

Flotation of Low-Grade Graphite Ore Using Collector Derived from Low-Density Polyethylene Waste



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1 Introduction

Polymorphs of carbon ranges from soft, blackish graphite to hard, transparent diamond. From the early fifteenth century itself graphite was widely used as it shows the properties of both metal and non-metal, has an extraordinarily low specific gravity, incredibly soft and cleaving with noticeably light pressure, exceptionally heat resistant and inert when in contact with other materials. That is why it is called as a “Mineral of Extremes” [1]. Crystalline forms of natural graphite have small flake size and as metamorphic grade increases it leads to microcrystalline forms. These flake graphites are graded based on the graphitic carbon content and flake size. Hexagonal crystal structure is the thermodynamically stable form of graphite which results in tremendous properties. The properties of graphite vary from place to place as the geography of the mined area play a crucial role in metamorphism.

Among various beneficiation techniques, froth flotation is more suitable for treating fines and naturally hydrophobic ores. Flotation is a surface phenomenon based on the surface hydrophobicity of the mineral surfaced to be separated [2–4]. Due to the natural hydrophobicity of graphite, this technique is adopted for beneficiation. The hydrophobic mineral particles which are attached to air bubbles floats on top as froth and is separated, while the remaining hydrophilic gangue particles that attach with water molecules stay in liquid [2–6]. Nanobubbles can be produced by ultrasonication, but this doesn’t have any effects on the floatation performance of graphite [7]. Ultrasonic-assisted flotation has effects on floatability which enhances the recovery flaky graphite from low-grade graphite ore [8]. The particle size has

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213

crucial roles in the overall multi-stage grinding-regrinding-flotation steps [9]. Selective adsorption of particular reagents on the mineral surface depends on the particle size of the mineral present in the pulp [10]. Controlled grinding is very important to achieve ideal cost-effective separation [11]. Surface chemistry can be affected by flotation. The purity of single graphite particles, on the other hand, is rarely compromised. Flotation reagents, viz., collectors, frothers, etc., are added to transform the mineral–water mixture suitable for flotation by controlling the relative hydrophobicity of particles and maintain froth characteristics [12]. These chemicals have critical role and importance in the entire process as they involve complex interactions. Graphite has natural affinity towards air bubbles. The chemical reagents commonly used in graphite flotation increase the selective hydrophobicity and a variety of non-polar hydrocarbon-based oils such as kerosene, diesel, and fuel oil are generally used collectors in combination with frothers such as pine oil, Methyl Isobutyl Carbinol (MIBC) or higher alcohol [13–15]. A jump-in phenomena exist between non-polar collectors and the hydrophobic surface, indicating the existence of an attractive force. Polar collectors form hydrogen bonding with water results in a weaker adhesive force. Jump-in distance, jump-out distance, friction force, and adhesion force are greater and play crucial role in the interaction of collectors with graphite surface [16]. Diesel oil as collector and MIBC as frother was found to yield best results in graphite flotation comparing other hydrocarbon oils like dodecane, kerosene, pine oil, iso octonal in terms of total carbon content and total carbon recovery of the rougher concentrate of graphite [13, 17]. In graphite flotation, the selectivity index between collector and graphite increases as the average droplet size of collector emulsions (e.g., Kerosene) lowers [18]. Conventional reagents are not economic when used in industrial scale due to the continuous price escalation of fuel oils.

Synthetic plastic, the world's most used polymer, whose disposal poses the utmost threat to environment as it is not readily bio-degradable and uses non-renewable resources as key ingredient in manufacturing of plastics. Around 12.7 tonnes per year of plastic waste is produced around the world which pollutes the entire ecosystem.

The present work evaluates the flotation performance efficacy of the oil (collector PE) derived using LDPE, i.e., low-density polyethylene waste as collector in combination with MIBC as frother and compares with the conventional reagent combination of diesel and MIBC for flotation of low-grade graphite ore (run-of-mine) from Tamil Nadu.

2 Material and Methods

A low-grade graphite ore (run-of-mine, R.O.M) from Tamil Nadu, India, was utilized in this study for recovery of graphite by flotation. The R.O.M graphite ore was size reduced in stages in a laboratory jaw crusher and a representative sample was drawn by riffle sampling. The preliminary laboratory scale tests for optimization of process parameters such as mesh-of-grind (grinding time), collector and frother dosages to recover graphite with reduced ash content were conducted.

2.1 Flotation Methodology

The flotation experiments were carried out in Denver D-12 laboratory flotation machine, at natural pH of the slurry (about 7) and impeller speed of 1240 rpm. The graphite slurry was conditioned with the reagents for 3 min each and the froth (float) was collected till froth formation ceased. The collected froth and tailings were dewatered, dried, weighed, and subjected to ash analysis. During the cleaning stages, no reagents were added and the froth from roughing stage was collected and subjected to cleaner flotation.

2.2 Flotation Reagents

Commercially available diesel, MIBC (LR grade), collector PE (oil-derived LDPE waste) were used as reagents in graphite flotation.

3 Results and Discussion

3.1 Proximate Analysis of Graphite Ore

The proximate analysis of R.O.M graphite ore was carried out to determine the (1) moisture, (2) volatile matter, consisting of gases and vapors driven off during pyrolysis, (3) fixed carbon, the non-volatile fraction of graphite, and (4) ash, the inorganic residue left over after combustion. The results are shown in Table 1, and it can be observed that ore is containing high ash content of 84.71% and fixed carbon content of 9.07% representing that the ore is of very low grade.

Table 1 Proximate analysis of graphite ore

Analysis	Value, %
Moisture	0.09
Volatile matter	6.13
Ash	84.71
Fixed Carbon	9.07

3.2 Characterization of Graphite Ore for Mineralogy and Morphology

The graphite ore was characterized by X-Ray Diffraction (XRD) shown in Fig. 1 for the identification of mineral phases of graphite and associated inorganic gangue minerals using copper-K α radiation with 1.54 Å wavelength are done using D2-Phaser of Bruker. The XRD results indicate the presence of graphite, quartz, pyrite, muscovite, and kaolinite mineral phases. Graphite has a distinct peak at $2\theta = 26.69^\circ$ in the X-ray Diffraction pattern and a minor peak at $2\theta = 40.42^\circ$ indicates 100 and 110 planes, respectively, for the graphite phases. The high intensity peaks of Quartz and the presence of clay mineral (Kaolinite) and mica mineral (Muscovite) indicate the high ash content of the graphite ore sample.

Scanning electron microscopy (SEM) was carried out using JCM-6000Plus in order to visualize the morphology of graphite ore sample as well as the concentrate which is separated from the gangue through flotation. The results in Fig. 2 show the clear difference of the sample's surface morphology. The SEM images in Fig. 2a show micro-scale graphite with thick flake size and layers, as well as partial porosity spots in the sample. The presence of minor associated gangue minerals is indicated by the different shades of light in mineral surface. However, in Fig. 2b of the graphite sample, the graphite concentrate shows minimized gangues resulting in exfoliated morphology formed after the removal of impurities like quartz and silica in the separation process that intrinsically intercalate graphite. Figure 2c shows the non-float of graphite which is the separated impurities.

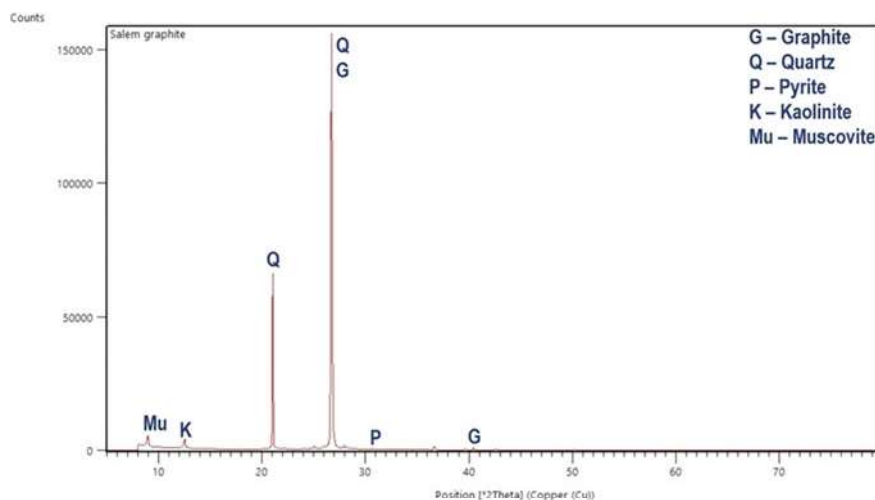
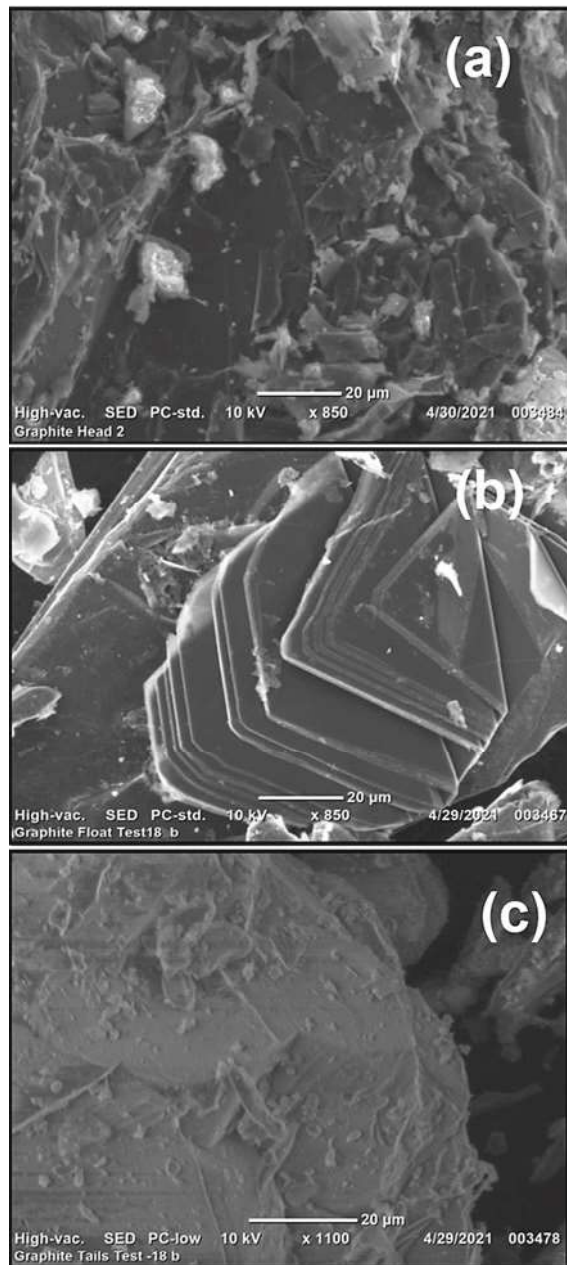


Fig. 1 X-ray diffractogram of graphite ore

Fig. 2 SEM images of **a** Graphite ore **b** concentrate **c** tailings



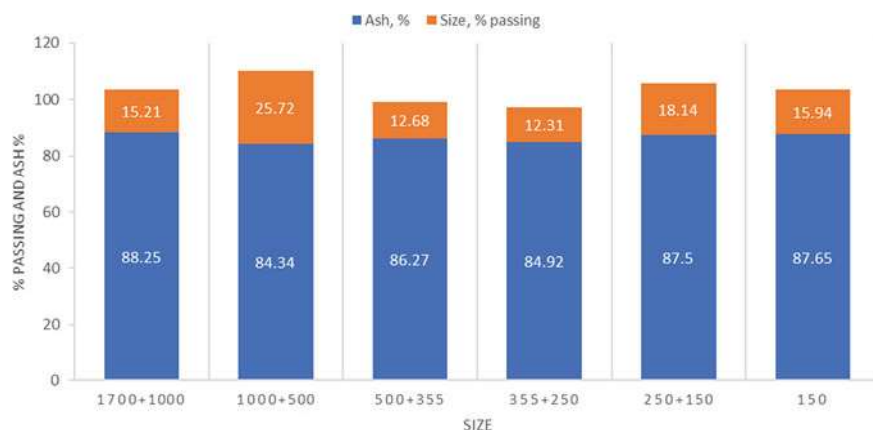


Fig. 3 Size distribution analysis of graphite ore

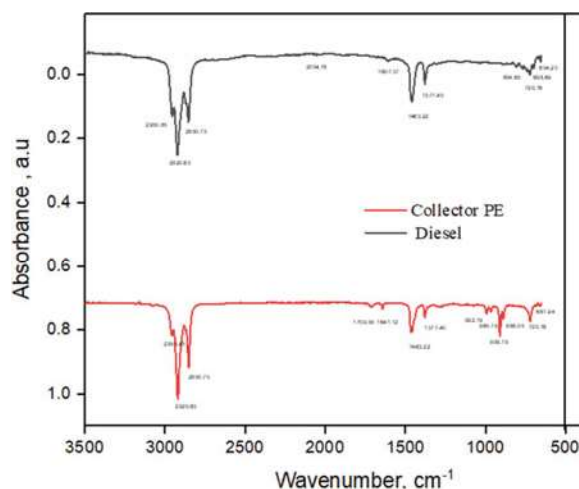
3.3 Size Distribution of Graphite Feed to Flotation

The particle size distribution of the -1.7 mm crushed graphite ore was carried out using a set of BSS screen/sieves with the top screen as $1700\ \mu\text{m}$ and the bottom sieve as $150\ \mu\text{m}$. The size distribution and the ash content in each size range are shown in Fig. 3. From the size analysis, 80% of the material (d_{80}) passes through $862.54\ \mu\text{m}$. This material is taken as feed to flotation at coarse size fraction study. The size distribution indicated that $-1000 + 500\ \mu\text{m}$ fraction is 25.72% by weight while rest of the fractions are found to be less than 20%. The size-wise ash analysis reveals that ash content of each size fraction is ranging from 84.34% to 88.25%. From the ash distribution, it is observed that the $-1000 + 500\ \mu\text{m}$ size fraction contributes to higher ash % among other size fractions. This size-wise ash distribution shows that liberation of graphite values from its associated gangue/ash has not occurred to a considerable level and hence this 100% passing $1700\ \mu\text{m}$ sized sample can be used directly as feed to flotation. So further grinding has to be adopted to attain better liberation thereby for better separation efficiency in flotation.

3.4 FTIR Analysis

The Fourier Transform Infrared Spectroscopy of the graphite ore sample was done using Bruker Alpha II Spectrometer. From the FTIR analysis of collector PE, two strong peaks at $2920\ \text{cm}^{-1}$ and $2850\ \text{cm}^{-1}$ are due to symmetric and asymmetric C-H stretching in CH_2 and CH_3 groups, typical of aliphatic carbons. The well-defined peaks at $1463\ \text{cm}^{-1}$ and $1377\ \text{cm}^{-1}$ are due to symmetric and asymmetric deformation vibrations experienced in C-H bond, i.e., C-H bending in C-H_2 and C-H_3 groups.

Fig. 4 FTIR Analysis of Collector PE and diesel



Peak at 908 cm^{-1} can be attributed to out-of-plane bending vibrations of C-H bonds. Another peak at 720 cm^{-1} can be attributed to C-H₂ rocking vibrations.

Diesel oil is a long alkane hydrocarbon chain which shows characteristic peaks at 2920 cm^{-1} and 2850 cm^{-1} due to symmetric and asymmetric C-H vibrations in CH₂ and CH₃ groups. Presence of alkyl group can be confirmed by bands at 1463.60 cm^{-1} and 1377 cm^{-1} corresponding to C-H bending vibrations. Peak at 720 cm^{-1} corresponds to the CH₂ rocking vibrations which are the characteristic feature of long-chain hydrocarbons. PE collector has similar peaks that of diesel oil resembling a mere long chain hydrocarbon (Fig. 4).

From the above observations, we can confirm that the collector PE is a long chain hydrocarbon which has similar backbone as that of the typical diesel oil. However, despite the fact that PE oil and diesel oil are synthesized from different sources, they still have some functional groups in common. The result obtained herein implies that both collectors are similar in terms of qualities and features. Hence, collector PE remains the best alternative for diesel oil in flotation.

3.5 Flotation Studies of Graphite Ore

3.5.1 Optimization of Grinding Time

Optimization of grinding time was carried out by grinding R.O.M graphite ore at different time intervals of 5, 10, 15, 20, and 25 min while maintaining a constant pulp density of 64.5% solids by weight. The ground product is then followed by flotation maintaining a constant collector (diesel) dosage of 0.56 kg/t and frother (MIBC) dosage of 0.07 kg/t. Results are depicted in Fig. 5.

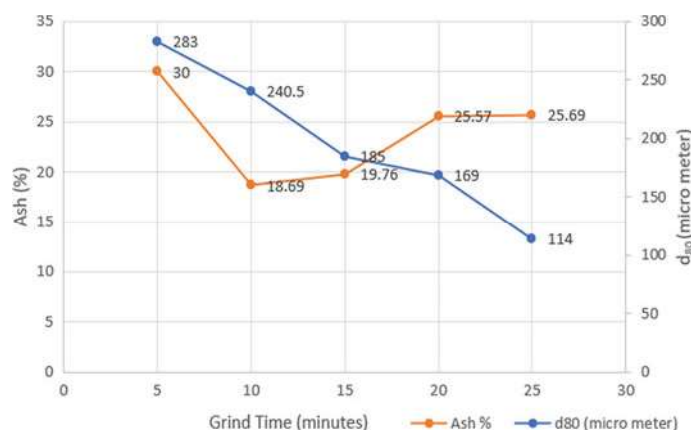


Fig. 5 Effect of grinding time and d_{80} size on ash content of concentrate

It is evident from the graph that the lowest ash value (18.69%) can be observed at 10 min grind time (d_{80} : 240.5 μm). The experiment results show that a float with 30% ash at 5 min of grinding time was obtained. This could be due to lack of liberation at relatively coarser size. The graphite used in this study was of low grade (with 84.71% ash content) and was found to be associated with the gangue minerals such as quartz. Also, the increase in ash % with increase in grinding time that was observed could be attributed to generation of more fines. Hence, grinding is one of the critical factors in liberation of values. Controlled grinding is very important to achieve ideal cost-effective separation [11]. Entrainment of gangue minerals depends closely on size of the particle [19]. The efficiency of flotation process depends mainly on the liberation and surface hydrophobicity of the values to be floated.

3.5.2 Optimization of Collector (Diesel) Dosage

The diesel collector dosage was optimized by carrying out flotation tests by varying collector dosages of 0.42, 0.56, 0.70, 0.85, 0.99 to 1.13 kg/t while maintaining a constant frother dosage (0.075 kg/t) and grind time of 10 min.

Figure 6 shows that at higher dose of collector (diesel) dilutes the grade of the concentrate with high ash content indicating the low selectivity of diesel at higher dosages. Lowest ash value (17.71%) with 15.23% recovery at 0.85 kg/t of collector was observed. This demonstrates that a collector dosage of 0.85 kg/t resulted in optimal selectivity of graphite particles in float and maximum rejection of gangue in non-float as rejects leading to an effective separation.

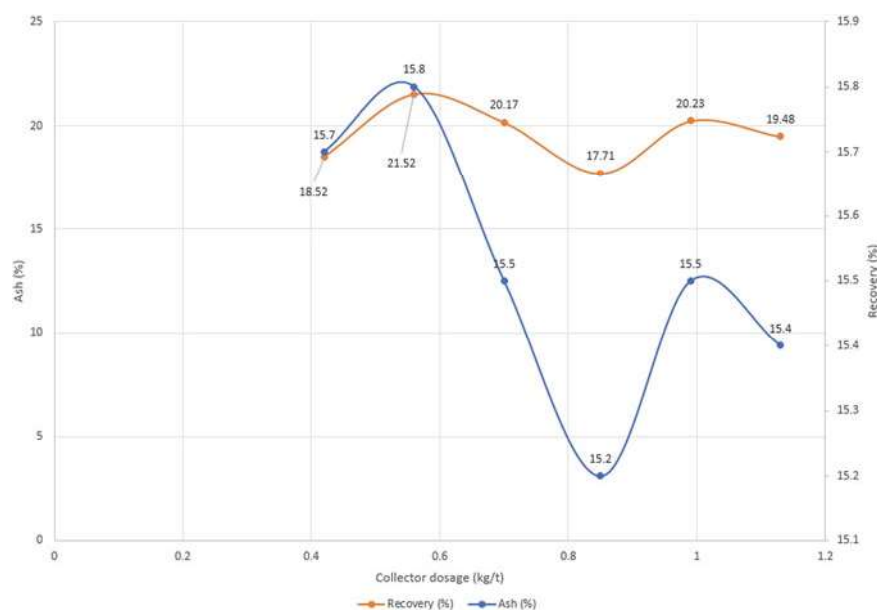


Fig. 6 Effect of Collector (diesel) on yield% and ash%

3.5.3 Optimization of Frother (MIBC) Dosage

The collector dosage was kept constant at 0.85 kg/t, and flotation tests were carried by varying frother dosages of 0.07, 0.11, 0.15, 0.19 kg/t. From the graph, it can be concluded that the lowest ash value of 17.71% was achieved with a recovery of 15.23% in concentrate (rougher concentrate) when 0.85 kg/t of diesel as collector with 0.07 kg/t of MIBC as frother was used. It also shows that high dosages of frother couldn't decrease the ash percentage but increased. The froth produced becomes more stable at higher froth dosages which carrying of gangue particles into float leading to high ash percentages in float. As the ash content was observed to be high, further cleaning of the rougher concentrate was carried out. After two-stage cleaning, a final concentrate was obtained with 12.66% weight recovery with 8.70% ash content (Fig. 7).

3.5.4 Optimization of Collector (Collector PE) Dosage

Collector PE dosage was optimized by varying the dosage (0.42, 0.57, 0.7, 0.85, 1.13 kg/t) and maintaining a constant frother dosage of 0.07 kg/t. Three stage cleanings were done to improve the grade of the concentrate. It can be observed from the graph that the lowest ash value of 8.9% with the highest recovery of 13.04% was achieved when treated with 0.57 kg/t of collector PE and 0.07 kg/t of MIBC (Fig. 8).

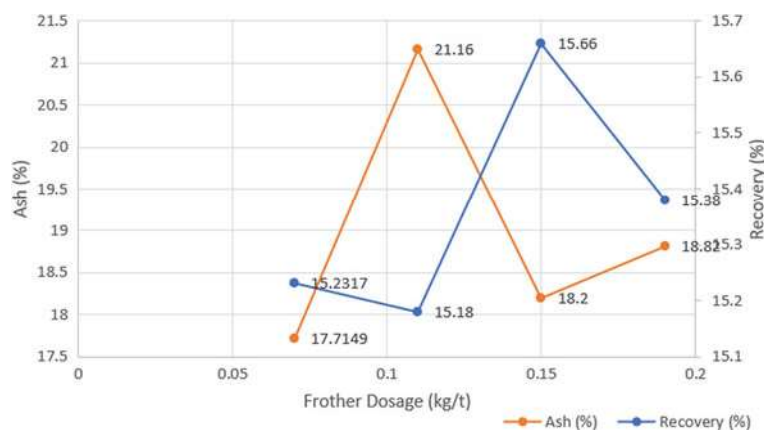


Fig. 7 Effect of Frother (MIBC) on yield% and ash%

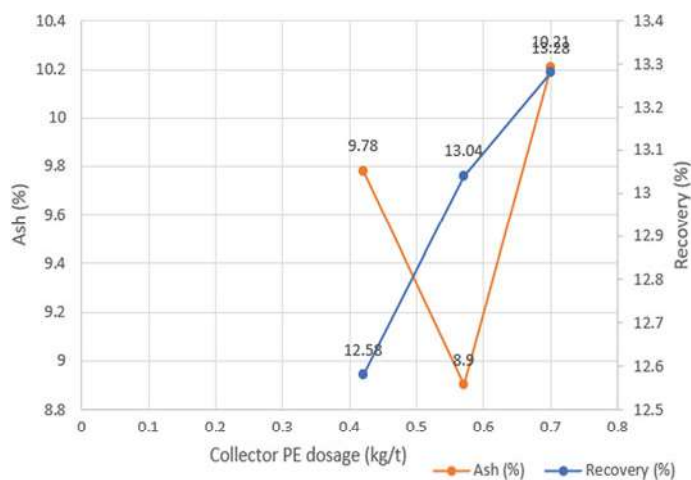


Fig. 8 Effect of Collector PE on yield% and ash%

3.5.5 Optimization of Frother (MIBC) Dosage

At fixed collector PE dosage (0.57 kg/t), MIBC frother dosage was optimized by varying dosage of 0.03, 0.07, 0.11 kg/t. It can be concluded from the graph that a yield of 13.04% with 8.90% ash was achieved with two-stage cleaning, when treated with 0.57 kg/t of collector PE and 0.07 kg/t of MIBC (Fig. 9).

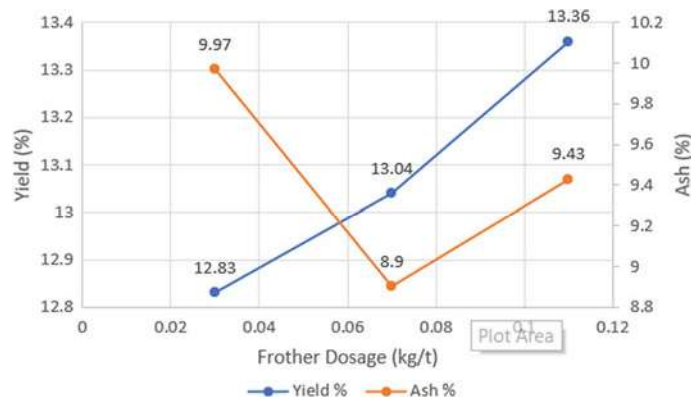


Fig. 9 Effect of Frother (MIBC) on yield% and ash%

4 Conclusion

The flotation studies of low-grade graphite carried out using the newly derived collector PE from the LDPE wastes and diesel indicates that the flotation efficiency of the collector PE is comparable with that of diesel and would be economical when used in large-scale industrial graphite flotation as the consumption amount of collector PE is also less than that of diesel. This would pave way for effective waste utilization of LDPE wastes and also to reduce the operational costs due to rapid cost escalation of diesel proving beneficial for graphite processing industries.

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