International Journal of Mineral Processing and Extractive Metallurgy
2025, Vol. 10, No. 2, pp. 38-48
https://doi.org/10.11648/j.ijmpem.20251002.11

Research Article

Eco-Friendly Collectors for Graphite Flotation: Performance Evaluation of *Elaeis guineensis* (Palm) Oil and *Arachis Hypogaea* (Groundnut) Oil

Babatola Osasona*, Fatai Olufemi Aramide, Oyelola Oladunni Alabi

Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure, Nigeria

Abstract

The increasing global demand for natural flake graphite, driven by its applications in green technology and the potential of graphene, offers a significant opportunity for Nigeria to effectively utilize its graphite resources. However, prioritizing sustainability in mineral processing is essential. The conventional collector, kerosene, is imported and non-biodegradable, presenting both economic and environmental challenges. This research aims to develop a sustainable graphite beneficiation process by exploring the use of locally sourced natural oils as alternative froth flotation collectors, focusing on Ningi graphite Run-of-Mine (R.O.M.) as a case study. The purity of the concentrate and processing efficiency were assessed using graphite burn-off assays and Energy Dispersive X-ray Fluorescence (EDXRF) analysis. The innovative eco-friendly froth flotation method achieved a graphite recovery rate of 82.40% using biodegradable oils, specifically *Elaeis guineensis* (palm) oil and *Arachis hypogaea* (groundnut) oil. This process resulted in a remarkable improvement in graphite purity—approximately 67-fold—while effectively reducing contamination from metal oxides. Additionally, this technique successfully separated graphite concentrate from non-combustible inorganic impurities, yielding a froth concentrate of 33.0% and achieving an impressive ash removal rate of 73.43%. This methodology addresses the economic and environmental concerns of traditional collectors while enhancing graphite purity. Further research is essential to optimize this novel approach.

Keywords

Graphite Mineral, Sustainable Froth Flotation, Bio-degradable Collectors, *Arachis Hypogaea* (Groundnut) Oil, *Elaeis Guineensis* (Palm) Oil, Comparative Beneficiation

1. Introduction

Graphite is the most common polymorph of naturally occurring crystalline carbon and is a fascinating mineral. Its unique properties, numerous industrial applications, increasing global demand, and potential value in Lithium-Ion Batteries, along with the scientific possibilities of graphene, highlight its significance for future engineering and economic development [1-3]. In Nigeria, graphite ore is found in several states; however, the total estimated reserves of these mineral deposits remain only partially investigated, resulting in inconclusive data. Nonetheless, some grades and characteristics have been empirically established [4-8].

Naturally occurring graphite has a wide range of purities de-

*Corresponding author: tolaosasona@gmail.com (Babatola Osasona)

Received: 9 July 2025; **Accepted:** 28 July 2025; **Published:** 21 August 2025

pending on its geological occurrence [9]. For graphite minerals to be commercially viable, the R.O.M. material must be concentrated to enhance its value per unit weight, without exceeding the importer's production cost [10, 11]. This processing should also minimize environmental impact while ensuring inter-generational equity [12]. Empirical studies demonstrate that the froth flotation technique is the most effective method for the beneficiation of graphite [13]. This technique is both industrially adaptable and cost-effective, utilizing the surface physicochemical properties of hydrophobic particles [9]. Given that graphite is inherently hydrophobic, it exhibits buoyancy when in contact with moist air bubbles. The efficacy of this process is further improved through the addition of specific reagents [13]. Consequently, the availability and pricing of intermediate froth flotation chemicals play a significant role in determining the overall cost of processing [14].

Graphite flotation is significantly influenced by the chemistry of the pulp, and its optimization relies on the presence of specific reagents which are environmentally unfriendly [9, 15]. Research indicates that kerosene, which is non-ionic and not biodegradable, serves as the most effective collector. Additionally, sodium metasilicate ($NaSi_3O_7$) has demonstrated exceptional efficacy as depressant, particularly with silicate minerals. Sodium carbonate (Na_2CO_3) is frequently employed as a potential of Hydrogen (pH) regulator, while methyl isobutyl carbinol (MIBC), pine oil, and polyglycolic ethers represent the most commonly used frothers in the flotation of graphite [16-18].

Vegetable oils are recognized as effective alternative fluids with industrial applications [19]. Oils such as palm oil, olive oil, cottonseed oil, groundnut oil, and sunflower oil are classified as oleic-linoleic acid oils, while kerosene is a non-polar, flammable fossil fuel with low biodegradability and toxic emissions. In contrast, groundnut oil and palm oil are abundant, edible, plant-based oils that are polar, biodegradable, and exhibit low ecotoxicity, making them eco-friendly alternatives for flotation. Additionally, kerosene, groundnut oil, and palm oil function as water-insoluble lubricants with similar density ranges [19-22].

Graphite has been recognized as a critical material in global mineral trade [23], and the devaluation of the Nigerian currency in 2023 has presented significant challenges, particularly for the mineral processing sector that relies heavily on foreign inputs. This economic situation has led to a decline in production, with a fall in capacity utilization [24]. In response to these challenges, this study seeks to enhance the economic competitiveness and environmental sustainability of the graphite beneficiation process for Ningi deposit as a case. The research will examine the efficacy of some locally abundant and biodegradable oils as potential substitutes for imported hydrocarbon froth flotation collectors. The anticipated outcomes of this investigation may reduce reliance on imported inputs, conserve foreign exchange, and promote environmental stewardship. Furthermore, this research may create opportunities for maximizing the utilization of productive factors, in alignment with classical trade theories of comparative advantage [11, 25]. To achieve these objectives, a comparative flotation study will be conducted using a specifically selected combination of frothers and collectors.

2. Experimental Details

2.1. Flake Graphite Sample

The material utilized for this experiment is the harmonized representative R.O.M. graphite extracted from the Ningi deposit, located in North-Eastern Nigeria. The samples are procured in lump form, prepared by pulverizing and drawn for analysis using Sampler (Jones Riffle). The specific properties of the unrefined crude ore and the experimental feed are comprehensively detailed in Tables 1 and 4, respectively. The unrefined Ningi R.O.M. graphite sample is categorized as low-grade in its raw state, primarily due to its elevated ash content (88.51 wt.%) and volatile matter content (8.32 wt.%). Notwithstanding these factors, the sample exhibits a favorable flake size distribution ranging from 10 µm to 350 µm, as observed through an optical microscope (LEICA DMEX). This distribution is characterized by fine granularity and weak interlocking within a quartz-silicate matrix, suggesting a potential for concentration via comminution. Therefore, substantial beneficiation will be required to render this graphite suitable for industrial applications [26].

Table 1. *Physicochemical Characterization of unrefined Ningi Graphite R.O.M.*

Graphite Sample	Fixed Carbon, %	Ash Content, %	Volatile Matter, %	Flake Size range, µm
Unrefined Ningi Graphite (R.O.M)	0.4	88.51	8.32	10-350

2.2. Size Analysis for Experimental Feed

The effective liberation size of Ningi graphite was assessed to be 63 µm. The crude Ningi R.O.M. sample was prepared in accordance with the ASTM (American Society for Testing and Materials) D3172-13 testing specification and subjected to a vertically vibrated automatic sieve shaker (Pascal Engineering) [27]. An analysis was conducted on the percentage by weight retained on each successive sieve screen, with the corresponding values for fixed carbon content presented in Table 2.

Table 2. Liberation size analysis of Ningi graphite Ore.

Nominal Sieve Size, µm	Fixed Carbon, %	Ash Content, %	Moisture content, %	Volatile Matter, %	Calorific Value, MJ/Kg
710	0.17	89.02	2. 51	8.29	0.102
500	1.01	88.49	2.81	7.69	0.606
355	0.75	88.43	2.61	8.21	0.450
250	0.16	89.07	3.32	7.45	0.096
180	1.26	88.02	2.52	8.20	0.757
125	1.01	88.11	2.77	8.11	0.606
90	1.32	88.71	2.81	8.14	0.793
63	1.92	87.50	2.72	7.86	1.153
<63 (Pan)	1.27	87.92	3.67	7.14	0.763

2.3. Mineral Concentration Test

The graphite samples were prepared to the specified economic liberation size of 63 µm for direct froth flotation using a Jaw Crusher (Fritsch pulverisette FAM8034-AK33), and Batch ball mill (Denver 12 by 5 inches) employing the same methodology utilized for proximate analysis. The samples were stored in a desiccator to maintain dryness. In the flotation process, analytical-grade Na_2CO_3 pellets acted as a pH controller, while powdered $NaSi_3O_7$ served as a depressant. Pine oil (*Pinus sylvestris*) and turpentine (*Pistacia terebinthus*) were used as frothers. Kerosene from Total Energies Nigeria, along with groundnut oil (*Arachis hypogaea*) and palm oil (*Elaeis guineensis*) obtained from local vendors, functioned as collectors. Laboratory-distilled water was employed, and room temperature was consistently maintained throughout the experiments.

Batch Micro flotation experiments involved the introduction of 200 grams (g) of graphite sample into a 3-liter Denver D-12 flotation cell. To achieve a slurry pulp density of 16.67%, 1000 milliliters (mL) of water was added, creating a mixture of 200 g of ore with 1000 g of water. The flotation machine was operated at a constant impeller speed of 1200 revolutions per minute (rpm). The experimental procedure followed the method outlined in Figure 1.

After an initial agitation period of 60 seconds (sec), the pulp pH was adjusted to 9 using Na_2CO_3. The slurry was then agitated for an additional 60 sec prior to the addition of 2.5 g of $NaSi_3O_7$. Following this addition, the pulp was conditioned for another 60 sec. Subsequently, 2 mL of a selected collector was introduced, with the pulp undergoing further conditioning for an additional 60 sec. Finally, 2 mL of the chosen frother was added to the pulp, followed by a conditioning period of 120 sec. Air was introduced at a rate of 6.0 liters per minute by opening the air inlet valve.

Following this step, the froth generated was skimmed for a duration of 2 minutes. It is noteworthy that a total of six flotation tests were conducted by varying the combinations of frothers and collectors, as illustrated in Table 3, while maintaining all other conditions and processes. The procedure was repeated for each selected combination of frother and collector after thoroughly cleaning the flotation chambers with distilled water and detergent between each test. Subsequent to the experiments, both the supernatant and depressed tailings were permitted to settle for 24 hours. They were then filtered, dried at a temperature of 75 ℃, weighed, and analyzed.

To evaluate the effectiveness of the various combinations of selected frothers and collectors, Ash content analyses were performed on the concentrates and tailings obtained from both conventional and eco-friendly flotation methods under optimal yield conditions. The constituents of these outputs were examined using bomb Calorimeter, and energy-dispersive X-ray fluorescence spectrometry (ED-XRFS). An empirical comparison of efficiencies was conducted utilizing the metallurgical accounting formula [28-29].

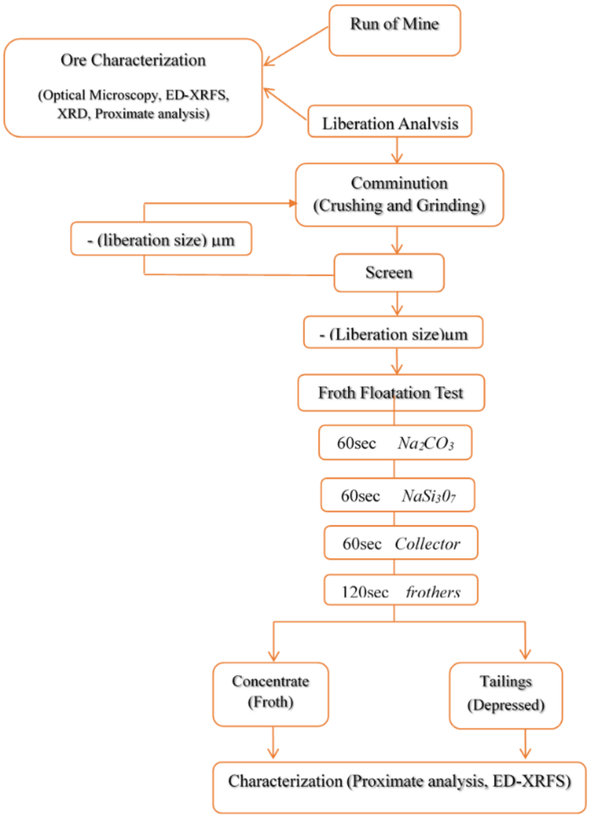

Figure 1. *Direct Froth Flotation Flowchart used in the processing of Ningi Graphite ore.*

Table 3. *Combination of selected Frothers and collectors used for the micro flotation tests.*

Frother/Collector	Kerosene	Palm-oil	Groundnut oil
Pine-oil	A	B	C
Turpentine	E	F	G

$$Ratio\ \ of\ \ concentration = \frac{mass\ \ of\ \ feed\ \ (F)}{mass\ \ of\ \ concentrate\ \ (C)} \tag{1}$$

$$Enrichment\ \ Ratio = \frac{\%\ \ graphitic\ \ carbon\ \ in\ \ concentrate\ \ (c)}{\%\ \ graphitic\ \ carbon\ \ in\ \ feed\ \ (f)} \tag{2}$$

$$Carbon\ \ recovery\ \ = \frac{\text{mass of concentrate} \times\% \text{ graphitic carbon in concentrate (Cc)}}{\text{mass of concentrate}+(\text{mass of tailing} \times\% \text{ graphitic carbon in the feed) (Ff)}} \tag{3}$$

$$\alpha = \frac{100.AF - \ \gamma.AC}{100.AF} \times 100 \tag{4}$$

Where AF is the ash content of the crude graphite ore,%, γ is the concentrate yield,%, and AC is the ash content of the concentrate,%.

2.4. ED-XRFS Measurement

The elemental composition of the samples was evaluated using an Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer (PANanalytical mini-Pal 4). The XRF analysis was conducted under an electrical configuration of 40 kV and 20 µA, utilizing a Silicon Drift Detector (SDD) to achieve high-resolution. The WinXRF software facilitated the identification and quantification of the elemental composition by analyzing the intensity of characteristic peaks.

3. Results and Discussion

3.1. Flotation Performance analysis: Conventional against Eco-Friendly

The results of the proximate analysis, conducted using a burn-off assay on flotation products, namely the froth (concentrate) and depressed (tailings), are documented in Tables 4a and 4b. Various combinations of conventional and eco-friendly collectors were utilized while maintaining consistent experimental conditions.

Table 4a demonstrates the amenability of Ningi graphite to froth flotation techniques, as indicated by the enhanced fixed carbon content of all concentrates in comparison to the fixed carbon content of the run-of-mine (R.O.M) material, as presented in Table 1. Among the six flotation systems evaluated, the conventional pine oil/kerosene system exhibited the highest purity in froth, achieving a fixed carbon content of 42.64 wt.%. Meanwhile, among the eco-friendly alternatives, the pine oil/groundnut combination yielded superior results with a fixed carbon content of 27.13 wt.%. This result is closely comparable to the fixed carbon content of the turpentine/palm oil system, which recorded 27.03 wt. %.

Table 4. *Experimental Data from Conventional Flotation and Eco-friendly Flotation: (a) Concentrates and (b) Depressed Materials/Tailings.*

(a)

EXPERIMENTAL FEED						
Sample (Frother/Collector)	Product	Fixed Carbon Content, %	Ash Content, %	Volatile Matter, %	Moisture Content, %	Calorific Value (MJ/Kg)
Pulverized, Homogenised, and Sieved (63 μm) Ningi ROM		10.8	80.46	0.90	7.84	6.65
CONVENTIONAL FLOTATION SYSTEM						
Sample (Frother/Collector)	Product	Fixed Carbon Content, %	Ash Content, %	Volatile Matter, %	Moisture Content, %	Calorific Value (MJ/Kg)
Pine oil/ Kerosene	Froth	42.64	38.80	17.35	1.21	25.61
Turpentine/ Kerosene	Froth	26.77	64.03	7.61	1.59	16.08
ECO-FRIENDLY FLOTATION SYSTEM						
Sample (Frother/Collector)	Product	Fixed Carbon, %	Ash Content, %	Volatile Matter, %	Moisture Content, %	Calorific Value, MJ/Kg
Pine oil/ Palm oil	Froth	27.13	64.78	6.70	1.39	16.29
Turpentine/ Palm oil	Froth	27.02	62.16	10.02	0.8	16.23
Pine oil/ Groundnut oil	Froth	24.69	68.30	5.70	1.31	14.83
Turpentine/ Groundnut oil	Froth	10.34	73.78	14.38	1.5	6.21

(b)

Sample (Frother/Collector)	**Product**	**Fixed Carbon Content, %**	**Ash Content, %**	**Volatile Matter, %**	**Moisture Content, %**	**Calorific Value (MJ/Kg)**
CONVENTIONAL FLOTATION SYSTEM						
Pine oil/ Kerosene	Depressed	4.62	91.67	2.30	1.40	2.77
Turpentine/ Kerosene	Depressed	2.49	91.00	5.81	0.70	1.50
ECO-FRIENDLY FLOTATION SYSTEM						
Pine oil/ Palm oil	Depressed	3.69	93.8	1.31	1.20	2.22

Sample (Frother/Collector)	Product	Fixed Carbon Content, %	Ash Content, %	Volatile Matter, %	Moisture Content, %	Calorific Value (MJ/Kg)
Turpentine/ Palm oil	Depressed	0.64	91.28	7.40	0.68	0.38
Pine oil/ Groundnut oil	Depressed	2.97	92.93	2.81	1.29	1.78
Turpentine/ Groundnut oil	Depressed	0.24	90.97	8.20	0.59	0.15

To further evaluate the performance of the various collectors utilized in the flotation process, we undertook a detailed comparison of the ash removal rates and concentrate yields. This analysis was based on the calculation results derived from equations 1 to 4, which are meticulously presented in Tables 5 and 6 and summarized in Figure 2 The conventional flotation system, which employs a combination of pine oil and kerosene, achieved a notable ash removal rate of 88.19%. This method also recorded a concentration ratio of 4.084 and an impressive recovery rate of 96.04%. However, it is important to point out that this system produced the lowest concentrate yield, measured at 24.49%. This lower yield suggests that the conventional method has a higher selectivity for valuable mineral components such as iron and silica, which may be advantageous in certain applications. In contrast, the eco-friendly combination of turpentine and palm oil demonstrated an ash removal rate of 77.03%. Additionally, it achieved a concentration ratio of 3.363 and a graphite recovery rate of 73.9%. This indicates that while it is less effective in removing ash compared to the conventional system, it still presents a viable alternative for sustainable practices in mineral processing, highlighting the trade-off between environmental considerations and operational efficiency.

Table 5. *Metallurgical account of Beneficiating Ningi graphite ore when utilizing conventional collectors in comparison to eco-friendly collectors.*

CONVENTIONAL COLLECTOR SYSTEM								
Sample	Total charge, g	Froth, g	Assay of Carbon in Froth, %	Depressed, g	Assay of Carbon in Depressed, %	Recovery, %	Enrichment ratio	Concentration Ratio
Pine oil/ Kerosene	200	48.97	42.64	151.03	4.62	96.04	3.92	4.084
Turpentine/ Kerosene	200	61.65	26.77	138.35	2.49	75.91	2.459	3.244
ECO-FRIENDLY COLLECTOR SYSTEM								
Sample	Total charge, g	Froth, g	Assay of Carbon in Froth, %	Depressed, g	Assay of Carbon in Depressed, %	Recovery, %	Enrichment ratio	Concentration Ratio
Pine oil/ Palm oil	200	66.025	27.13	133.975	3.69	82.40	2.493	3.029
Turpentine/ Palm oil	200	59.465	27.02	140.535	0.64	73.90	2.483	3.363
Pine oil/ Groundnut oil	200	63.52	24.69	136.48	2.97	72.13	2.269	3.149
Turpentine/ Groundnut oil	200	58.265	10.34	141.735	0.24	27.71	0.95	3.433

Table 6. *Flotation Performance: The Outcomes of Conventional Flotation and Environmentally Sustainable Flotation Experiments.*

	Froth/Collector	Concentrate yield/%	Ash Content of Concentrate/%	Ash Content of tailings/%	Ash removal rate/%
R.O.M	Feed		80.46		
Conventional Flotation	Pine oil/ Kerosene	24.49	38.80	91.67	88.19
	Turpentine/ Kerosene	30.83	64.03	91.00	75.44
	Pine oil/ Palm oil	33.01	64.78	93.8	73.42
	Turpentine/ Palm oil	29.73	62.16	91.28	77.03
Eco-Friendly Flotation	Pine oil/ Groundnut oil	31.76	68.30	92.93	73.03
	Turpentine/ Groundnut oil	29.13	73.78	90.97	73.28

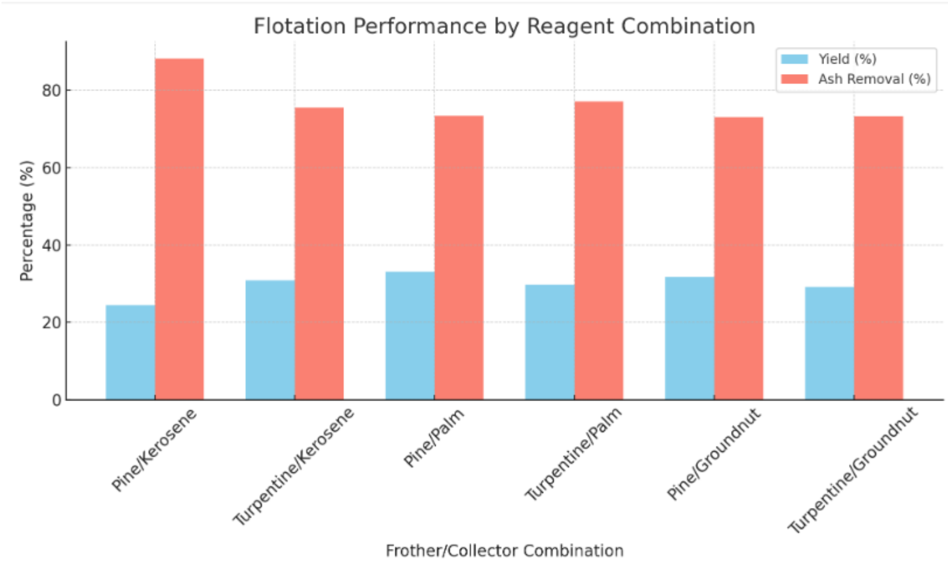

Figure 2. *The Concentrate Yield (%) and Ash Removal Rate (%) demonstrate the trade-off between recovery and purification in both conventional and environmentally friendly flotation systems.*

3.2. Elemental Composition Analysis of Flotation Feed and Products

The results of the Energy-Dispersive X-Ray Fluorescence analysis for the experiment are presented in Table 7. The feed sample (R.O.M) shows a significant concentration of silica (SiO_2: 81.5%). Additionally, the sample contains moderate amounts of potassium (K_2O: 8.47%) and iron (Fe_2O_3: 6.92%), along with trace levels of impurities such as titanium (Ti), ruthenium (Ru), vanadium (V), sulfur (S), and chromium (Cr). This composition highlights the dominance of gangue silicates and iron oxides, emphasizing the need for effective impurity rejection during flotation processes.

The elemental compositional analysis of the products (concentrates and tailings) obtained from the concentration tests conducted on Ningi graphite ore shows an overall improvement across all six evaluated frother/collector systems, although the froth did not meet the stipulated metallurgical standards in a single-stage process. Notably, the eco-friendly flotation system, which utilizes a combination of pine oil and groundnut oil, successfully reduced the weight percentage of silica in the feed ore to 63.20% in the froth concentrate, a decrease from the initial 81.50%. This reduction exceeds that achieved by the pine oil/palm oil eco-friendly flotation system, which lowered the silica content to 63.70%, and the pine oil/kerosene conventional flotation system, which reduced it to 69.60%.

Table 7. *Results of ED-XRFS analysis for Ningi Graphite products obtained through the concentration process utilizing both Conventional Collectors and Eco-Friendly Collectors.*

EXPERIMENTAL FEED										
Elemental Composition	Sample	Si, SiO_2	K, K_2O	Ti, TiO_2	Fe, Fe_2O_3	Ru, RuO_2	V, V_2O_5	S, SO_3	Ba, BaO	Cr, Cr_2O_3
	R.O.M.	81.5	8.47	1.19	6.92	0.58	0.32	0.2	0.16	0.15
CONVENTIONAL COLLECTOR SYSTEM										
Frother/Collector	Product	Si, SiO_2	K, K_2O	Ti, TiO_2	Fe, Fe_2O_3	Ru, RuO_2	V, V_2O_5	S, SO_3	Ba, BaO	Cr, Cr_2O_3
Pine oil/Kerosene	Froth	69.6	16.1	1.85	10	BDL	0.70	0.52	0.3	0.16
	Depressed	79.6	11.1	1.85	5.44	0.61	0.44	0.48	BDL	0.097
Turpentine/ Kerosene	Froth	67.9	16.4	1.86	10.5	1.31	0.72	BDL	0.38	0.18
	Depressed	83.3	9.65	1.70	3.65	0.527	0.36	0.41	BDL	0.069
ECO-FRIENDLY COLLECTOR SYSTEM										
Frother/Collector	Product	Si, SiO_2	K, K_2O	Ti, TiO_2	Fe, Fe_2O_3	Ru, RuO_2	V, V_2O_5	S, SO_3	Ba, BaO	Cr, Cr_2O_3
Pine oil/Palm oil	Froth	63.7	11.4	1.01	5.95	0.672	0.41	BDL	0.18	0.11
	Depressed	82.01	10.7	1.41	4.05	0.564	0.40	0.20	0.05	0.083
Turpentine/ Palm oil	Froth	72.6	13.9	1.79	9.36	0.87	0.637	BDL	BDL	0.15
	Depressed	71.7	8.04	1.30	3.38	0.384	0.30	0.32	BDL	0.063
Pine oil/ Groundnut oil	Froth	63.2	11.8	1.17	6.24	0.718	0.44	BDL	0.27	0.11
	Depressed	69.7	9.36	1.29	3.48	0.420	0.35	0.32	0.09	0.073
Turpentine/ Groundnut oil	Froth	71.7	15.4	1.62	8.58	1.08	0.63	BDL	BDL	0.16
	Depressed	82.9	9.69	1.63	4.11	0.4	0.37	0.40	BDL	0.071

Conventional Flotation

In the context of conventional flotation utilizing a combination of Pine Oil and Kerosene, the froth product exhibited a decreased silica content (SiO_2: 69.6%) alongside increased levels of potassium (K_2O: 16.1%) and iron (Fe_2O_3: 10%) when compared to the feed sample. Conversely, the depressed product demonstrated an elevated silica content (SiO_2: 79.6%) and a reduced iron content (Fe_2O_3: 5.44%), suggesting enhanced gangue rejection capabilities. The presence of ruthenium oxide (RuO_2) was below the detection limit in the froth but was identified in the depressed product, indicating a selectivity for heavier impurities within the tailings.

When assessing the flotation performance with a combination of Turpentine and Kerosene, it was observed that a higher concentration of impurities was carried into the froth, with increased levels of iron (Fe_2O_3: 10.5%) and ruthenium (RuO_2: 1.31%), thus indicating a less effective cleaning process. Nevertheless, the depressed product achieved a greater silica content (SiO_2: 83.3%) and a lower iron content (Fe_2O_3: 3.65%) in comparison to the Pine Oil and Kerosene combination, although it demonstrated reduced selectivity regarding titanium and chromium. Therefore, it can be concluded that the combination of Pine Oil and Kerosene exhibits superior selectivity for the removal of iron and silica in conventional flotation processes, compared to the Turpentine and Kerosene combination.

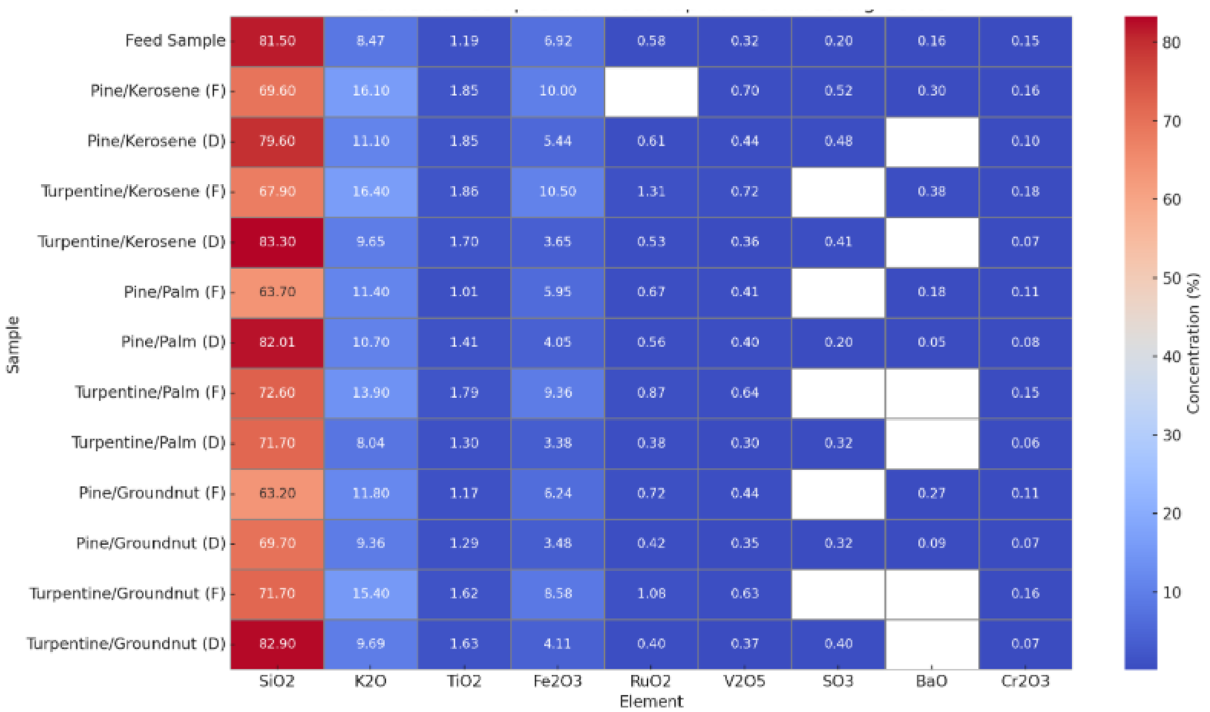

Figure 3. *The heat map delineates the elemental composition of the Ningi graphite feed sample, establishing a correlation with both the froth (F) and depressed (D) products derived from conventional and environmentally sustainable graphite flotation systems.*

Eco-Friendly Flotation

For eco-friendly collectors employing a combination of pine oil and palm oil, the froth demonstrates the lowest silicon dioxide (SiO_2) content at 63.7% and a reduced iron oxide (Fe_2O_3) concentration of 5.95%, indicating effective cleaning performance. The depressed sample exhibits a high SiO_2 concentration of 82.01% and a low Fe_2O_3 level of 4.05%, which reflects successful gangue recovery.

In a system utilizing a combination of turpentine and palm oil, the froth displays a higher Fe_2O_3 content of 9.36% and a SiO_2 concentration of 72.6%, signifying lower selectivity. Conversely, the depressed material maintains a silica concentration of 71.7% while exhibiting a lower Fe_2O_3 content of 3.38%.

Analysis of groundnut oil systems indicates that the combination of pine oil and groundnut oil yields the lowest SiO_2 content in the froth at 63.2%, thereby facilitating grade improvement. In contrast, the combination of turpentine and groundnut oil results in a higher froth Fe_2O_3 content of 8.58% and a moderate SiO_2 concentration of 71.7%, suggesting less effective separation in this instance. A comparative summary is presented in Table 8.

Table 8. *Summary of Impurity Rejection Trends.*

System	Best Froth Purity (Low SiO_2)	Best Iron Rejection (Low Fe_2O_3)	RuO_2 Selectivity
Pine/Kerosene	Yes (1st)	Yes (1st)	Yes (BDL in froth)
Pine/Palm oil	Yes (2nd)	Yes (2nd)	Yes
Pine/Groundnut oil	Yes (3rd)	Yes (1st)	Moderate
Turpentine systems	No (higher impurity in froth)	No (less selective)	Poor

The eco-friendly flotation systems utilizing Pine oil in conjunction with Groundnut oil as collector and Pine oil with Palm oil exhibit superior performance in the reduction of silica and iron concentrations within the concentrate. These systems present both environmental and economic advantages being biodegradable and locally sourced over traditional kerosene-based methods. Furthermore, the depressed tailings consistently displayed a concentration of gangue minerals, confirming the efficiency of the separation process.

4. Conclusion

The findings indicate that a comprehensive array of frother and collector combinations can effectively process the fine-grained, low-grade Ningi graphite deposit through froth flotation techniques. Kerosene, the conventional collector, has been identified as the most effective option, facilitating a substantial enhancement in the value of unrefined Ningi graphite R.O.M. by increasing its carbon purity from 0.4 wt.% to 42.64 wt.%. This results in a remarkable 100-fold increase in value in conjunction with pine oil as a frother. Additionally, the environmentally friendly application of palm oil and groundnut oil as alternative collectors presents a promising avenue for research. Notably, the highest purity levels were achieved with palm oil as the collector, resulting in a 67-fold increase in purity when utilized within both the pine oil/palm oil and turpentine/palm oil flotation systems. A comparative analysis of the flotation systems demonstrated the superiority of kerosene as a collector in the conventional pine oil/kerosene system, which exhibited an ash removal rate of 88.19%, a concentration ratio of 4.084, and a recovery rate of 96.04%. Concurrently, palm oil emerged as a more effective eco-friendly alternative than groundnut oil, providing a balanced option within the turpentine/palm oil flotation system, characterized by an ash removal rate of 77.03%, a concentration ratio of 3.363, and a graphite recovery rate of 73.9%. While the biodegradable collector systems utilizing palm oil and groundnut oil present notable environmental advantages and demonstrate effectiveness in reducing concentrations of silica and iron within Ningi graphite ore, their overall efficacy in the beneficiation of the Ningi graphite sample remains inferior to that of conventional non-biodegradable kerosene. Nevertheless, these biodegradable alternatives could be viable in scenarios where global supply chains for conventional, non-biodegradable, and imported hydrocarbon collectors are disrupted. This study concludes that pine oil is the preferred frother for the beneficiation of Ningi graphite, showcasing distinct advantages over turpentine in both conventional and environmentally sustainable flotation systems. Moreover, there is an urgent need for further research into the effects of reagent dosage, electromagnetic pretreatment, the mechanisms of adsorption (both physical and chemical), and the interactive effects of palm oil and groundnut oil on graphite ore to enhance mineral recovery rates. Furthermore, cost and economic considerations are essential for optimizing practices within the industry.

Abbreviations

ROM	Run-off-mine
EDXRFS	Energy Dispersive X-ray Flourescence Spectrometry
MIBC	Methyl Isobutyl Carbinol
ASTM D	American Society for Testing and Materials
3172-13	Standard Practice for the Proximate Analysis of Coal and Coke
rpm	Revolution Per Minute
mL	Milliliter
℃	Degree Centigrade
SDD	Silicon Drift Detector
BDL	Below Detection Level
$NaSi_3O_7$	Sodium Metasillicate
Na_2CO_3	Sodium Carbonate
MJ	Megajoules
Kg	Kilogram
µm	Micrometer
sec	Seconds
pH	Potential of Hydrogen
g	Gram
wt.	Weight

Acknowledgments

This research received support from the HBO Foundation grant (001/2021) for Pre-Concentrated Graphite Nigeria. We extend our sincere gratitude to Mr. Akinyele Olabode Samuel for his invaluable collaboration during the laboratory experiments conducted at the Mineral Processing Laboratory of the Federal University of Technology (FUTA) in Akure. Furthermore, we wish to acknowledge the Nigerian Metallurgical Development Center (NMDC) in Jos for their generosity in providing access to their laboratory facilities.

Author Contributions

Babatola Osasona: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Writing - original draft

Fatai Olufemi Aramide: Supervision, Validation, Writing - review & editing

Oladunni Oyelola Alabi: Conceptualization, Data curation, Methodology, Supervision, Writing - review & editing

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] Crossley P. Graphite - high-tech supply sharpens up. *Industrial Minerals* 2000, November 31-47.

[2] Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nature Materials* 2007, (6), 183-191.

[3] Jagiellom J.; Judek, J.; Zdrojek, M.; Aksienionek, M.; Lipinska, L. Production of graphene composite by direct graphite exfoliation with chitosan. *Materials Chemistry and Physics* 2014, 148, 507-511.

[4] Nwoke, M. A. U.; Uwadiale, G. G. O. O.; Kollere, M. A. Flotation of low-grade Birnin Gwari and Alawa graphite. *Nigeria. Miner. Metall. Process.* 1997, 14, 54-58.

[5] Fatoye, F. B.; Gideon, Y. B. Geology and mineral resources of the Lower Benue Trough, Nigeria. *Advances in Applied Science Research* 2013, 4(6), 21-28.

[6] Mohammed, A. M.; El-Nafaty, U. A.; Bugaje, I. M. Characterization of Graphite from Sama-Borkono Area of Bauchi State-Nigeria. *International Journal of Recent Development in Engineering and Technology* 2014, 3(2), 157-162.

[7] Oruonye, E. D.; Ahmed, Y. M. Challenges and prospects of mining of solid mineral resources in Taraba State, Nigeria. *International Research Journal of Public and Environmental Health* 2018, 5(1), 1-7.

[8] Osasona, B.; Alabi, O. O.; Aramide, F. O.; Akinyele, S. O. The Grindability of Ningi Graphite Ore in Nigeria. *Journal of Scientific and Engineering Research* 2019, 6(7), 195-200.

[9] Gamaralalage, R. A. K.; Herath Mudiyanselage, G. T. A. P.; Buddika K.; Mantilaka Mudiyanselage, M. G. P. G. M.; Rajapakse Mudiyanselage, G. R,; Hsin-Hui, H.; K. Kanishka, H. D.; Masamichi, Y. The Development of a chemical free floatation technology for the purification of vein graphite and characterization of the products. *Scientific Reports* 2021, (11), 22713. https://doi.org/10.1038/s41598-021-02101-9

[10] Lai, H.; Zhu, S. C. Technology, endowments, and factor content of bilateral trade. *Journal of International Economics* 2007, 71, 389-409.

[11] Davis, G. A. Trade in Mineral resources: Background paper to the 2010 world Trade report," WTO staff working paper ERSD-2010-01, World trade organisation-Economic research and statistics Division, Geneva, Switzerland; 2010.

[12] Henckens, M. L. C. M.; Van Ierland, E. C.; Driessen, P. P. J.; Worrell, E. Mineral resources: Geological scarcity, market price trends, and future generations. *Resources Policy* 2016, 49, 102-111. https://doi.org/10.1016/j.resourpol.2016.04.012

[13] Vasumathi, N.; Vijaya Kumar, T. V.; Nayak, B.; Subba Rao, S.; Prabhakar, S.; Bhaskar Raju, G. Beneficiation of low-grade graphite ore of Eastern India by two-stage Grinding and Flotation. *Journal of Mining and Metallurgy* 2014, 50 A (1), 9-17.

[14] Leamer, E. E. Sources of International Comparative Advantage: Theory and Evidence. *MIT Press*, Cambridge, MA; 1984.

[15] Bulatovic, S. M. Handbook of Flotation Reagents: Chemistry, theory, and practice. Volume 1, *Elsevier Science & Technology Books*. Amsterdam; 2007.

[16] Ravichandran, V.; Eswaraiah, C.; Manisankar, P. Beneficiation of low-grade graphite ore deposits of Tamilnadu (India). *Ultra Chemistry* 2012, 8, 159-168.

[17] Chelgani, S. C.; Rudolph, M.; Kratzsch, R.; Sandmann, D.; Gutzmer, J. A. Review of Graphite Beneficiation Techniques. *Mineral Processing and Extractive Metallurgy Review* 2016, 37(1), 58-68.

[18] Mengfei Lui et. al. A comprehensive investigation of microcrystalline graphite flotation using the innovative reagent MOS. Minerals Engineering. 2025; (22) -109234. https://doi.org/10.1016/j.mineng.2025.109234

[19] Kayisoglu, B.; Ulger, P.; Akdemir, B.; Aytac, S. A Research on Determining Some Performance Values by Using Proportional Mixture of Vegetable Oils and Diesel Fuel at a Diesel Engine. *J. Tekirdag Agric* 2006, 3(1), 16-24.

[20] Aluyor, E. O.; Obahiagbon, K. O.; Ori-jesu, M. Biodegradation of vegetable oils: A review. *Sci. Res. Essay* 2009, 4, 543-548.

[21] Atasie, V. N.; Akinhanmi, T. F.; Ojiodu, C. C. (2009). Proximate Analysis and Physicochemical Properties of Groundnut. *Pak. J. Nutr.*, 2009, 8(2), 194-197.

[22] Karmakar, G.; Ghosh, P.; Sharma, B. K. Chemically Modifying Vegetable Oils to Prepare Green Lubricants. *Lubricants* 2017, 5(4), 44. https://doi.org/10.3390/lubricants5040044

[23] European Commission. European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Grohol, M., & Veeh, C. Study on the critical raw materials for the EU 2023, final report, Publications Office of the European Union. https://data.europa.eu/doi/10.2873/725585

[24] Wilson E. Nigeria in 2023: Bridging the productivity gap and building economic resilience. *Brooking* 2023. https://www.brookings.edu/articles/nigeria-in-2023-bridging-the-productivity-gap-and-building-economic-resilience/

[25] Davis, D.; Weinstein, D. An Account of Global Factor Trade. *American Economic Review* 2001, 91: 1423-1453.

[26] Osasona, B.; Alabi, O. O.; Aramide, F. O. Characterization of Graphite Mineral of Ningi in North-Eastern Nigeria. *Journal of Materials Science Research and Reviews* 2021, 8(4): 258-264.

[27] American society for testing and materials. Standard Practice for Proximate Analysis of Coal and Coke, ASTM International, West Conshohocken, PA, United State of America; 2013.

[28] Wills, B. A.; Napier-Munn, T. Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery (7th Edition). *Elsevier Science & Technology Books. Amsterdam* 2006.

[29] Zheng, Tong; Jing, Lu; Xinnan, Hu; Xiangning, Bu.; Yujin, Sun; Yuran, Chen; Saeed Chehreh, Chelgani. (2024). Ultrasound Pretreatment for Enhancing Fine and Ultrafine Flake Graphite Flotation Beneficiation. ACS Omega 2024, 9(9), 10717-10726. https://doi.org/10.1021/acsomega.3c09316