–C symmetric and asymmetric stretching vibration respectively. Additionally, it also indicates peaks at 1065 and 1273 cm^{-1} , corresponding to C=S and C–N stretching respectively. Similarly, the chalcocite spectrum depicts peaks at 895 cm^{-1} and 764 cm^{-1} , implying P–O–C symmetric stretching vibrations. A semi-broad peak is also observed at

1192 cm^{-1} , indicating C–O–C asymmetric stretching. However, bornite indicates two strong peaks at 1208 and 1351 cm^{-1} : C–N stretching and C–O–C asymmetric stretching respectively. The characteristic peaks related to DBD were also observed at 633 and 745 cm^{-1} . These spectra reveal that DBD is more strongly adsorbed than the SIBX collector on chalcopyrite and chalcocite. Similarly, the adsorption of the SIBX collector is stronger for bornite as compared to DBD. The infrared spectroscopy results are consistent with the zeta potential and Hallimond flotation results. All the information regarding the bands and peaks are summarized in Table 1.

Table 1. The FTIR bands of dithiophosphate, Cu-dithiophosphate precipitate, xanthate and chalcopyrite, chalcocite and bornite (before and after adsorption of dithiophosphate/dithiophosphate-xanthate blend, 1:1).

Spectrum Name	Bands (cm^{-1})	Significance	References
Dithiophosphate (DBD)	531	ν_s (P–S)	[32,33]
	614	ν_s (P=S)	[32,33]
	735	ν_s (P–O–C)	[28,32]
	787	ν_s (P–O–C)	[32,33]
	828	ν_s (P–O–C)	[28,32]
	860	ν_s (P–O–C)	[32]
	907	ν_{as} (P–O–C)	[32]
	984	ν_{as} (P–O–C)	[32]
Cu-dithiophosphate	1036	ν_{as} (P–O–C)	[32]
	523	ν_s (P–S)	[32,33]
	642	ν_s (P=S)	[32]
	746	ν_s (P–O–C)	[33]
	833	ν_s (P–O–C)	[32,33]
Xanthate (SIBX)	970	ν_{as} (P–O–C)	[32,33]
	1168, 1255	ν_{as} (P–O–C)	[32]
	1047	ν_s (C=S)	[34]
	1065	ν_s (C=S)	[32,34]
	1086	ν_s (C=S)	[32,33]
	1169	ν_{as} (C–O–C)	[32,33]
Chalcopyrite + DBD	1254	ν (C–N)	[32,34]
	1508	ν (C–N)	[34]
	530	ν_s (P–S)	[32,33]
	571	ν_s (P–S)	[32]
	692	ν_s (P–O–C)	[32,34]
Bornite + DBD	777	ν_s (P–O–C)	[32,33]
	964	ν_{as} (P–O–C)	[32,33]
	486	ν_s (P–S)	[32,33]
	623	ν_s (P=S)	[32,34]
	635	ν_s (P=S)	[32–34]
Chalcocite + DBD	814	ν_s (P–O–C)	[32,33]
	949	ν_{as} (P–O–C)	[32,33]
	625	ν_s (P=S)	[32]
	683	ν_s (P–O–C)	[32,33]
Chalcopyrite + DBD + SIBX	773	ν_s (P–O–C)	[32,33]
	953	ν_{as} (P–O–C)	[32,33]
	1024	ν_{as} (P–O–C)	[32,33]
	584	ν_s (P–S)	[32]
Bornite + DBD + SIBX	883	ν_s (P–O–C)	[32–34]
	985	ν_{as} (P–O–C)	[32,33]
	1065	ν_{as} (C–O–C)	[32,33]
	589	ν_s (P–S)	[32–34]
Chalcocite + DBD + SIBX	663	ν_s (P–O–C)	[32]
	1208	ν (C–N)	[33]
	1351	ν (C–N)	[34]
	1428	ν (C–N)	[32,33]
Chalcopyrite + DBD + SIBX	717	ν_s (P–O–C)	[32,33]
	848	ν_s (P–O–C)	[32,33]
	935	ν_{as} (P–O–C)	[32,33]
	1186	ν_{as} (C–O–C)	[32–34]

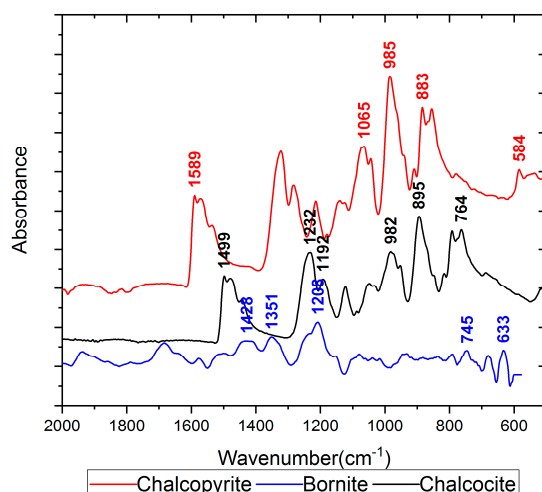


Figure 20. The DRIFT spectra of the dithiophosphate and xanthate collector blend (1:1) adsorption on copper sulphides at pH 8 and a total concentration of collector 3×10^{-5} M.

3.6. Correlation among the Pure Mineral Studies with Respect to Collector Concentration

Figure 21 shows the correlation between the Hallimond flotation recovery, Zeta Potential results and adsorption densities for the mixed collector system (SIBX:DBD = 1:1) on the three copper minerals at collector concentration 3×10^{-5} M at pH 8. Figure 21a–c indicates a significant decrease in the zeta potential values at the total collector concentration (3×10^{-5} M); at the same concentration, the floatability of the Cu-minerals increased. The adsorption of DBD is approximately constant above collector concentration 3×10^{-5} M. Xanthate adsorption is less pronounced at this concentration. Thus, a good correlation is observed among all the pure mineral results on all the three copper minerals.

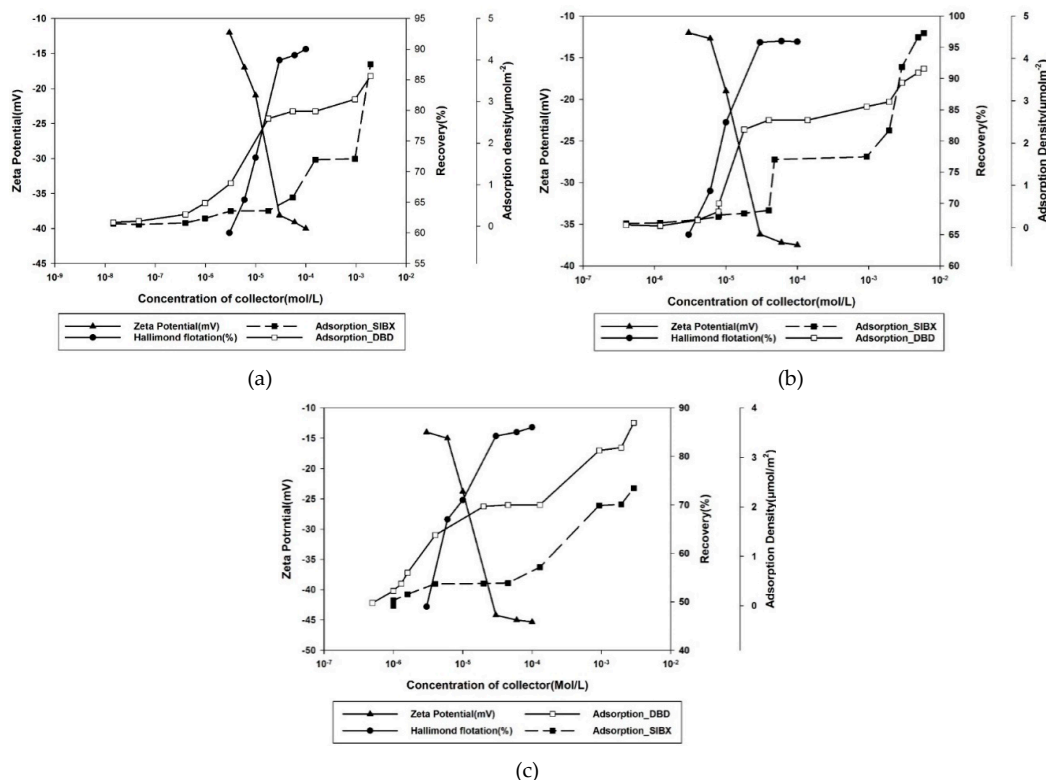


Figure 21. The correlation between the Hallimond flotation recovery, zeta potential results and adsorption densities for (a) chalcopyrite, (b) chalcocite, and (c) bornite at a total collector concentration 3×10^{-5} M (SIBX:DBD ratio 1:1) at natural pH.

3.7. Bench Scale Flotation

The natural ore flotation was carried out using DBD as the collector and MIBC as frother as a function of pH. Lime or any other additive was not employed in the current study because the ore does not contain iron sulphide gangue minerals. The feasibility of copper sulphide flotation with the collector DBD and mixtures of DBD and SIBX for the coarse grind samples ($-105 \mu\text{m}$) were tested and are reported in this study. As per the mineralogical studies, the copper sulphides are liberated ($>80\%$) in this size range; the major middlings' percentage are copper sulphide-copper sulphide associations.

The results are presented in Table 2. At pH 4, recovery is considerable and close to 90% with a total concentrate grade of 17%. In the alkaline region, at pH 12, the grade is low, approximately 10.7%, but the recovery is above 90%. At natural pH (pH 8), the recovery is maximum, approximately 95% with a concentrate grade of 19.4%. The flotation response of Nussir ore with SIBX as a reagent produced a highest concentration grade of 14% [19], Thus, the copper concentrate grade is significantly improved by using DBD as a collector due to the high selectivity of the collector towards copper minerals. The results are consistent with the pure mineral studies. Table 3 represents the recovery and grade results for the mixed collector systems at natural pH. The table indicates that all results of the collector combinations are better as compared to a single collector system. Thus, the results are in agreement with the previous findings in the literature [35], understandably due to the synergistic action of reagents which leads to higher flotation of copper sulphides. Overall, the best results were obtained for SIBX:DBD = 1:3 at natural pH, which showed a recovery of 96.3% with a concentrate grade of 24.7%. The results can be correlated with the pure mineral studies. It was observed in the microscopic analysis that the ore has bornite in major quantity. Therefore, the mixture with DBD at a higher proportion in the reagent mixture is the best suited reagent scheme proposed for this ore.

The reagent mixture, with total concentration $3 \times 10^{-5} \text{ M}$, produced the best grades and recoveries. Thus, the reagent concentration can be reduced by using the mixed collector system with improved metallurgical results.

Table 2. The grade and Recovery results with respect to varying pH at collector concentration $5 \times 10^{-5} \text{ M}$. Feed grades 2.2%–2.5%.

Samples Conc/Tail	pH	Copper Grade (%)	Copper Recovery
Conc_1	4	34	86.7
Conc_2		1.3	3.3
Tail		0.2	9.4
Head Bal.		17.4	90.0
Total Mass Bal.			99.4
Conc_1	6	42.6	93.3
Conc_2		1.1	2.0
Tail		0.1	4.5
Head Bal.		19.4	95.3
Total Mass Bal.			99.8
Conc_1	8	32.2	92.8
Conc_2		0.9	1.8
Tail		0.1	4.72
Head Bal.		19.4	94.6
Total Mass Bal.			99.3
Conc_1	12	46	83.1
Conc_2		1.1	7.3
Tail		0.1	8.6
Head Bal.		10.7	90.4
Total Mass Bal.			99.0

Bal., Balance.

Table 3. The grade and Recovery results with respect to varying collector concentration. Feed grades 2.2%–2.5%.

Samples Conc/Tail	Collector Conc.	Copper Grade (%)	Copper Recovery
Conc_1		42.8	93.4
Conc_2		1.05	2.41
Tail	2×10^{-5} M(D)	0.1	3.3
Head Bal.	1×10^{-5} M(S)	21.4	95.8
Total Mass Bal.			99.2
Conc_1		30.1	90.4
Conc_2		2.21	3.95
Tail	1×10^{-5} M(D)	0.1	4.7
Head Bal.	2×10^{-5} M(S)	19.6	94.4
Total Mass Bal.			99.1
Conc_1		47.3	93.5
Conc_2		1.5	3.01
Tail	2.25×10^{-5} M(D)	0.07	3.01
Head Bal.	0.75×10^{-5} M(S)	24.7	96.3
Total Mass Bal.			99.4
Conc_1		27.9	94.8
Conc_2		2.1	1.91
Tail	0.75×10^{-5} M(D)	0.1	4.42
Head Bal.	2.25×10^{-5} M(S)	22.3	96.6
Total Mass Bal.			99.3

D, DBD; S, SIBX; Bal., Balance.

4. Conclusions

The copper mineralogy of Nussir copper ore primarily comprises chalcopyrite, chalcocite and bornite. Microscopic analyses showed the copper sulphides are more than 80% liberated in the –105 μm size fraction samples. It was also revealed that approximately 10%–17% of copper sulphides are associated with each other or other gangue minerals and that these mineral mixtures were difficult to float with xanthate collectors. Therefore, an attempt was made to employ a dithiophosphate collector (DBD) and a mixture of DBD-SIBX collectors to float these copper minerals from the ore.

The zeta potential studies of copper minerals after interaction with DBD showed that the mineral surfaces acquired a comparatively more negative charge due to the chemical adsorption of the collector on the surface, chiefly on the Cu-sites. In the case of chalcopyrite, chalcocite and bornite, the zeta potential values significantly decrease with a higher proportion of DBD in the reagent mixture. Another important observation was that at alkaline pH values, the zeta potential values of copper minerals were less influenced by increases in the collector concentration; this is due to the prevalence of metal hydroxide, which diminishes the adsorption of collector on the copper minerals.

Single mineral flotation results indicate a low recovery of all the three copper minerals at pH 4 while the best recovery was found in the pH range 6 to 10 and the recovery decreases marginally at very alkaline pH (>10). The recovery of chalcopyrite was consistently higher until pH 10, which decreases insignificantly beyond this pH value. However, the flotation response of gangue minerals (calcite and quartz) are negligible at natural pH. Based on data from the pure mineral studies, it can be stated that the copper sulphides can be floated in the natural pH region at a DBD concentration of 5×10^{-5} M. When xanthate and dithiophosphate mixtures were employed as collectors, the recovery was always higher than a single collector system. The highest recoveries of all the three copper minerals were observed for SIBX:DBD at 1:2, when the proportion of DBD was greater in the mixture.

The FTIR spectral studies indicated that the interaction of dithiophosphate on copper sulphides was due to chemical reactions. The adsorption results obtained with chalcopyrite, chalcocite and bornite indicate the surface species formed to be Cu-(DBD). The spectra of copper sulphides

conditioned with a mixed collector (1:1) show both the xanthate and dithiophosphate characteristic bands on the three copper minerals. However, strong peaks of the more selective collector DBD are observed on the chalcopyrite and chalcocite spectra, while strong peaks of SIBX are observed on the bornite spectrum. The quantitative adsorption results showed that DBD was adsorbed on the chalcopyrite and bornite surface at far lower concentrations (1×10^{-6} M), whereas the onset of adsorption on chalcocite was at a relatively higher concentration (1×10^{-5} M). All the three isotherms depict less than monolayer coverage; however, a higher concentration of collector was required for bornite to achieve saturation. The adsorption of the mixture of dithiophosphate and xanthate in the ratio 1:1 on the three copper sulphides indicated that DBD adsorbs preferentially on chalcopyrite and chalcocite surfaces, whereas SIBX adsorbs preferentially on the bornite. The results were substantiated by the area under the alkyl chain region and the intensity of characteristic peaks of DBD and SIBX in the FTIR spectra. Thus, it is clear from these results that the more selective collector adsorbs first on the copper mineral surface followed by the less selective collector.

The bench scale flotation results of a Nussir ore sample with a DBD collector indicated that at natural pH and collector concentration 5×10^{-5} M, the optimum cumulative concentrate grade obtained was 19.6% copper with a recovery of 94.9%. The bench scale flotation with a mixed collector scheme showed the synergistic action of the collectors and the grade is improved for the various proportions of collector mixture at lower total collector concentration. A higher proportion of DBD in the collector blend resulted in a higher cumulative recovery (96%) and grade (24.7%) of copper. The pure mineral studies are consistent with the bench scale flotation results. In summary, the copper minerals in the Nussir deposit could be exploited with better metallurgical results using dithiophosphates and xanthate collector mixtures.

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