



Degree project in Materials Science and Engineering

Second cycle, 30 credits

# Purification of Engineered Graphite for Advanced Application

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## **Abstract**

Graphite has important applications in several key industries, which has been listed as a “critical raw material” considered to be supply-risk by European since 2020. Purification of engineered graphite is one of the essential processes for the manufacturing of high-quality graphite. In this work, the production process and the existing methods to purify the three major types of graphite are evaluated and compared. Then purification method focusing on acid washing to remove iron from bio-graphite is investigated. The results showed that the impurity removal efficiency of acid washing increases with the increase of temperature, but efficiency decreased because of HCl volatilization when the temperature reaches 100 °C. High concentrations of hydrochloric acid and other strong acids can improve the ability of acid washing. The smaller the graphite particle size, the more iron impurities are removed. Finally, through multi-steps acid washing with hydrochloric acid and aqua regia at 80 °C, bio-graphite with a purity of 99.67 % as obtained. This meets the requirements of metallurgical electrodes and other applications. The acquisition of ultra-high-purity graphite still needs more further work.

**Key words:** Graphite; Purification; Acid washing; Biomass; Biochar

## **Sammanfattning**

Grafit har viktiga tillämpningar i flera nyckelindustrier, som har listats som en "kritisk råvara" som anses vara en försörjningsrisk av Europa sedan 2020. Rening av teknisk grafit är en av de väsentliga processerna för tillverkning av högkvalitativ grafit. I detta arbete utvärderas och jämförs produktionsprocessen och de befintliga metoderna för att rena de tre huvudtyperna av grafit. Därefter undersöks reningsmetod med fokus på syratvätt för att avlägsna järn från biografit. Resultaten visade att effektiviteten för avlägsnande av föroreningar vid syratvätt ökar med ökningen av temperaturen, men effektiviteten minskade på grund av HCl-förångning när temperaturen når 100 °C. Höga koncentrationer av saltsyra och andra starka syror kan förbättra förmågan till syratvätt. Ju mindre grafitpartikelstorlek, desto mer järnföroreningar avlägsnas. Slutligen erhöles biografit med en renhet på 99,67 % genom syratvätt i flera steg med saltsyra och aqua regia vid 80 °C. Detta uppfyller kraven för metallurgiska elektroder och andra applikationer. Förvärvet av grafit med ultrahög renhet kräver fortfarande mer arbete.

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# 1. Introduction

## 1.1 Introduction

Graphite is an allotrope of the crystalline carbon, which contains only  $sp^2$  hybrid orbitals and  $\pi$  bonds in its structure [1]. Its structural model is shown in Figure 1. Good electrical and thermal conductivities are obtained in the layers because of the in-plane  $\pi$  metallic bonding which allows free delocalized electrons able to move in the plane direction. The two-dimensional planes of graphite are called graphene. However, in the perpendicular direction, the thermal and electrical conductivity is not high. This is because the layers are connected via Van der Waals forces, which are weak [2].

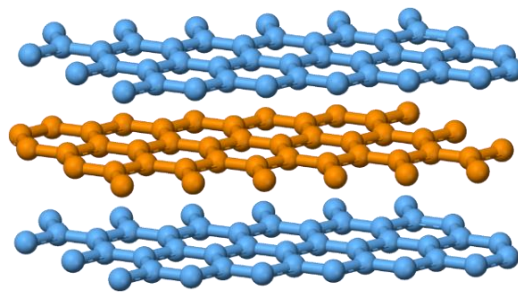


Figure 1. Schematic diagram of graphite structure [3].

In addition to the excellent electrical and thermal conductivity given by the structure, graphite also has strong stability. At atmospheric pressure, graphite will not melt and will sublime directly when the temperature reaches approximately 4000 K. Only at 100 atmospheres pressure, the melting of graphite can be observed when the temperature reaches 4200 K [1]. At the same time, graphite also has good corrosion resistance and lubricity [4].

These unique physical and chemical properties of graphite make it applicable in many applications shown in Figure 2 including industrial pencil leads, refractory materials, metallurgical electrodes, lubrication, batteries, etc [5][6].

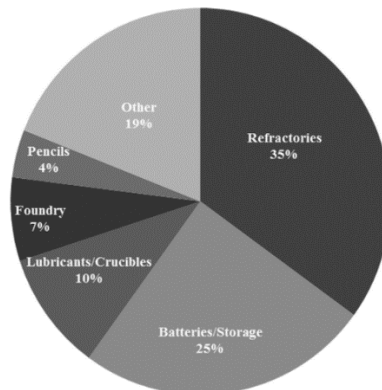


Figure 2. Common applications of graphite [5][6].

Graphite is also applied in some advanced technology fields, but these applications often require ultra-high purity graphite. To directly separate graphene from graphite, the carbon content of graphite is required to reach 99.9 % [7]. In the field of fuel cell electrodes, it is generally believed that graphite with a purity of more than 99 % should be used [8]. When graphite is used in lithium battery anodes, its carbon content should reach 99.9 % [9].

The ultra-high requirements on purity for advanced technologies of graphite makes the purification process of graphite more and more important. This article will analyze the types and contents of impurities in graphite products from the production process of natural graphite, synthetic graphite and bio-graphite and introduce and compare various graphite purification methods and impurity removal efficiencies. Some influencing factors on impurity removal results of the acid washing method for bio-graphite will be studied and analyzed.

## **1.2 Objective**

The overall aim of this project is to study the purification methods of engineered graphite for advanced applications. Specifically:

1. To review the production process of three major types of graphite including the manufacturing process parameters and the general impurity content.
2. To review the existing methods applied to impurity removal of the three major types of graphite. The removal efficiency of different methods will be evaluated and compared.
3. To investigate the influence of acid concentration, temperature, and graphite particle size on the iron removal efficiency of bio-graphite derived from biochar.

## 2. Literature review

### 2.1 Production of graphite

In general, there are three main sources of graphite, natural graphite mined directly from minerals, synthetic graphite, and bio-graphite. Natural graphite is the most important source of graphite materials today, but it often contains too many impurities and is difficult to be applied directly.

Another graphite is synthetic produced graphite, which refers to the graphite obtained by a high temperature over 2800 °C graphitization process of the materials. The main raw materials for the large-scale industrial production of synthetic graphite are calcined petroleum coke and coal tar pitch [10].

Nowadays, with the development of sustainable energy and the requirements of environmental protection, bio-graphite has gradually become a research hotspot. Bio-graphite is mainly obtained by pyrolysis and high-temperature catalytic graphitization of carbon-containing organics. The industrialization of bio-graphite will greatly alleviate the crisis of fossil energy depletion and it has the opportunity to become the most important source of graphite in the future.

#### 2.1.1 Natural graphite

Natural graphite is the largest source of graphite and is distributed all over the world. According to statistics in 2019, the global exploitable graphite content can reach 300 million tons and recyclable graphite resources can even reach 800 million tons [11]. There are three types of natural graphite: amorphous graphite, flake graphite, and veined graphite, which depend on the metamorphism of the carbon-rich precursor material at different pressures and temperatures (Simandl et al., 2015) [11]. Table 1 shows the features and comparison of the three types of natural graphite [12].

Table 1. The features and comparison of the three types of natural graphite [12].

Natural graphite type	Amorphous graphite	Flake graphite	Veined graphite
Ore	Seams, frequently folded and faulted	5 – 30 % graphite, strata-bound, tabular, or lenses	90 % and above graphite, veins, and fractures
Purity after beneficiation	< 85 %	80 % - 99 %	> 98 %
Origin	Syngenetic, contact and/or regional metamorphism	Regional metamorphism	Epigenetic, regional metamorphism

When natural graphite is mined from the mineral, its carbon content is generally low (except for vein graphite). Therefore, the production of natural graphite needs to go through many enrichment and impurity removal processes, which mainly include crushing, beneficiation, and graphite refining stages. The simplified process is shown in Figure 3 below.

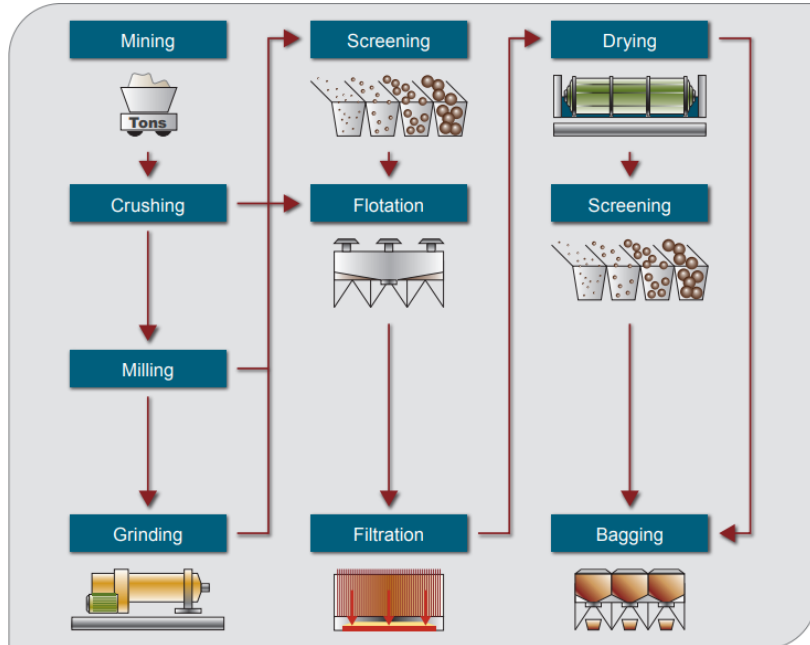


Figure 3. The simplified production process of natural graphite [13].

The first crushing process is the most important, and its function is to release graphite flakes from the mineral parent rock to improve the subsequent beneficiation efficiency. The size and carbon content of graphite flakes are the most important factors in determining the final graphite grade. Therefore, in the crushing stage, the crushing methods, ball mills, hammer mills, air-jet mills, and rod mills, should be determined according to the type of graphite ore. The second stage is grinding and screening to maximize the recovery of graphite flakes. The last stage is refining, which is the purification process of graphite [13]. The most common ways are flotation, acid washing, acid-base, and high-temperature purification. These methods will be described in detail in the following chapters.

### 2.1.2 Synthetic graphite

Synthetic graphite is also called artificial graphite, which is mainly produced by heat treatment of amorphous carbon materials, such as calcined petroleum coke and coal tar pitch. When the graphitization temperature is reached, the microscopic morphology of the synthetic graphite will gradually converge towards flake-like during the graphite growth process (see Figure 4) [14]. Compared with natural graphite, synthetic graphite has no cost advantage. However, instead of the large number of mineral impurities contained in natural graphite, synthetic graphite has higher carbon content, better

cyclability, more balanced performance, and better compatibility with electrolytes [15]. This is also the reason why it is more favoured in solar energy storage and electric arc furnaces [16].

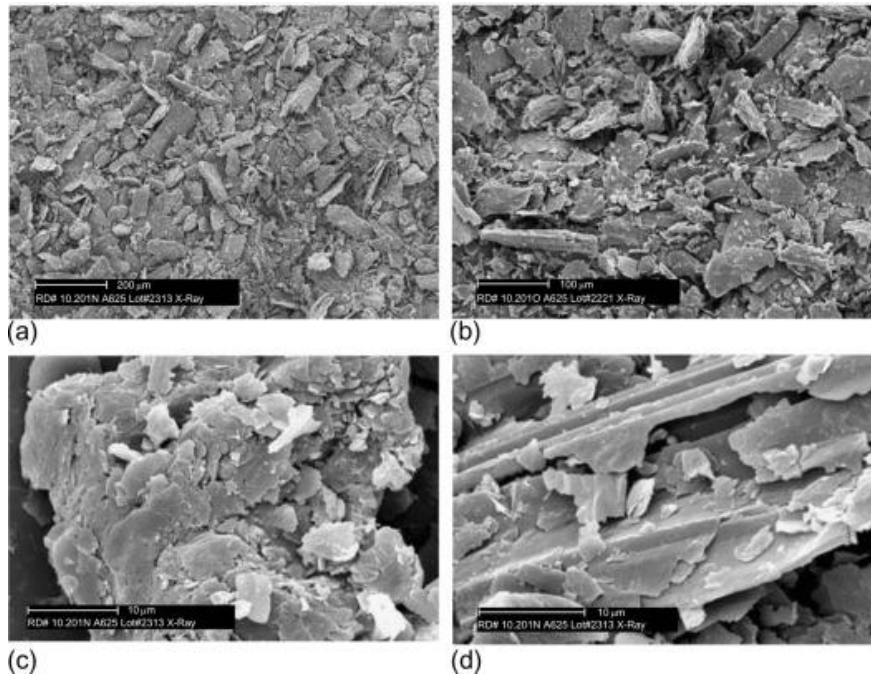


Figure 4. Convergence towards flake-like morphology of synthetic graphite [17].

The manufacturing technology of synthetic graphite is very mature, which is shown in Figure 5. Its production process can be summarized into the following five stages: powder preparation, shape-forming, baking, pitch impregnation, and graphitization [18]:

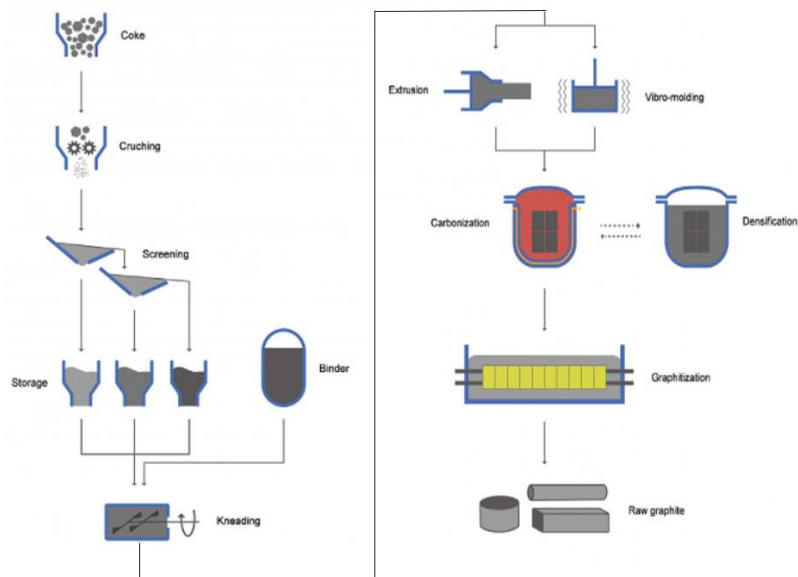


Figure 5. The process of the production of synthetic graphite.

➤ Powder preparation: This step is mainly the processing of raw materials. After

calcined petroleum coke is crushed, ground, and sieved, coal tar pitch or petroleum pitch is used as a binder and mixed with suitable coke powder to form a paste.

- Shape forming: Several shape forming techniques are used in this step, where the paste is compacted and extruded through a die into the required shape. The most common methods include Extrusion, vibration molding, and cold isostatic pressing.
- Baking: After shape forming, the product is heated in an oxygen-free environment at 900 - 1200 °C. At this temperature, the pitch is carbonized, the newly generated carbon is tightly combined with the previous carbon powder, and a part of the organic matter is volatilized.
- Pitch impregnation: This step usually uses a low viscosity pitch, such as petroleum pitch, to impregnate the baked product again to fill the pores caused by the carbonization of the binder during the baking process. The pitch impregnated product will be calcined and carbonized again to make it densified. Some high-density graphite products will even be repeatedly baked and impregnated several times.
- Graphitization: During this process, the temperature is raised to 2700 to 3000 °C, then the amorphous precursor carbon crystallizes and transforms into graphitic crystallites, which continue to grow and eventually become a stable graphitic structure. At the same time, at such a high temperature, most of the impurities will volatilize to achieve the purification of graphite.

### **2.1.3 Bio-graphite**

With the continuous increase in the demand for graphite and the requirements for environmentally friendly production, bio-graphite which refers to graphite derived from biomass has become a more attractive research topic [19]. So far, various methods have also been used to produce bio-graphite, such as laser ablation [20] and high-temperature heating [21]. Banek et al. [20] used a high-intensity laser method to convert lignocellulosic feedstock into bio-graphite. Firstly, the lignin was pyrolyzed at 600 °C in the N<sub>2</sub> atmosphere to obtain biochar, and then a high-intensity laser was used to graphitize the mixture of biomass char and iron powder. According to the analysis results, the quality of bio-graphite is high, but the disadvantage is a higher requirement of the high-strength lasers.

Another more common method is high-temperature graphitization; its process is shown in Figure 6. After obtaining biochar from biomass pyrolysis, the high-temperature treatment is used to convert the mixture of biomass and catalyst into bio-graphite. The addition of the catalyst can sharply reduce the graphitization temperature from 3000 °C to more than 1000 °C. Regularly used catalysts for graphitization are transition elements such as Ti, Al, Fe, Co, Ni, and metal compounds [21]. In the study of Zhao et al, glucose was pyrolyzed into biochar at 1100 °C, and then Mg powder as a catalyst is doped into

biochar. The mixture was heat-treated in a tube furnace at 800 – 1000 °C for 2-3 hours to obtain bio-graphite [22].

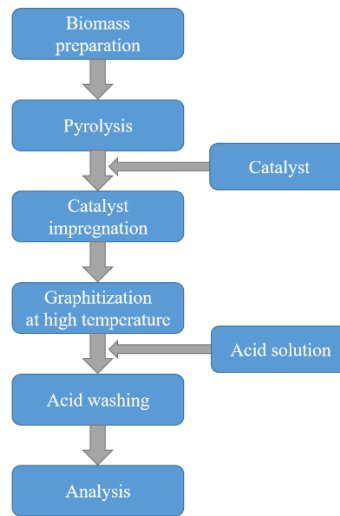


Figure 6. The simple process of producing graphite from biomass.

## 2.2 Purification of graphite

The different sources and production methods of the three types of graphite make the types and contents of impurities they contain different. Natural graphite is to separate mineral impurities, synthetic graphite is to remove volatiles and oils, and bio-graphite focuses on removing the catalyst added before graphitization. Different impurities determine their different impurity removal methods.

### 2.2.1 Purification of Natural graphite

Nowadays, various purification methods have been applied to reduce the impurity content in the natural graphite including floatation, acid washing method, acid-base method, and high-temperature method. Flotation is the simplest purification method but compared with the other methods, the purity of graphite obtained after flotation is lower, which cannot meet the minimum requirements of many applications. Acid-base method and acid method are both chemical treatment methods, they can remove more impurity content in graphite by chemical reaction with the impurity. The high-temperature purification method can obtain higher purity graphite. However, the huge energy required and the environmental pollution are the disadvantages that cannot be ignored.

Although the structures of different natural graphite are not the same, their compositions of impurities are similar. These impurities mainly consist of potassium, sodium, calcium, magnesium, and aluminium silicate minerals [23]. The following analysis of flake graphite mined in Nanjiang (China) shows the various mineral components and main chemical components in natural graphite ore [24].

Table 2. Mineral compositions of raw fine flaky graphite ore from China (wt%) [24].

Species	Feldspar	Graphite	Quartz	Mica	Tremolite	Chlorite	Phosphorite	Others
Content, %	28	25	25	10	6	2	2	3

From Table 2, the Feldspar, Quartz, Mica, and Tremolite have a relatively high content in natural flake graphite and the graphite content can only reach 25 %. After understanding the mineral composition, Table 3 lists the main chemical composition of graphite flakes.

Table 3. Chemical compositions analysis of flaky graphite from China (wt%) [24].

Composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TFe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
Content, %	47.85	8.17	4.84	2.26	2.59	1.87	2.46
Composition	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	H <sub>2</sub> O	SO <sub>3</sub>	Loss	Carbon
Content, %	0.54	0.28	0.034	0.13	2.04	28.43	25.95

According to the chemical composition analysis in Table 3, the content of SiO<sub>2</sub> in flake graphite is very high, and other impurities include Al<sub>2</sub>O<sub>3</sub>, TFe<sub>2</sub>O<sub>3</sub>, CaO, and so on. Therefore, the natural graphite purification process is to find a suitable method to remove these impurities.

### 2.2.1.1 Flotation

Flotation is a physical impurity removal method. The principle is the hydrophobicity of graphite on the cleavage planes due to its low surface energy. The measure of its surface hydrophobicity is mainly the contact angle of graphite in the air-water-mineral system, which depends on the pH of the solution and the surface treatment process [25]. With the help of a surfactant-froth agent that can generate a large number of bubbles, when blow air into the solution, the hydrophobic end of the surfactant is inserted into the air, and the hydrophilic end still stay in the solution to create air bubbles. In order to improve the separation efficiency, depressants are also necessary. Depressants have a mineral-philic group on one end and a hydrophilic group on the other, which keeps mineral impurities in the solution. At the same time, some selective collectors are added to the solution, and they will be adsorbed on the surface of the graphite powder. The hydrophobic end of the collectors is inserted into the bubble so that the graphite is brought to the interface of the liquid during the rise of the bubble to achieve the separation of graphite from the hydrophilic impurities [26]. The schematic diagram of flotation is shown in Figure 7.

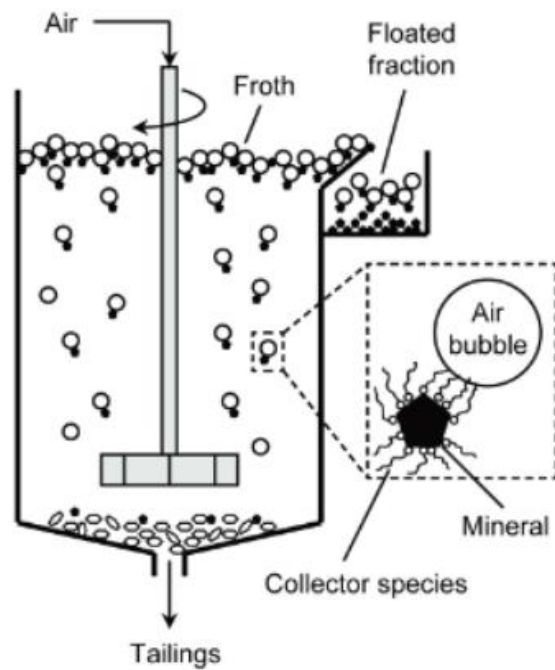


Figure 7. Schematic diagram of mineral flotation [27].

The flotation process usually consists of multiple coarse flotations and fine flotation, including multi-step grinding and cleaning processes. Figure 8 shows the multi-step flotation process for flake graphite ore [24]. Such a flotation process design can reduce a huge amount of slag caused by damage to the graphite sheet during the regrinding process [26].

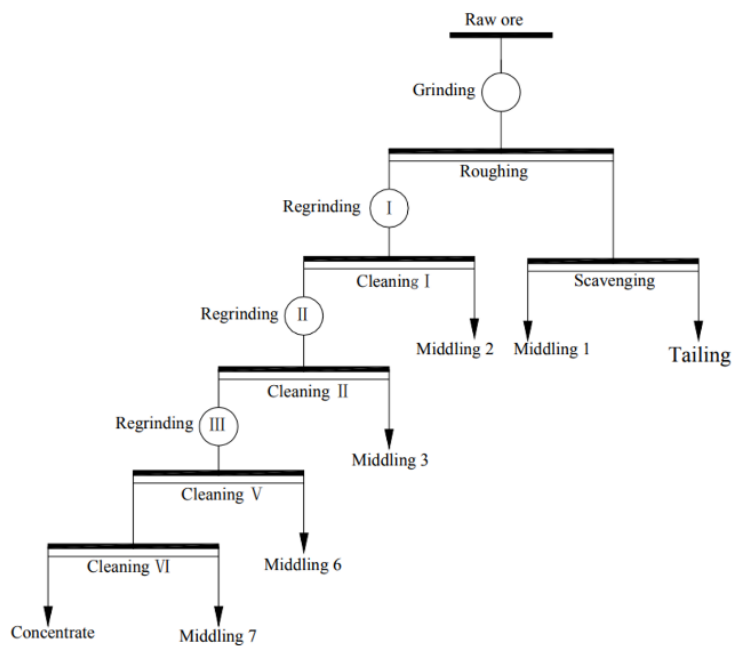


Figure 8. The flowchart of a typical grinding-flotation technique for graphite [24].

The purity of graphite can be increased to about 95 % by using flotation, which can remove most of the hydrophobic minerals. Graphite at this purity can be applied in refractory materials, industrial pencil leads and foundry coatings, etc [28]. However, there is still an improvement in purifying graphite through chemical methods [26].

### 2.2.1.2 Acid-washing method

In the purification of natural graphite, after flotation, it is necessary to use chemical methods to further remove the hydrophobic impurities. Acid washing is one of the commonly used methods including hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), nitric acid (HNO<sub>4</sub>), and hydrofluoric acid (HF). Its mechanism is the chemical reaction between the various acids and impurity substances.

Acid washing can not only further purify graphite but also serve as a pre-treatment before flotation to reduce the impurity content and further improve the hydrophobicity of graphite [29].

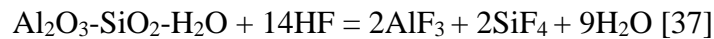
Table 4 summarizes some of the results of acid washing for different natural graphite [30 - 35]. The first three rows of data show the impurity removal ability of acid washing as a pre-treatment of flotation [30], and the rest data are the results of further impurity removal after flotation using different types of acids [31 - 35].

Table 4. Purity of natural graphite by acid washing with different acids [30 - 35].

Sample	Size (µm)	Acids	Time (h)	Temperature (°C)	Feed FC %	Product FC %	Impurities
Inebolu (Turkey) [30]	150	HCl+HF	4	85	23.5	40.1	Pyrite, clay, quartz
Akdagmadeni (Turkey) [30]	150	HCl+HF	4	85	37.9	60.5	Calcite, feldspar, clay, quartz
Coraklidere (Turkey) [30]	150	HCl+HF	4	85	42.3	59.5	Gypsum, pyrite, clay, quartz
Birin Gwari (Nigeria) [31]	75	H <sub>2</sub> SO <sub>4</sub>	1	120	90.0	98.0	Apatite, pyrite, clay
Liaoning (China) [32]	200	H <sub>2</sub> SO <sub>4</sub> + HNO <sub>4</sub>	50 min	100	94.2	99.5	Quartz, clay
Kangwon (South Korea) [32]	200	H <sub>2</sub> SO <sub>4</sub> + HNO <sub>4</sub>	50 min	100	92.9	98.8	Quartz, clay
Neimeng (China) [33]	100	HCl+HF	4.5	100	88.9	99.9	Quartz, pyrite, clay
Natural graphite (Brazil) [34]	20	NH <sub>x</sub> F <sub>y</sub> + H <sub>2</sub> SO <sub>4</sub>	4	90	98.5	99.9	Fe, Al
Bogala (Sri Lanka) [35]	53	HCl	1.15	65	98.5	99.4	Fe, Cu, Mg, Ca

It can be seen from the table that the purity of graphite after acid washing can reach up to 99.9 %. The combination of several acids can improve the purification result, for example, only using H<sub>2</sub>SO<sub>4</sub> can get 98 % graphite, but when HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> are mixed, the purity of graphite can be increased to 99.5 %. When the impurities contain quartz (the main component is SiO<sub>2</sub>), the impurity removal efficiency of HF is obviously higher.

Hydrofluoric acid is reported to be the most effective acid, dissolving most impurities and organics. Especially, its ability to react with SiO<sub>2</sub> makes it the most commonly used acid in acid washing treatments in industrial production.



However, HF is highly corrosive, and some of the fluorides produced are also toxic, so it causes some environmental problems [38]. Another problem that cannot be ignored is that HF is difficult to clean sulphide impurities, which results in a higher S content in the final graphite product. Therefore, further purification of graphite by other methods is required.

### ***2.2.1.3 Acid-base method***

After flotation or acid washing, the removal of sulphide impurities such as FeS is still a difficult problem. Some researchers have shown that calcining graphite at a higher temperature (around 500 - 900 °C) can directly convert sulphides to generate SO<sub>2</sub>. However, sulphide gas has seriously polluted the environment and the emission cost is expensive [39]. The acid-base method by mixing NaOH with graphite and roasting at a high temperature can convert the metal impurities, sulphides, and silicon oxides impurities into silicates, sodium salts, oxides, and hydroxides which can be dissolved in water/acid. Then acid washing is carried out to clean these impurities. By using this method, it can not only remove the sulphide effectively, but the NaOH can also reduce the calcination temperature [40].

Research by Allah D. Jara et al. [41] investigates a three-step acid-base method to purify graphite shown in Figure 9. In the first step, mix 100 g 10 % H<sub>2</sub>SO<sub>4</sub> and 2.5 g 30 % H<sub>2</sub>O<sub>2</sub> with 10 g graphite powder and then sonicate at room temperature for one hour. After that, the mixture was taken out and washed with distilled water until PH=7 and dried at 115 °C overnight. In the second step, add 20 % NaOH evenly to the mixture and bake in a muffle furnace at 550 °C. Finally, continue to wash with distilled water until neutral and dry. In the third step, the dried samples were acid-washed with 18 % HCl or 5 % HF, then cleaned with distilled water until pH = 7.

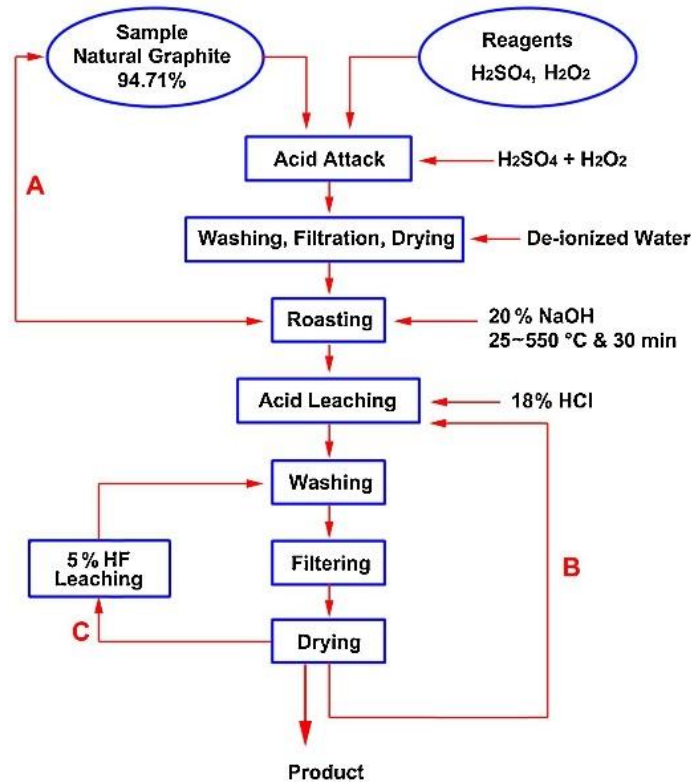


Figure 9. Flowchart of a three-step acid-base method for purification of graphite [41]. From Table 5, the purity and ash content of graphite after treatment by different methods/paths can be seen. Path A is roasting using caustic soda. Both path B and path C add a step of acid washing based on Path A. Path B uses HCl to wash the base-treated graphite and obtains 99.68 % purity graphite, while path C uses HF to improve the purity of graphite to 99.72 %. The impurity removal results between path B and path C are relatively similar, but HF has a great impact on the environment. Therefore, path B is considered to be a more optimal acid-base treatment method.

Table 5. The carbon content, volatile content, and ash content after purification [41].

Process Flow	Sample	Carbon Content	Volatile Matter	Ash Content
Before Chemical Purification	Natural Graphite	94.71 %	2.19 %	3.10 %
After Chemical Purification	Path A	98.91 %	0.00	1.09 %
	Path B	99.68 %	0.00	0.32 %
	Path C	99.72 %	0.00	0.28 %

Compared with the other two methods, the advantage of the acid-base method is that the sulphide in the natural graphite can be removed in the form of salt, which reduces the pollution of the environment. At the same time, NaOH can also react with the silicon oxide impurities that are difficult to remove among the impurities. However, its

disadvantage is that a large amount of caustic soda consumption (400-500 kg NaOH for 1ton selected graphite ore [38]) will cause serious environmental problems.

#### 2.2.1.4. High-temperature method

The theoretical basis of the high-temperature method is that the boiling point of graphite is higher than that of other impurities. After being heated to a high temperature (around 3000 °C) in a protective atmosphere, the impurities will be gasified and taken away, leaving pure graphite. Although there are differences in the types of graphite, the main impurities are similar including Fe, Ca, Cu, K, Mg, Mn, Ni, Zn, Na, SiO<sub>2</sub>, and so on. Table 6 lists their boiling points.

Table 6. The boiling point of main components in graphite.

Components	Fe	Ca	Cu	K	Mg
Boiling points	2862	1484	2562	758.8	1091
Components	Mn	Ni	Zn	Na	SiO <sub>2</sub>
Boiling points	2061	2730	907	882.8	2230

The high-temperature method is not used alone in the actual application process but is often used in combination with other methods. Some impurities in graphite can react with specific gases and be removed in the form of volatile chlorides at a high temperature, which can reduce the maximum temperature required of the method. The research of Chenguang Bao et al [42] aimed at different impurities removing in graphite by introducing corresponding gases at different reaction temperatures to achieve ultra-high-purity graphite production. The types of inlet gas at different temperatures are shown in Table 7. The final results show, that except for a very small amount of B, all other impurities are basically removed during the temperature is kept at 3000 °C for 12 hours.

Table 7. The relationship between temperature and types of gas feed [42].

Temperature (°C)	Gas feed	Impurity removal
T < 2000	Ar	Na, K, Zn etc.
2000 < T < 2400	Cl <sub>2</sub>	Si, Al etc.
2400 < T < 3000	Freon	B, V, Ti etc.

The high-temperature method can be considered as excellent further graphite purification method after flotation or chemical impurity removal. When using graphite with a purity of more than 99 % as raw material, the graphite content can reach an astonishing 99.995 % after high-temperature purification [43].

Although graphite with extremely high purity can be obtained by the high-temperature method, it requires relatively high purity of graphite as raw materials. At the same time, ultra-high temperature heating requires a huge initial investment in equipment and a large amount of energy consumption. Considering the protection of the environment,

exhaust gas treatment is also a very serious problem. These shortcomings lead to the fact that high-temperature purification of graphite is often used in small-scale production in a few specialized industries, and it is difficult to be applied in large-scale industrialization [44].

### 2.2.2 Purification of synthetic graphite

Since synthetic graphite is usually graphitized at a high temperature above 2500 °C, this treatment process is similar to the high-temperature impurity removal process [45]. Most of the impurities in synthetic graphite can also be removed during this process, so the purity of synthetic graphite is very high, and usually, no further impurity removal process is required. However, the carbon content of the raw material has a great influence on the purity of its final product.

Petroleum coke is an important raw material for the production of synthetic graphite, which is the remaining carbonaceous solids in the refining coking process [46]. Petroleum coke after the direct coking process is called raw petroleum coke, which has a carbon content of around 80 %, some volatiles, and moisture residues [47]. In order to obtain raw materials with higher carbon content, raw petroleum coke is usually calcined at 1250 to 1350 °C (shown in Figure 10) to obtain calcined petroleum coke with a carbon content of more than 98 % [47]. After calcined petroleum coke with high carbon content is graphitized at high temperature, the carbon content of graphite products can reach more than 99 %.

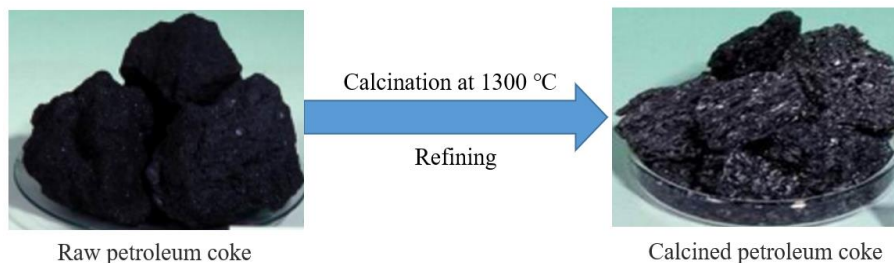


Figure 10. Calcination and purification of petroleum coke [17].

### 2.2.3 Purification of bio-graphite

The main components of impurities in bio-graphite obtained from biomass come from two parts: one part is the trace elements contained in the biomass, and the other part is the metal element catalyst added in the process of graphitization. These impurities can be treated at different stages of bio-graphite production.

#### 2.2.3.1 Acid leaching for biomass

In several works the study of obtaining graphite from numerous types of biomass precursors, including wood, cellulose, husks, and so on is reported. For different types

of biomasses, the types of impurities are not the same [48]. The content of inherent impurities contained in biomass can usually be reduced by acid leaching at the raw material preparation stage [49]. The main content of ash in biomass is shown in Table 8.

Table 8. The main content of ash in the wood-derived biomass.

Composition	Ca	Al	K	Fe	Na	Mg
Content (mg/kg)	2170	2080	1520	986	690	429

Selected 10 wt% acetic acid was heated to 85 °C in a constant temperature reflux reactor (as shown in Figure 11), and then mixed with the preheated biomass and leached at 85 °C for 90 minutes. Finally, it was cooled to room temperature and vacuum filtered to separate the biomass. According to the elemental analysis, the ash content was reduced from 3.5 % to 0.8 % [49].

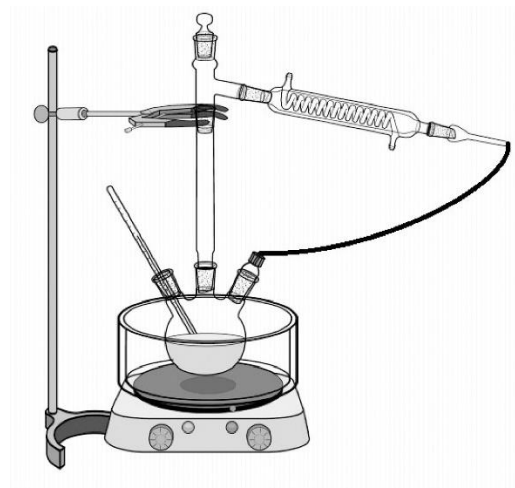


Figure 11. The reflux apparatus for acid leaching.

### 2.2.3.2 Acid washing for bio-graphite

The principle of the acid washing process of bio-graphite is the same as that of natural graphite, which is the chemical reaction between acid and impurities. Nathan A. Banek et al. [50] used the laser method to obtain coarse graphite products with iron content above 50 %. After that, the graphite with a purity of 99.95 % was obtained by refluxing treatment with 50 % volume of hydrochloric acid and mixed acid washing with HNO<sub>3</sub> and HCl. The purity of such graphite can reach commercial battery levels.

### 3. Experiments

#### 3.1 Materials

The raw material used in this study is biochar provided by the company Envigas. The ash analysis of the biochar is listed in Table 9. It shows that the biochar has fewer impurities, and the carbon content can reach 99 %. At the same time, the very small Fe content in biochar will not affect the subsequent determination of the Fe content in graphite.

Table 9. The main content of ash in biochar.

Impurities	Ca	K	SiO <sub>2</sub>	Mg	Na	Mn	P	Fe	Al
mg/kg	2300	1600	1300	530	340	280	160	150	120
Content (wt%)	0.23	0.16	0.13	0.053	0.034	0.028	0.016	0.015	0.012

For the production of bio-graphite,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  is chosen as the catalyst to reduce the graphitization temperature. This catalyst exists in crystalline form and will be mixed with biochar by dissolving it in distilled water. The pictures of catalyst and biochar are shown in Figure 12.



Figure 12.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  catalyst (left) and biochar feedstock (right).

#### 3.2 Method

##### 3.2.1 Graphitization of biochar

In the process of catalytic graphitization,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  is selected as the catalyst for providing Fe ions. The amount of catalyst added should ensure that the mass fraction of Fe is 22.4 wt% of biochar. The weighed  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  crystal was completely dissolved in distilled water firstly, and then the mixture of the catalyst solution and biochar was stirred for 3 h using the magnetic stirrer. After that, the mixed solution

should be fully dried in a drying oven. The magnetic stirrer and drying oven used are shown in Figure 13.



Figure 13. The photos of the magnetic stirrer (left) and drying oven (right).

The dried mixture of the biochar and catalyst was then put into a ceramic crucible and put the crucible into the horizontal furnace for high-temperature graphitization. The configuration of the horizontal furnace is shown in Figure 14. During this process, blew through nitrogen ( $N_2$ ) into the furnace and checked the airtightness at the beginning. The graphitization temperature was set at  $1300\text{ }^\circ\text{C}$  and kept at this temperature for 3 h. Under this temperature, the biochar will gradually transfer into bio-graphite. After cooling to room temperature, samples were removed and subjected to structural analysis.

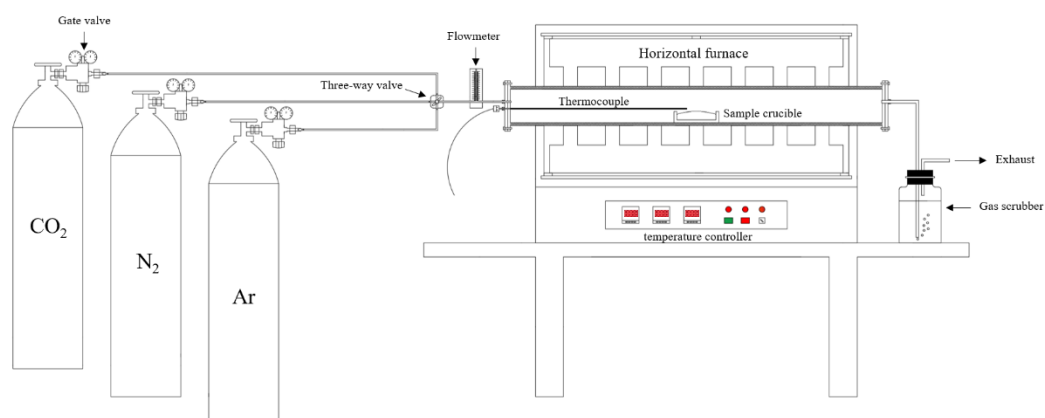
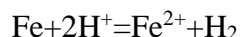


Figure 14. The schematic diagram of the horizontal furnace for graphitization.

### 3.2.2 Acid washing

Taking into account the environmental factors and waste liquid treatment issues, hydrochloric acid (HCl) is selected as the main solution for acid washing instead of hydrofluoric acid (HF). The main principle of acid washing is the oxidation-reduction

reaction between acid and metal elements, and the major reaction chemical equation list below:



Ideally, graphite contains only 22.4 wt% Fe impurities. Under this condition, 8 mol HCl is required to completely remove the impurities in 1 kg of graphite, that is, 8 L HCl solution with a concentration of 1 mol/L is required. But in practice, other impurities in graphite cannot be ignored and a high-temperature water bath promotes HCl volatilization, so the ratio of graphite and HCl added is set as M: V = 1: 10 (g/ml) in this experiment. Meanwhile, in order to fully react to Fe impurities, the reaction time of HCl solution and graphite is set as 2 h.

In order to explore the conditions with higher impurity removal efficiency, the influence of variables such as water bath temperature, acid solution concentration, and graphite particle size on the impurity removal efficiency was investigated. The main equipment is the magnetic heating stirrer (AREX Digital PRO Hot Plate Stirrer) which is shown in Figure 15.



Figure 15. The magnetic heating stirrer used for acid washing [51].

### ***3.2.2.1 Temperature***

The chosen acid solution is 1 mol/L HCl solution. 10 g graphite sample was weighed for each experiment, followed by the addition of 100 ml of HCl solution. The temperature of the water bath was set at 20, 40, 60, 80, and 100 °C, respectively. After the temperature of the water bath was stabilized, the acid and graphite were mixed into a beaker and heated and stirred by the magnetic heating stirrer for 2 hours. The mouth of the beaker needs to be sealed with polyethylene film to reduce the volatilization of HCl. After stirring and waiting time for the beaker to cool down to room temperature, the next step of separation is proceeded.

### 3.2.2.2 HCl concentration

In this group of experiments, the water bath temperature was kept at 80 °C throughout the whole experimental time. In each experiment, 10 g of graphite and 100 ml of HCl solution was added. The HCl concentrations were varied between 1 mol/L, 3 mol/L, and 6 mol/L. After the water bath temperature stabilized, different concentrations of acid and graphite were mixed in a beaker and heated and stirred by the magnetic heating stirrer for 2 h. After stirring, and waiting time for wait for the beaker to cool down to room temperature, to proceed to the next step of separation is proceeded.

### 3.2.2.3 Graphite particle size

In this part of the experiment, the particle size of the graphite was altered. The graphite was sieved into three batches according to the particle size: > 200 μm, 100 - 200 μm, and < 100 μm. To 10 g of graphite of each particle size, 100 ml of 1 mol/L HCl solution was added. The temperature of the water bath was stabilized at 80 °C. After that, keep stirring for 2 h by using the magnetic heating stirrer. After stirring, and waiting time for wait for the beaker to cool down to room temperature, to proceed to the next step of separation is proceeded.

### 3.2.3 Filtering

After the acid washing process, the solid and liquid phase was separated by suction filtration which is shown in Figure 16. After that, the graphite was washed several times with distilled water and filtered until the filtrate from the last washing no longer contained Fe<sup>2+</sup>. To verify this, potassium hexacyanoferrate solution is dropped into the filtrate, if the solution turns blue, it still contains Fe<sup>2+</sup>. If there is no discoloration, the Fe<sup>2+</sup> was removed. At this point, the clean graphite is placed in the drying oven to remove the remaining moisture.

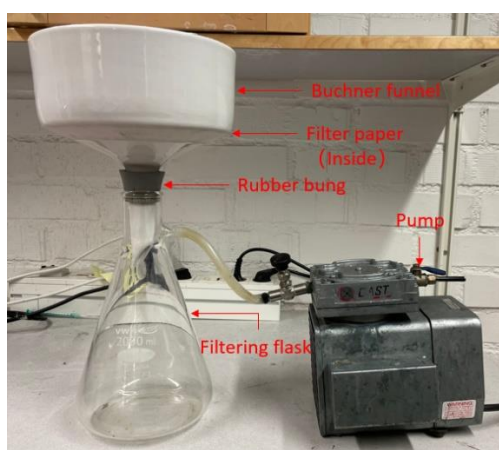


Figure 16. The picture of suction filtration equipment.

### 3.2.4 Analysis

In this study, various analytical methods were used to characterize the structure of graphite and to measure the ash content and impurity removal efficiency of acid washing.

- A scanning electron microscope (SEM) uses a focused electron beam to scan a surface to create an image of a sample [52]. The structure and distribution of iron impurities on the graphite surface before and after acid washing were characterized by SEM.
- The ash species and contents of biochar and graphite will be analyzed and determined by the Eurofins company. Its analytical methods mainly include inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-OES), etc., to determine the content of 25 elements and 10 oxides.
- The Fe content in graphite samples was analyzed by using the muffle furnace which is shown in Figure 17. First, used the analytical balance to weigh about 0.5 g of graphite sample into a crucible, and then the crucible and the sample were placed in the muffle furnace. Raise the temperature of the muffle furnace to 900°C and hold it for 3 h, C will react with oxygen to generate the gas and escape. After cooling, the remaining Fe turns into red powder  $\text{Fe}_2\text{O}_3$  in the air, weigh it and calculate the mass of iron. Finally, the content of iron in graphite can be obtained.



Figure 17. The photo of the Working Muffle Furnace.

## 4. Results

### 4.1 Removal of impurity

Table 10 shows the composition and content of ash in bio-graphite catalyzed by  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . Where Fe is the element with the highest content with 24 wt%. Other impurities are mainly  $\text{SiO}_2$ , Ca, Al, Mn, P, and so on. Most of these impurities can react with HCl to form soluble salts which can be removed by filtration. In this study, the emphasis was on optimizing the conditions for acid washing to improve the removal efficiency of the iron.

Table 10. The ash content in bio-graphite before acid washing.

Impurities	Fe	$\text{SiO}_2$	Ca	Al	Mn	P
mg/kg	240000	1700	740	410	360	130
Content (%)	24	0.17	0.074	0.041	0.036	0.013
Impurities	Mg	K	Na	Co	Cu	
mg/kg	130	<100	58	56	11	
Content (%)	0.013	<0.01	0.0058	0.0056	0.0011	

The SEM micrographs of bio-graphite before acid washing was shown in Figure 18. It can be seen from the figures that a large number of Fe impurity particles are attached to the surface of the graphite, and their distribution does not appear to be agglomerated but is relatively uniform. The uniform distribution of Fe particles can increase the contact area between Fe impurities and HCl solution, and improve the impurity removal efficiency of acid washing. Meanwhile, as can be seen from the micrograph on the left, many iron particles exist in the form of spherical morphologies. This indicates that iron impurities may have melted into a liquid state at 1300 °C and solidified again when the temperature was lowered.

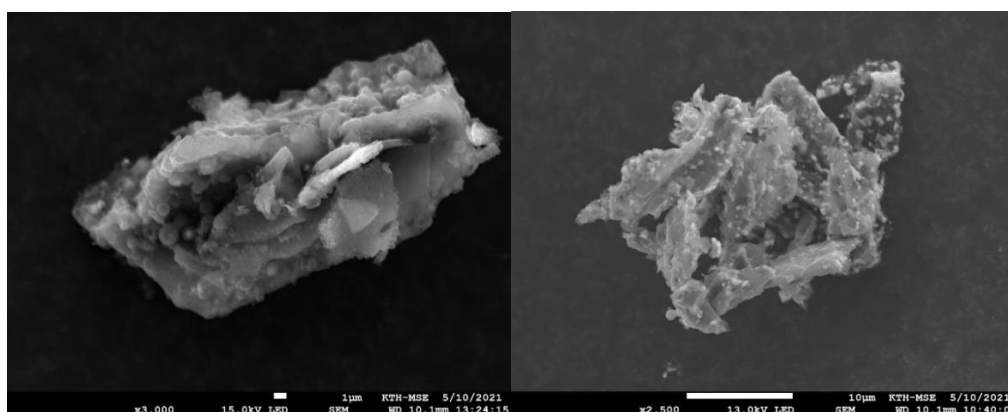


Figure 18. The SEM photomicrographs of bio-graphite before acid washing.

The crude graphite was purified by 1 mol/L HCl solution at 80 °C, filtered, and washed to obtain fine graphite. Table 11 shows the ash composition and content of bio-graphite after acid washing. The content of Fe impurities was significantly reduced, from 24 wt%

to 0.31 wt%. Also, from the SEM micrograph shown in Figure 19, it can be seen that the Fe particles attached to the graphite surface have basically disappeared. At this time, graphite with relatively high purity was obtained.

Table 11. The ash content in bio-graphite after acid washing.

Impurities	Fe	SiO <sub>2</sub>	Ca	Al	Mn	P
mg/kg	3100	1000	390	100	8.4	<20
Content (%)	0.31	0.1	0.039	0.01	0.00084	<0.002
Impurities	Mg	K	Na	Co	Cu	
mg/kg	<20	<100	<50	0.1	2	
Content (%)	<0.002	<0.01	<0.005	0.00001	0.0002	

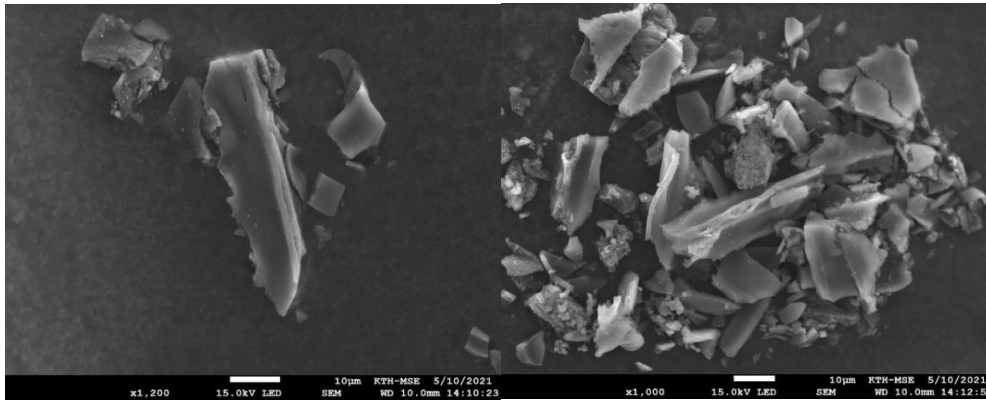


Figure 19. The SEM photomicrographs of bio-graphite after acid washing

In addition to Fe impurities, other impurity contents are also shown in table 11. The content of elements such as P, Mg, K, and Ca cannot reach the minimum limit of the test method after acid washing, and the contents of Co and Cu elements are so small that they can be ignored. Figure 20 intuitively shows the content changes in several impurity elements excluding Fe. It can be seen from the graph that the impurity content has decreased significantly, but the content of SiO<sub>2</sub> is still relatively high. This may be because hydrochloric acid and SiO<sub>2</sub> do not react.

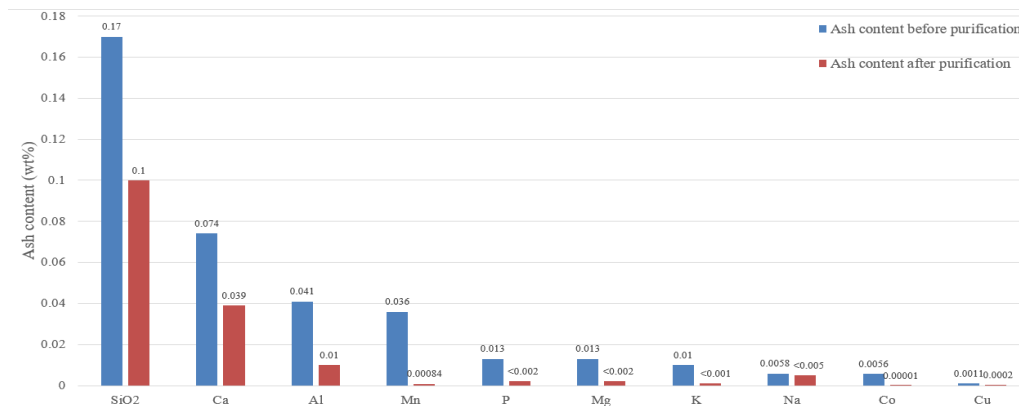


Figure 20. Content change in ash excluding Fe in graphite before and after acid washing.

## 4.2 The influence of temperature

The effect of temperature on the impurity removal efficiency of acid washing was studied by conducting experiments at different temperatures in a water bath. The iron content in the sample and iron removal efficiency was calculated by the following formula:

$$Fe \% = m(Fe_2O_3) \cdot \frac{111.694}{159.69} \cdot \frac{1}{m(sample)} \%$$

$$\eta = \frac{Fe\%_{Initial} - Fe\%_{After}}{Fe\%_{Initial}} \%$$

Fe % - Iron mass fraction in the sample;

$m(Fe_2O_3)$  - Weight of  $Fe_2O_3$  remaining after sample roasting;

$m(sample)$  - The weight of the sample;

$\eta$  - Iron removal efficiency;

Fe %<sub>Initial</sub> - Iron content before acid washing;

Fe %<sub>After</sub> - Iron content after acid washing.

After analysis and calculation, the mass fraction of iron in the graphite before acid washing was 24.25 %. Table 12 records the results after acid washing at 20, 40, 60, 80, and 100 °C. The mass fractions of iron impurities are all below 1 %, which means that the purity of graphite reaches 99 %. The removal efficiency of iron impurities has also reached more than 97 %, which shows that the impurities removal ability of HCl is great.

Table 12. The influence of different temperatures on iron removal efficiency.

Water bath temperature (°C)	20	40	60	80	100
$m(Sample)/g$	0.51019	0.52837	0.52311	0.55641	0.54412
$m(Fe_2O_3)/g$	0.00455	0.00451	0.00402	0.00367	0.00408
Iron content after acid washing (%)	0.62	0.60	0.54	0.46	0.52
Iron removal efficiency (%)	97.43	97.54	97.78	98.12	97.84

From Figure 21, it can be seen intuitively that with the increase in temperature, the iron content decreases and the impurity removal efficiency increases continuously until 80 °C, indicating that a higher water bath temperature can improve the impurity removal efficiency of HCl. However, blindly increasing the temperature is not always effective in improving efficiency. As shown in Figure 21, when the temperature reaches 100 °C, the impurity removal efficiency begins to decline instead. According to the experimental phenomenon, it is speculated that the excessively high temperature will

cause a large amount of HCl to volatilize, thereby affecting the impurity removal efficiency.

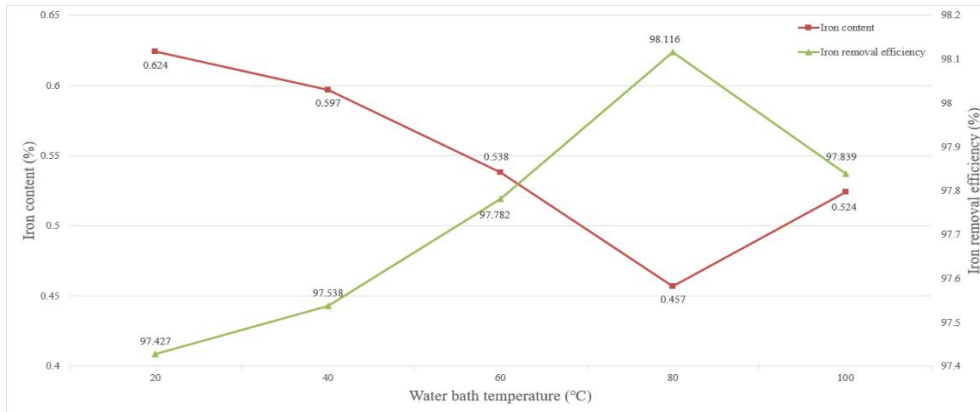


Figure 21. The influence of temperature on iron removal by acid washing.

### 4.3 The influence of acid

#### 4.3.1 The influence of HCl concentrations

In the experiments for HCl concentration, the content of graphite before treatment was 24.67 wt%, and the temperature of the water bath was controlled to be 80 °C. After that, use HCl with concentrations of 1mol/L, 3mol/L, and 6mol/L for acid washing and impurity removal. As can be seen from Table 13, after acid washing with 1 mol/L, 3 mol/L and 6 mol/L of HCl for 2 h, the mass fractions of iron in the graphite were 0.54 %, 0.50 %, and 0.46 %, respectively.

Table 13. The influence of different HCl concentrations on iron removal efficiency.

Water bath temperature (°C)	80		
HCl concentration (mol/L)	1	3	6
$m(\text{Sample})/\text{g}$	0.51085	0.52161	0.51956
$m(\text{Fe}_2\text{O}_3)/\text{g}$	0.00395	0.00375	0.00341
Iron content after acid washing (%)	0.54	0.50	0.46
Iron removal efficiency (%)	97.81	97.96	98.14

It can be seen from Figure 22 that with the increase of the concentration of HCl, the iron impurity concentration decreases, and the impurity removal efficiency increases after acid washing. However, such an improvement does not have a great impact on the application of graphite.

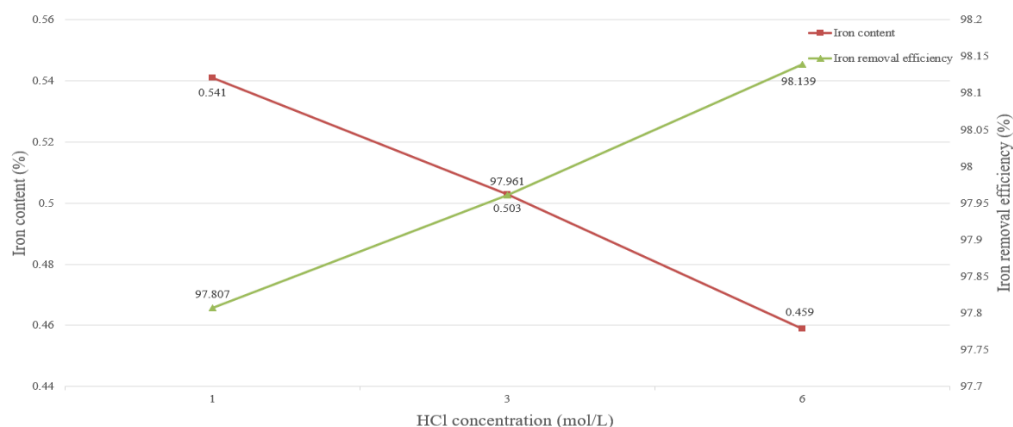


Figure 22. The influence of HCl concentrations on iron removal by acid washing.

### 4.3.2 Multi-step acid washing treatment

In order to further remove impurities and try to improve the purity of graphite to reach 99.9 %. After the first acid washing, two more steps were performed for further impurity removal. The first acid washing was carried out using 6 mol/L HCl at an 80 °C water bath for two hours. In the second step, acid washing was carried out using exactly the same conditions as in the first step. In the end, use aqua regia prepared with 12 mol/L HCl solution and 12 mol/L HNO<sub>3</sub> solution ( $V_{\text{HCl}}: V_{\text{HNO}_3} = 3:1$ ), and heat and stir with graphite for two hours. The results are shown in Table 14.

Table 14. The iron impurity content after multi-steps acid washing.

	First washing	Second washing	Third washing
Iron content after acid washing (%)	0.46	0.44	0.33

As can be seen from the results, after the second acid washing, the iron content decreased by only 0.02 wt%. After using aqua regia, the iron content decreased from 0.44 wt% to 0.33 wt%. That means the strong acidity and strong oxidizing properties of aqua regia further could improve the purity of graphite through acid washing.

### 4.4 The influence of particle size

In the above experiments, it obtained a more suitable acid washing temperature (80 °C) and concentration (6 mol/L) of HCl to produce the bio-graphite with higher purity. Under this treatment, the purity of graphite reaches more than 99.5 %, which can meet the requirements of various applications such as electrodes.

In this group of experiments, the graphite before acid washing was sieved into <100µm, 100 - 200 µm, and > 200µm according to particle size, and its Fe content was measured after acid washing in a water bath. Table 15 lists the impurity removal efficiencies of various particle sizes of graphite. It can be seen that when the particle size of graphite

is  $> 200 \mu\text{m}$ , its impurity removal efficiency is 97.66 %. With the decrease of graphite particle size, the impurity removal efficiency by acid washing can reach 98.12 % under the same conditions. This proves that the particle size of graphite has a certain influence on the iron removal of graphite during the acid washing process.

Table 15. The influence of different graphite particle sizes on removal efficiency.

Water bath temperature ( $^{\circ}\text{C}$ )	80		
Particle size ( $\mu\text{m}$ )	$> 200$	100 - 200	$< 100$
Initial Fe content (%)	24.52	24.53	24.25
Iron content after acid washing (%)	0.58	0.50	0.46
Iron removal efficiency (%)	97.66	97.95	98.12

## 5. Discussion

Through the experiments of several sets of control variables, this article studied the factors affecting the acid washing purification of iron-catalyzed bio-graphite and tried to further improve the purity of the bio-graphite. The advantages and disadvantages of using acid to remove impurities from bio-graphite are obvious. Its advantages mainly include the following:

- The principle of purification and process is relatively simple. The main reactions are the chemical reactions between the acid and the metal and metal oxide, which can achieve the removal of most impurities in bio-graphite.
- Lower cost. Graphite with a purity of about 99.5 % can be obtained by using low-concentration HCl, and the cost is relatively low compared to HF treatment and high-temperature treatment.
- Less impact on the environment. The H<sub>2</sub> generated by the reaction has little impact on the environment, and the waste liquid is easy to deal with. The filtered washing liquid can be collected to recover the FeCl<sub>2</sub> in it, to realize the reuse of resources.

The biggest disadvantage of this method is that its ability to remove Fe impurities is limited, and it is difficult to obtain bio-graphite with purity above 99.9 %.

From the results, the temperature of acid washing, the concentration of the acid solution, and the size of graphite all have influence on the final impurity removal efficiency.

Regarding the temperature, the increase in acid washing temperature is accompanied by some improvement of iron removal efficiency. This may be because as the temperature increases, the thermal motion of the molecules is more vigorous, making the reaction easier. And the increase in temperature can also speed up the reaction rate so that the stirring time of acid washing is greatly shortened. However, the temperature rise caused the problem of the volatilization of HCl. Excessive temperature makes the volatilization of HCl affect the reaction to a large extent, resulting in a decrease in the impurity removal efficiency.

Another influencing factor is the concentration of the acid solution. The increase of the acid concentration represents the increase of the H<sup>+</sup> concentration in the solution, which makes the reaction proceed to the production side to improve the impurity removal efficiency. The results of multi-step acid washing show that aqua regia with strong acidity and strong corrosiveness can further improve the purity of graphite to about 99.7 %, but this improvement is limited. At the same time, the use of strong acid will inevitably bring waste liquid treatment problems and cost problems.

The influence of graphite particle size on the acid washing is mainly by reducing the size and increasing the contact area between iron impurities and acid solution to improve the reaction efficiency and increase the degree of reaction. The smaller the

graphite particle size, the more the iron is in contact with the acid, and the easier it is to react.

Theoretically, as long as the amount of HCl is large enough, iron and metal impurities in graphite should be removed totally. According to the ash analysis results, the final ideal graphite purity can reach above 99.8 %. However, such results did not appear in the experiments' results. Several possible reasons are listed below:

- Some iron impurities are embedded in the graphite structure, the acid did not completely react with them.
- Some FeCl<sub>2</sub> attached to the graphite was not washed away after several times of washing using distilled water.

## 6. Sustainable development goals

Sustainable development has always been an important concept and research direction in today's society. The seventeen Sustainable Development Goals (SDG) were proposed by the United Nations in 2015 and are also known as the Global Goals. These goals cover many aspects and provide references and directions for the development of various fields of society. This project also matches several aspects of the SDGs, which are discussed in detail below:

### ➤ **Goal 9: Industry, innovation and infrastructure**

Exploring efficient purification methods to obtain high-purity bio-graphite, will become an important means of obtaining graphite in the future. Its raw material can be waste biomass, which greatly reduces the harm of mining fossil minerals. This technological innovation is fully in line with SDG 9.

### ➤ **Goal 12: Responsible consumption and production**

The main raw material of bio-graphite is biomass, which can be obtained by recycling and utilizing waste organic matter. This is without a doubt a responsible production method, fully compliant with SDG 12.

### ➤ **Goal 13: Climate action**

Technological innovations to obtain bio-graphite from biomass and purify it to meet the requirements of advanced technological applications have the potential to replace natural graphite obtained through mining in the future. This can greatly reduce the impact of mining on the climate and the environment, in line with the requirements of SDG 13.

## 7. Conclusion

In this work, the graphite produced by iron catalysis was purified using acid washing. This method is a relatively simple and efficient treatment, and its influencing factors have been studied in detail in this study. It shows that the increase of acid washing temperature in a certain range, the increase of acid concentration, and the decrease of graphite particle size can improve the impurity removal efficiency to a certain extent.

Bio-graphite with a purity of 99.67 % was obtained by multi-steps acid washing at a water bath temperature of 80 °C. At this temperature, graphite with a particle size of fewer than 100  $\mu\text{m}$  is treated with 1 mol/L HCl solution, and its purity can also reach 99.5 %. This allows the bio-graphite after purification to meet the requirements of a variety of applications such as metallurgical electrodes and refractory materials. Nevertheless, acid washing cannot increase the purity of graphite above 99.9 % for advanced technology applications. How to achieve further in-depth impurity removal is still a problem worth investigating.

## **8. Acknowledgement**

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