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Research Article

Spectroscopic analysis of Sri Lankan vein graphite, industrially purified using green and chemical approaches

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ABSTRACT

Sri Lanka is well known for high-quality vein graphite, which can be exported with value addition at a higher price than the raw form to remain competitive in the global market. The present study aims at industrial scale production of Sri Lankan vein graphite above 99.9% purity level using eco-friendly and chemical methods. For the first time a novel mechanical floatation method was followed to purify vein graphite above 99% on mass scale. Acid leaching method was followed subsequently to remove most of the impurities from graphite at industrial scale as well. Subsequently, alkali-acid method was followed for further purification of graphite. The raw and treated graphite were subjected to X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analysis to verify any structural change resulting from the treatment process. XRD analysis showed that the crystalline structure of graphite has not significantly changed upon treatment. XPS and FTIR spectroscopic analysis also revealed that there is no apparent functional groups attached to graphite structure after treatment. SEM images demonstrated a flaky appearance of graphite without any clear changes in morphology even after the treatment with acids at commercial level quantitates. The results illustrated that combination of the flotation technique and chemical treatment allow graphite purification well above 99.9% carbon without significant structural changes.

Keywords: *Sri Lankan vein graphite, Floatation, Acid leaching, XPS, XRD, FTIR and SEM analysis*

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1. INTRODUCTION

Graphite is a mineral of sp^2 hybridized elementary carbon atoms of crystalline and polymorphic form [1]. Graphite is also an allotrope of carbon such as diamond. Graphite is made up of layers of carbon atoms that are connected by Van der Waal forces arranged in multiple hexagonal honeycomb lattice structures with a separation of 0.142nm. Van der Waals bonding forces of energy of graphite are 0.2 eV/atom [2][3]. Graphite inter-planer spacing is 0.335nm [4]. In graphite, carbon atoms are bonded covalent to three other carbon atoms, resulting in strong, two-dimensional layers of hexagonal structure forms [1][4].

Graphite is valuable when it is free from any form of structural defects which change the sp^2 hybridized carbon to sp^3 or with attached impurities. Removing impurities physically attached to graphite results added value to natural graphite for various applications.

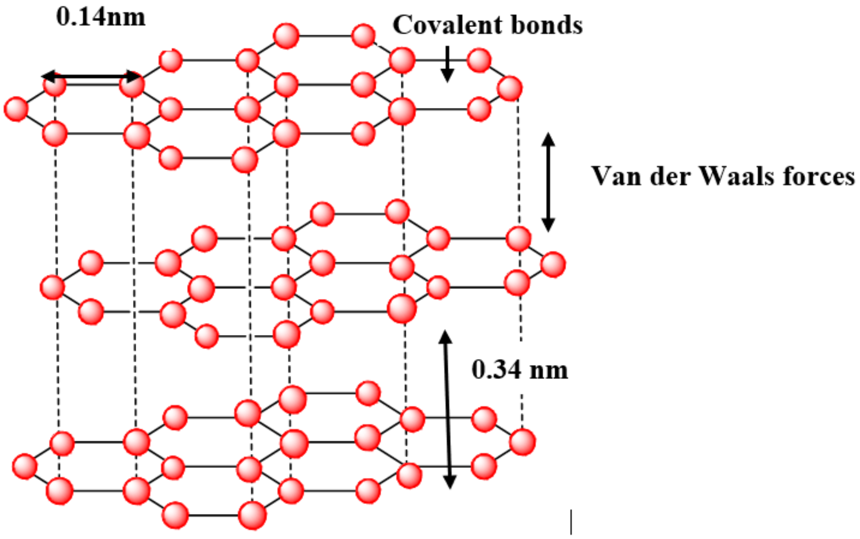


Figure 1: Chemical structure of graphite

Sri Lanka is known for its high-quality natural vein graphite, which is a key mineral export product. Sri Lankan graphite is the purest in the world, with a carbon content above 90%. The demand for graphite is increasing due to the growing market for electric vehicles, lubricants, energy storage, and electronics [5][6]. Generally, quartz is associated with graphite because it is found in granulite-hosted veins. The main impurities found in graphite are SiO_2, Al_2O_3, Fe_2O_3, CaO, S, MgO, MnO, K_2O, Na_2O, P_2O_5, TiO_2, and trace elements [7][8]. Among them Fe, Mg, and Ca are abundant in Sri Lankan vein graphite. Some impurities are mechanically attached to graphite and also intercalated those impurities in the graphite layers. However, the purity level of the graphite decreases with various impurities [6][8].

To produce high-purity vein graphite, it is desirable to remove silicate minerals from graphite first since silicate minerals represent major impurities in graphite [8]. Natural graphite has been purified through physical methods such as comminution, flotation, electrostatic separation, air classification, microwave, thermal purification, and gravity separation to remove silicate based impurities [5]. Floatation is a common physical method to achieve purity about 90% carbon. Recently, flotation methods and reagents used have been reviewed by Vaumathi *et.al*. [9] The froth floatation technique is more effective as a first step in the purification process [5][6][10]. However, the floatation technique is not sufficient for removing the intercalated matters in graphite layers [7]. Mechanically attached and intercalated impurities in natural graphite have been removed using thermal and chemical purification techniques [11]. Chemical methods including alkali roasting and acid leaching enable further purification of graphite above 99.9%. Alkali roasting removes silicate and sulfide impurities, while acid leaching removes acid-soluble impurities like iron [5][12][13]. Despite, the alkali roasting technique and acid leaching are observed to be more effective in purification of graphite [13][14][15]. Most of these published methods have achieved significant purity levels using chemicals or non-chemical methods[10][13][14][15]. Despite, industrial scale production of graphite with purity above 99.9% is challenging. In the present study a mechanical floatation technique using step wise stirring with controlling speed was followed for the first time to purify graphite at industrial quantities as eco-friendly purification process. Subsequently, an optimization of chemical treatment processes such as the alkali roasting technique and acid leaching were followed for further purification of graphite above 99.9% carbon as a value addition to vein graphite.

2. EXPERIMENTAL PROCEDURE

2.1. Floatation Method

Powdered graphite was mixed with distilled water and few drops of a volatile organic material were added. Compounds with least environmental impact such as ether-alcohol based materials have been used in this regards [9]. The resulting graphite slurry was agitated by using a magnetic stirrer (for laboratory scale production) and an overhead stirrer (for industrial scale production) with controlling speed so that graphite particles attached to the bubbles reach to the surface in high yield. The froth was collected for analysis. Depending on the initial purification level, the process was repeated several times to obtain purer form of graphite. The non-floated gravel remaining in the bottom was discarded in each step. Water is obtained from national water supply for the industrial scale purification process without further purification.

2.2. Acid Leaching Method

Graphite purified using floatation method was further purified using acid. A floated graphite sample was stirred using overhead stirrer for 8h with 10% H_2SO_4 at optimized ratio of 1:2 compared to prior art [12]. Resulting graphite was washed with water. Then residue sample was separately collected and dried for analysis. In this manner, mass scale purification of graphite was achieved using acid treatment.

2.3. Alkali Roasting and Acid Leaching Method

Alternatively, graphite purified using floatation method was further purified using alkali roasting method followed by acid treatment. Graphite and ceramic crucibles were used to roast graphite. Graphite was mixed with 25% NaOH at an optimized ratio and roasted at 270^{o}C for an hour compared to prior art [13][14].

2.4. Characterization

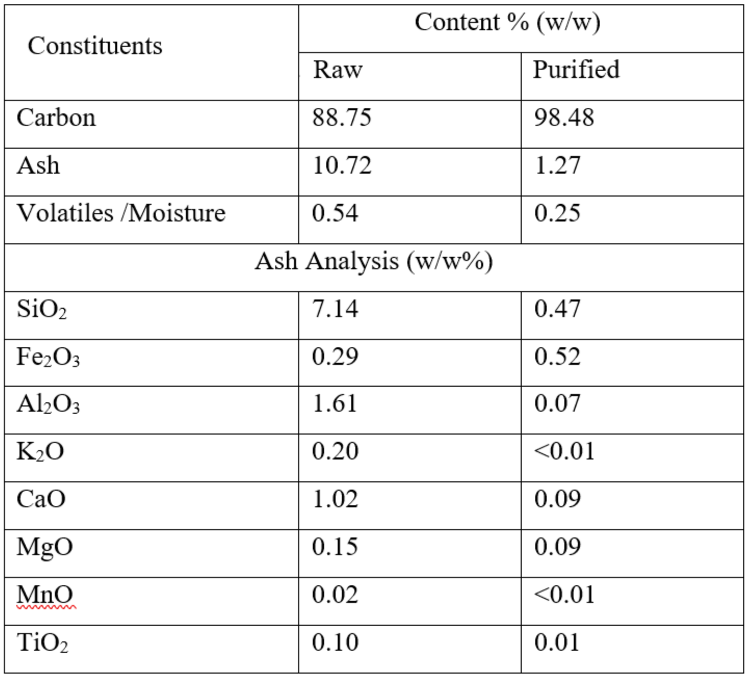
The surface morphology of the samples was imaged using a ZEISS EVO scanning electron microscope (SEM). XRD analysis was conducted using a RIGAKU Ultima-IV X-ray Diffractometer operated at 40 kV voltage, 30 mA current using Cu $K\alpha_1$ - 1.4506 Å (XRD) FTIR analysis was done using a BRUKER Tensor 27 FTIR. X-ray photoelectron spectroscopic (XPS) analysis was carried out using a Thermo Scientific, Nexsa spectrometer (England).

3. RESULTS AND DISCUSSION

In the present study mechanical floatation was followed as initial step of purification of graphite which was found to be feasible at industrial scale production as well. Froth flotation is a commonly used technique in the mining industry to physically separate hydrophobic materials from hydrophilic materials in liquid phase through froth formation. Therefore, minerals such as graphite is possible to separate using froth floatation technique due to inherent hydrophobic nature [16][17][18][19]. August and Adolph have used this technique for purification of graphite in 1877 for the first time [20][21]. When air bubbles are generated in graphite suspension, graphite attached to air bubbles are moving upwards and float on the surface of water. This unique property of graphite allows separation of graphite easily from other minerals in the bulk. Two types of froth floatation techniques have been used for industrial scale purification of graphite; mechanical method and air bubbling through a column [9]. In mechanical floatation process, froth has been created by agitation with a rotating impeller, releasing air bubbles in to the graphite suspension [22]. In column floatation which is a commonly used method, air bubble generation is done from the bottom of the column. In the present study, a stirrer with controlling speed was followed for the first time to float graphite at industrial scale which is also a mechanical method to purify graphite. In addition, reagents such as collectors are used to increase the efficiency of the froth formation process and effective collection of graphite from other impurities [23]. A similar chemical free mechanical floatation method has been used to purify graphite in prior art [10] which is infeasible in mass scale producing pure graphite due to low yield. In the present overhead stirring method with controlling speed, significant improvements in graphite recovery efficiencies found using few drops of single volatile organic compound. It is interesting to note that a higher yield is observed recovering almost all graphite. In general, waste graphite generated from common floatation technique using bubble generator is about 40%. The results indicated that the present method can be used to recover graphite from even waste graphite of 40% carbon up to well above 98% by increasing the flotation speed and cycles. However, the present study limited to maximum 2-3 cycles at industrial scale production of pure graphite to minimize the cost and therefore, the initial purity above 75% was used as shown later.

Table 1 shows chemical analysis of raw and two times floated Sri Lankan vein graphite. Graphite sample is consisting of impurities such as SiO_2, Al_2O_3, CaO, MgO, and Fe_2O_3 which could appear in mineral forms of quartz, mica, carbonates and pyrites [24]. Major impurities are silicate compounds which represent more than 70%, while alumina and calcium compounds represent next highest non-graphitic materials. It is interesting to note that the vein graphite studied is free from sulfur containing compounds which may have added value in some applications. Almost all major and minor impurities have been reduced to trace level during the floatation process. It is noted that considerable amounts of silicate compounds are still remaining in graphite. In the industrial scale production, water from national supply was used without further purification and as a result, ion content has presumably increased slightly after floatation. Filtered water or distilled water may be more suitable.

Table 1: Chemical analysis of raw and floated graphite



Constituents	Content % (w/w)	
	Raw	Purified
Carbon	88.75	98.48
Ash	10.72	1.27
Volatiles /Moisture	0.54	0.25
Ash Analysis (w/w%)		
SiO_2	7.14	0.47
Fe_2O_3	0.29	0.52
Al_2O_3	1.61	0.07
K_2O	0.20	<0.01
CaO	1.02	0.09
MgO	0.15	0.09
MnO	0.02	<0.01
TiO_2	0.10	0.01

Despite it is costly for industrial scale production. Floatation method followed in the present study enabled purification of graphite well above 99% at industrial scale production as shown in the Table 1, which has significant improvement compared to the prior art. Various spectroscopic techniques were followed to analyze any structural or morphological changes happening in the floatation and chemical purification of graphite.

3.1 XRD analysis

XRD is a widely used nondestructive technique to determine crystalline phases and structural properties such as lattice parameters, particle size and phase composition of materials. In the present work, natural graphite and purified graphite was subjected to XRD analysis. inter-planar distance (*d*-spacing) were compared to identify phase changes on physical and chemical treatments.

The XRD spectra of the raw, acid treated, and alkali-acid treated graphite are presented in Figure. 2. There is a prominent sharp peak at $2\theta \sim 26.7^{o}$ and a smaller peak at $2\theta \sim 54.9^{o}$ specific to (002) and (004) planes for raw graphite. Corresponding inter-planar distances (*d*-spacing) are 0.332 nm and 0.168 respectively. Vein graphite appears in a well-defined layered structure with a highly crystalline structure. The lists of *d*-spacing values after purification of graphite using floatation and chemical methods have been shown in Table 2.

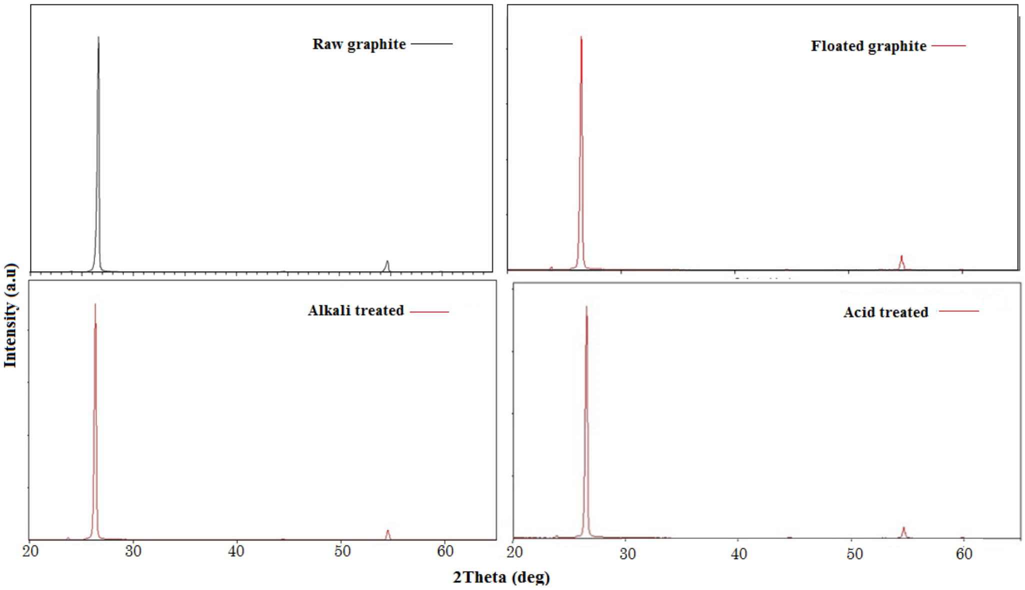


Figure 2: XRD spectra of raw graphite and purified graphite

Table 2: *d*-spacing values for raw and purified graphite

	2θ Angle		***d*-spacing (nm)**	
	(002)	**(004)**	**(002)**	**(004)**
Raw Graphite	26.7°		0.332	
		54.9°		0.168
Floated Graphite	26.5°		0.335	
		54.7°		0.168
Acid-treated Graphite	26.5°		0.336	
		54.6°		0.168
Alkali-acid Treated Graphite	26.4°		0.337	
		54.5°		0.168

The 2θ Angle corresponding to both (002) and (004) planes of treated graphite has slightly reduced from 26.7° to 26.4° compared to raw graphite upon three different treatment processes while increasing inter layer spacing specific to (002) plane from 0.332 to 0.337. Parallel increase in corresponding *d*-spacing obviously indicates inclusion or intercalation of some other materials as shown in the FTIR analysis. Apart from that there is no significant change in the crystal structure of graphite on flotation or chemical treatment.

3.2 FTIR analysis

FTIR analysis is effective in determining functional groups presence in organic materials and identification of various organic materials through their vibrational frequencies. FTIR spectra was used to identify any non-carbonaceous group attached to graphite structure upon physical and chemical treatment.

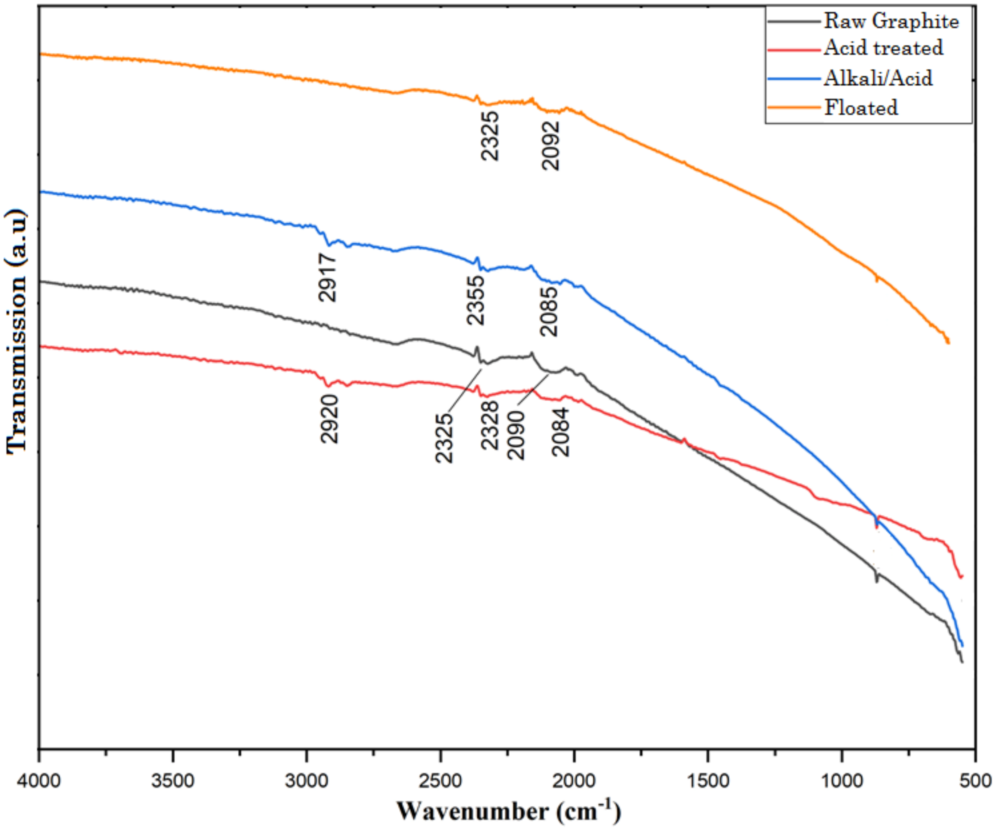


Figure 3: FTIR spectra of raw and purified graphite

Figure 3 illustrates the FTIR spectra of raw and graphite purified using three different methods. There is no any prominent peak in FTIR spectra of raw and floated graphite except doublet at 2325cm^{-1} bands attributable to absorption of atmospheric CO_2 in graphite [25]. Chemically purified graphite compared with raw graphite shows two additional minor peaks for asymmetric C–H stretching vibration of saturated carbon at 2920 cm^{-1} and 2848 cm^{-1} for acid treated graphite while at 2917 cm^{-1} and 2849 cm^{-1} for alkali acid treated graphite which are attributable to organic materials added in the floatation process of graphite. Apart from that, the FTIR analysis of graphite does not show significant functionalities upon treatment, suggesting that the graphite structure remains almost unchanged even after the chemical treatment [25].

3.3 SEM analysis

The surface of raw graphite particles has rough and irregular morphology due to different orientations. SEM images can give visual evidence of impurities in graphite, while it does not reveal information on the specific composition, or the nature of impurities present in the sample. SEM images of purified graphite show evenly distributed compact morphology of particles similar to raw graphite without any apparent changes except for the alkali treated graphite. The latter shows rougher surface presumably due to removal of alkali soluble impurities like silica. Finally, it is proven that, both floatation and acid leaching techniques are feasible in purification of graphite without significant morphological changes.

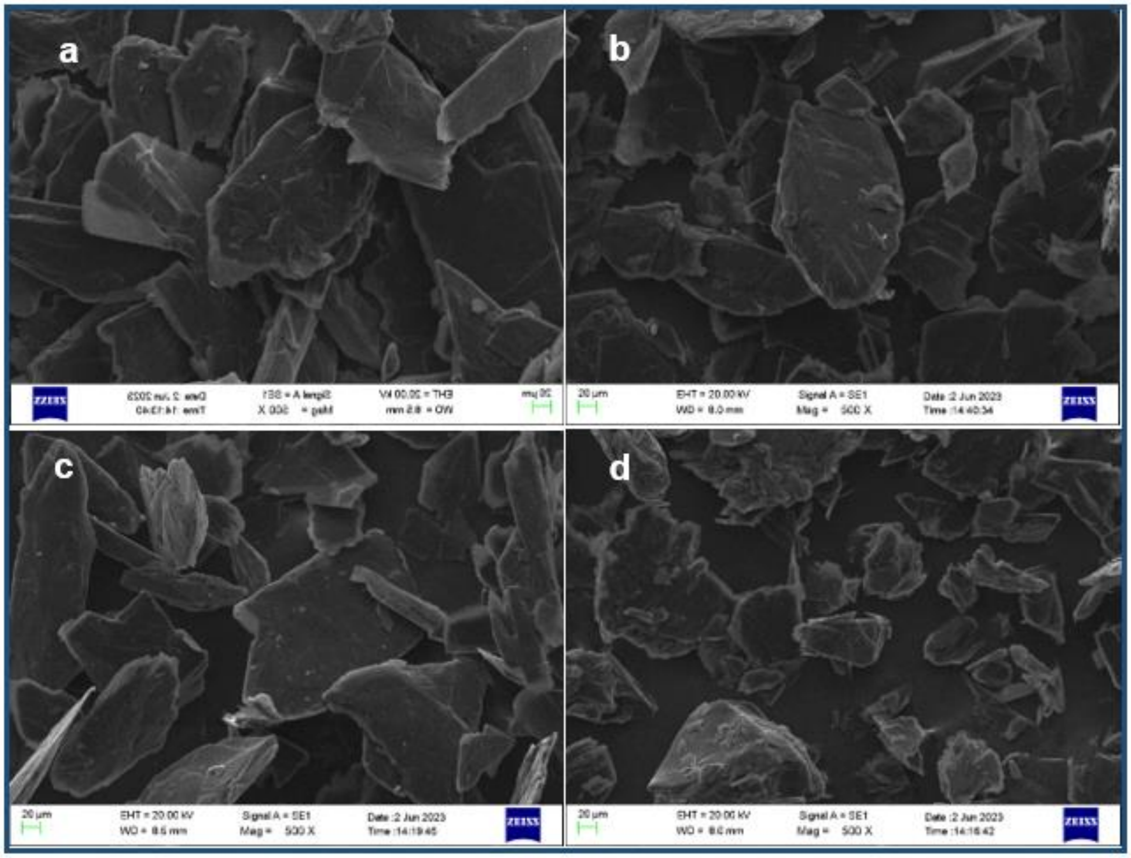


Figure 4: SEM image of (**a**) raw, (**b**) floated, (c) acid treated and (d) alkali-acid treated graphite

3.4 XPS Analysis

XPS is a spectroscopic technique for surface analysis that provides valuable details on the surface chemistry of graphite such as elemental composition, chemical state, and electronic structure; particularly, sp^2 and sp^3 hybridized carbon content in graphite [26][27][28][29]. Graphite has a trigonal structure consisting of sp^2 hybridized carbon bonding in which *p*-orbitals overlaps between carbon atoms. [28]

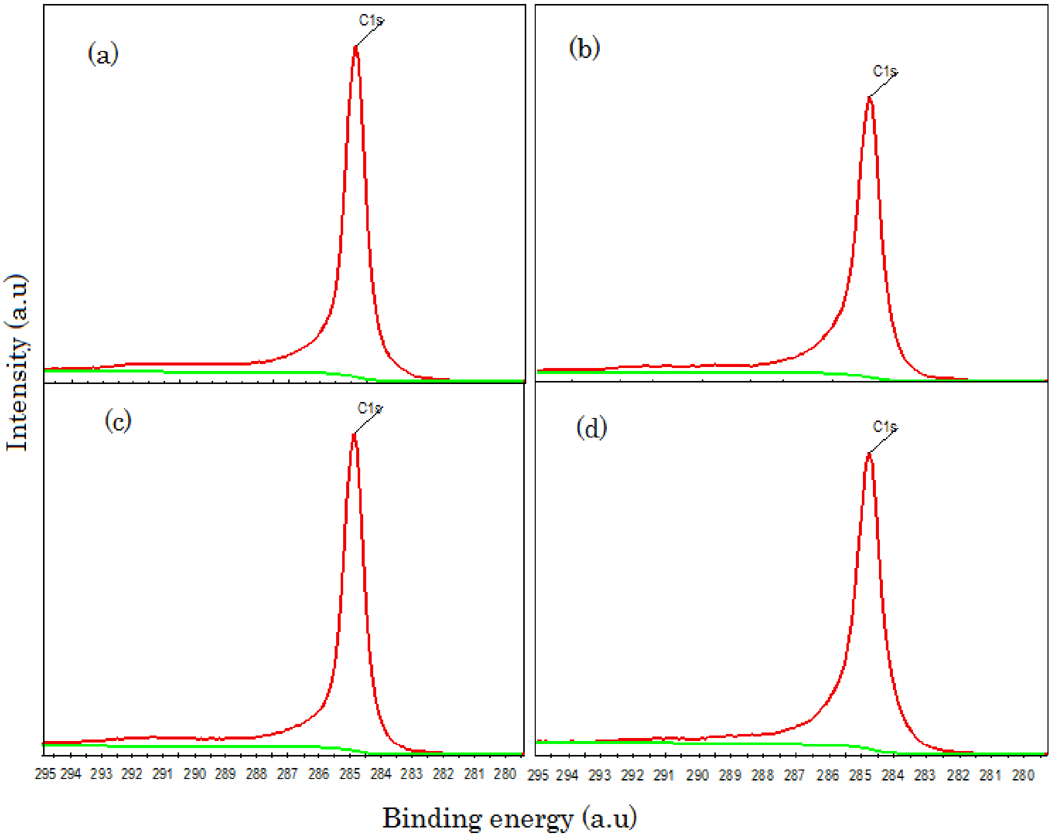


Figure 5: XPS analysis of (a) natural graphite (b) floated graphite (c) acid-treated graphite and (d) alkali-acid treated graphite

High resolution XPS spectra for C1s of graphite and purified graphite are shown in Figure 5. All four spectra show a single peak with asymmetric tail towards high binding energy direction. The peak appears at 284.7 eV is generally associated with sp^2 hybridized carbon atoms in graphite, [30][31][32].The spectra have not deconvoluted, since main features are clearly visible. The tail to the high binding energy direction associated to a host of oxygen-related functional groups are not prominent in all spectra. It is also reported that π-bonding would also lead to a broad π to π* satellite in the binding energy range of 288-294 eV and known to be a signature of sp^2 carbon since no any other peak is expected in this binding energy region [28]. Therefore, XPS spectra also verifies that the structure of graphite remains almost unchanged upon different physical and chemical treatment.

3.5 Graphite Floatation

Table 3: Graphite purity achievement using floatation and chemical methods.

Initial purity (%)	Treated method	Final purity (%)
75.68	Floatation	98.02
84.65	Floatation	99.07
96.95	Acid leaching after floatation-No. 1	99.30
97.83	Acid leaching and floatation-No. 2	99.51
99.38	Acid leaching and floatation-No. 3	99.79
99.44	Alkali roasting in graphite crucible & acid treating (after floatation)	99.87
99.44	Alkali roasting in ceramic crucible & acid treating (after floatation)	99.97

According to Table 3, low purity graphite such as 75% was purified up to 98% using floatation technique. Here we have used two floatation cycles to optimized the production cost without affecting the quality. Further purification can be achieved by increasing the number of floated cycles, Floated graphite was subsequently used for further purification using chemical methods.

3.6 Acid treatment

Acid leaching removes any other remaining acid soluble impurities in floated graphite. As shown in the Table 3, acid leaching enabled further purification of graphite up to 99.5%. Sulfuric acid was used as the acid in the graphite purification process. The impurities containing Fe, Mg, Ca, and Al are dissolving in acid as shown in equation [1] to [4].

$$Fe_2O_{3(s)} + H_2SO_{4(aq)} \longrightarrow Fe_2(SO_4)_{3(aq)} + 3H_2O \quad \text{eq [1]}$$

$$MgO_{(s)} + H_2SO_{4(aq)} \longrightarrow MgSO_{4(aq)} + H_2O \quad \text{eq [2]}$$

$$CaO_{(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(aq)} + H_2O \quad \text{eq [3]}$$

$$Al_2O_{3(s)} + 3H_2SO_{4\,(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3\,H_2O \quad \text{eq [4]}$$

$Fe_2(SO_4)_3$, $MgSO_4$, $Al_2(SO_4)_3$ are salts soluble in water [15] and can be removed by dissolving in water. Amphoteric Aluminum oxide reacts with sulfuric acid by forming Aluminum sulfate and water which dissolve in water and forms Aluminum hydroxide. Washing process enables removing all water-soluble impurities and excess acid in treated graphite. Silica does not react with sulfuric acid and therefore, unable to remove using acid treatment. Acid leaching allows reducing the content of impurities in graphite to significant levels. XPS Quantitative analysis results of acid treated graphite samples are indicated in Table 4. It also confirms that the main impurity in the acid treated graphite is also silicate compounds while removing all the other mineral impurities in graphite.

Table 4: XPS quantitative analysis of acid treated graphite

Name	Peak BE	FWHM eV	Atomic %	Title
C1s	284.88	0.74	97.15	C1s Scan
O1s	532.5	2.1	2.31	O1s Scan
Si2p	102.59	1.73	0.54	Si2p Scan

3.7 Alkali-acid treatment

In alkali roasting process, chemical reaction occurs in between silicate impurities and NaOH by forming silicate, sodium salt, oxides which can be dissolved in water. [14][15] Table 1 indicated that, the silica is the main impurity in raw graphite. And other impurities could be removed in the form of water-soluble alkali silicates. Sodium aluminate and Sodium silicate are water soluble.[15] Water-soluble form of impurities was removed from graphite on subsequent washing process after the alkali roasting.

$$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_{3(aq)} + H_2O_{(l)} \qquad \text{eq [5]}$$

$$Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)} \qquad \text{eq [6]}$$

$$TiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2TiO_{3(aq)} + H_2O_{(l)} \qquad \text{eq [7]}$$

In the present study alkali roasting was conducted using ceramics and graphite crucibles. Most commonly graphite crucibles are used in alkali roasting process of graphite due to chemical stability and the resistance to acids and alkaline solutions. In addition, graphite crucibles are used because of their specific characteristic such as, thermal conductivity, high temperature resistance, low thermal expansion coefficient for high temperature applications etc. The non-reactive nature of these graphite and ceramics crucible makes them ideal to use in the alkali roasting process. It is also high resistance to both chemical and thermal attacks and hence can withstand high temperature.

Table 3 also indicates purity achieved from two different types of crucibles. The results indicated that the crucible used in alkali roasting process significantly affect the final carbon content of graphite, because silicate materials present in crucible can react with alkaline compounds and contaminate graphite.

A carbon content of graphite was achieved up to 99.97% by using ceramic crucible as shown in the Table 3. We have noticed slight damage in the graphite crucible after the alkali roasting process. Impurities in the crucible might have added to graphite resulting a lower purity level than expected. Therefore, the present study revealed that the ceramic crucible is more effective to purify graphite compared to graphite vessel in this study. However, slight damage to ceramic crucible is also noticed in this study since ceramics also contains aluminate and silicate compounds which may react with NaOH. We have noticed refloatation after alkali treatment is effective in removing added impurities from these vessels. Therefore, efforts are on the way to improve the graphite crucible which is the most suitable cost effective vessel for purification of graphite using alkali roasting method.

4. CONCLUSION

The present study revealed that Sri Lankan vein graphite contains Si, Al, and Ca compounds as main impurities while Fe, Mg, Mn and Ti compounds are in trace levels which can easily be removed using floatation method based on stirring with controlling speed and purifying graphite up to 99% at industrial levels. The floatation process can be considered as green approach and might suitable for applications where high natural purity is expected such as in energy storage devices. Acid treatment of graphite could remove further impurities and purify graphite to a level 99.5% on mass scale. Alkali roasting followed by acid treatment allow further purification to a level 99.97%. Further study is in progress to achieve purity above 99.99% on industrial scale production. XRD, FTIR, and XPS spectroscopic analysis revealed that purified graphite is free from substantial structural damages while SEM analysis shows no significant morphological changes on chemical treatment except in the alkali roasted process. The investigation is pave the path for using Sri Lankan high purity vein graphite in diverse industrial applications on expectation level of purity.

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