Journal of Mining and Environment (JME) Vol. 16, No. 2, 2025, 371-385

Shahrood University of Technology

Journal of Mining and Environment (JME)

Journal homepage: www.jme.shahroodut.ac.ir

Iranian Society of Mining Engineering (IRSME)

Purification of Natural Flake Graphite with Acid Leaching Method using a Two-step Method of Introducing Additives

Jiaye Li[1, 2], Jing Zhao[1, 2*], Zebin Wang[1, 2], Huan Liu[1, 2], Qing Wen[1, 2], Jinling Yin[1, 2], Ze Li[3], Yang Lei[3], and Guiling Wang[1, 2]

1. Key Laboratory of Superlight Materials and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, P. R. China, Guiling Wang, Jing Zhao

2. b Heilongjiang Hachuan Carbon Materials Technology Co., LTD, National Quality Supervision and Inspection Center Of Graphite Products, No. 88 Kangxin Road, Jiguan District,Jixi City, Heilongjiang Province, 158100, P. R.Chinac

3. Heilongjiang transportation investment group Co., LTD, No. 899, Innovation 3rd Road, Songbei District, Harbin, Heilongjiang Province, 150025, P. R. China

Article Info

Received 8 March 2024

Received in Revised form 1 August 2024

Accepted 8 November 2024

Published online 8 November 2024

DOI: 10.22044/jme.2024.14294.2670

Keywords

Graphite

Purification

Alkali-acid process

Response surface methodology

Auxiliary agent

Abstract

Traditional graphite has safety and environmental issues, associated with fluorine purification. To address these issues, an energy-saving and efficient graphite purification process can be explored through the acid leaching method with composite additives. The acid leaching process was studied and optimized in detail using the controlled variable method including the effects of the soaking time and temperature on the graphite purification process. Then the response surface method was used to simulate the orthogonal experiment of graphite purification to verify the correctness of the single-factor, experiment. The purity and micromorphology of the graphite samples at each stage were characterized and tested. The experimental results showed that the optimal liquid-to-solid ratio of the acid solution and graphite was 20:1, which could make the fixed carbon content reach 99.77%. On the basis of these optimal process conditions, the addition types were further explored. The experimental result showed that the best addition was ascorbic acid and EDTA, which could reduce the content of various impurities in the graphite raw material without destroying the microstructure of the graphite. Benefitting from the addition of compound additives in the two-step process, almost all the metal ions were leached from the graphite. After the acid and water leaching, the fixed carbon content of graphite could reach 99.96%. The process parameters proposed in this paper were scientifically verified by both the single-factor and multi-factor experiments, and innovative and effective additives were introduced in different steps to make the graphite purity break through 99.9%, which was difficult to reach by the traditional method.

1. Introduction

Graphite is a significant mineral resource that provides diverse technological applications in the industries such as lithium-ion batteries, fuel cells, refractory materials, and electric vehicles [1]. Although China possesses the world's largest graphite reserves, and can engage in a large-scale graphite production, the technological proficiency of the graphite industry in the country remains lower compared with other major producing nations [2]. Numerous graphite enterprises in China have not yet mastered the cutting-edge graphite technologies, and the level of graphite processing remains at a rudimentary stage, with a minimal involvement in the advanced processing sectors. Consequently, the product prices are extremely low, resulting in substantial resource wastage and outflows [3]. Moreover, at the present stage, China is vigorously developing the industries like the high-tech materials and new energy, which require substantial quantities of high-quality, high-purity graphite. Unfortunately, the exploration and practical production applications of graphite materials are not satisfactory [4]. With the increasingly stringent

---

✉ *Corresponding author: zhtdzhn@hrbeu.edu.cn (J. Zhao)*

requirements for the graphite purity in various fields, China is unable to independently produce the high-end graphite products, due to the expensive imported high-purity raw materials [5]. The graphite industry does not match the current rapid technological strength and economic level, which greatly limits the economic development [6].

High-purity graphite is the prerequisite for the subsequent processing of graphite materials, so the graphite purification is the decisive key to the development of the graphite industry. Flotation of the graphite ore is a preliminary processing step, and further purification processes are required to produce the high-quality graphite. Commonly, there are four typical industrial graphite purification methods such as the alkaline acid method [7], the hydrofluoric acid method [8], the chloride roasting method [9], and the high temperature method [10]. Among these methods, hydrofluoric acid is highly toxic, and a dangerous carcinogen [11]. Additionally, the chlorination roasting method is difficult to process the waste gas [12], and causes a severe damage to the equipment and environment. These two methods are inconsistent with the development concept of green and environmental protection, so they are not advocated. The high-temperature method can produce ultra-high-purity graphite with a carbon content of 99.99%. However, this method has a high energy consumption and cost, and is only used in specific fields such as the aerospace and nuclear industry. Among them, the alkaline-acid purification of flotation of the graphite concentrate has the advantages of being a simple process, low cost, and complete graphite microstructure. It is the most widely used method in the graphite purification and production [13]. However, the traditional acid-base method for purifying graphite still has problems such as low graphite purity, a high-energy consumption, and a serious equipment corrosion [14]. Jara conducted a study, examining the effects of acid type and liquid-solid ratio, the reaction time, and the temperature on the carbon content of Ethiopian natural flake graphite. The obtained purified graphite exhibited a carbon content of 99.72% [15]. Wang and his research team upgraded a 90.2%; a graphite concentrate to 99.0% by the traditional alkaline acid method [16]. However, the purity of graphite is still not enough to meet the needs of the high-end applications. As the main process in the acid-base purification of graphite, acid leaching has an absolute qualitative impact on the graphite purification effect [17].

Herein, this work explores the optimal process conditions of the acid leaching process through experiments, and realizes the preparation of the high-purity graphite by the acid-base method through the two-step method of introducing additives. The impurity content and graphite micromorphology in each stage are tested and characterized to reveal the purification process. This innovative methodology holds the promise of significantly enhancing the quality of the final graphite product.

2. Materials and Methods

2.1. Materials

The raw material used in this work was the concentrate of the flotation of the natural large-scale graphite from Jixi Liumao, and the fixed carbon content of the raw material was 94%. Sodium hydroxide (of analytical grade), hydrochloric acid (12 mol/L), ascorbic acid (wt% > 99%), and ethylenediaminetetraacetic acid disodium (EDTA) (of analytical grade) were of analytical reagent. The employed solvent was deionized water, which was obtained from the ultrapure water machine BASIC-Q15.

2.2. Experimental methods

The first step in the experiment was alkali fusion. Weigh graphite and sodium hydroxide with a mass ratio of 1:1.3, and then add deionized water according to a solid-liquid ratio of 1:1.1 to prepare a sodium hydroxide solution. The sodium hydroxide solution and graphite powder were mixed, and the stirred evenly in a beaker, ultrasonicating at 50 °C for 30 minutes. The sample obtained after the ultrasonic treatment was added to an air-drying box to dry the moisture, then placed in a tube furnace, and baked at 500 °C for 120 min. The graphite sample prepared in the above alkali fusion step was transferred to a beaker, adding an appropriate amount of deionized water to immerse the sample. The samples were soaked for 30 min under magnetic stirring at 50 °C (rotation speed 750 rpm), and filtered with vacuum filter. The above steps were repeated until the filtrate was neutral (pH = 7), and then the filter cake was dried, and the graphite materials were collected.

The second step of the experiment was acid leaching. 2 g of alkali fused graphite were added to the solutions of different concentrations (0.5 mol/L, 1 mol/L, 1.5 mol/L, 2 mol/L, 2.5 mol/L, and 3 mol/L). The solid-phase temperature range was set as 35 °C, 50 °C, 65 °C, 80 °C, and 95 °C. The solid-liquid ratio range was set as 1:10, 1:15, 1:20, 1:25, and 1:30, and the reaction time was set as 40 min, 60 min, 80 min, 100 min, and 120 min. The graphite sample prepared by the acid leaching step was pumped and filtered, and the graphite collected by washing the filter cake was added with an appropriate amount of deionized water. The graphite sample became neutral after pumping and filtering at 50 °C for 30 minutes. After washing, the graphite sample was dried, and the finished product was obtained.

Then the influence of the type of additives and the site of adding additives on the purity of graphite was discussed. Ascorbic acid and EDTA were added to the acid-leaching process to further improve the purity of graphite. Finally, the influence of the number of additives on the effect of acid-leaching graphite was discussed by the control variable method.

2.3. Characterization and testing methods

To remove the impurities in graphite, a series of characterization analyses were carried out. The X-Ray Diffraction (XRD) patterns were obtained using a Rigaku D/Max-TTR III X-ray diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) in the 2θ range of 10-80°. The Scanning Electron Microscope (SEM) images were acquired using a JEOL JSM-6480A.The X-Ray Fluorescence (XRF) data was acquired using the Bruker S8 Tiger [18].

To understand the mineral composition and crystallization status of graphite, the raw material, an X-Ray Diffraction (XRD) analysis, of graphite raw material was carried out. Optical microscopy is an effective method to observe the microscopic structure of graphite, which can observe the optical properties and microstructure of the graphite raw materials. Scanning electron microscopy analysis was used to test the microscopic morphology characteristics of graphite in the purification process. XRF analysis spectroscopy was performed on the samples at each stage of the graphite purification. To test the content of each oxide impurity in the composition, the fixed Carbon Content (GC%) of the graphite samples was employed as the main basis for judging the purification effect of graphite. According to the graphite chemical analysis method GB/3521-2008, the fixed carbon content of the graphite samples obtained during the experiment was determined. The purity of graphite enhanced with the increasing GC%, demonstrating that the purity of graphite, was effectively improved.

3. Results and Discussion

3.1 Characterization

The XRF, XRD, and SEM were employed to present the characters of the graphite samples at each stage. The proportion of ingredients of the samples were shown in Table 1. It is clear that the two-step method of introducing additives has a significant effect on the graphite purification, which can make the carbon content of the graphite reach 99.9621%.

Table 1. Carbon content of purified graphite after different process conditions.

	C%	SiO_2%	Fe_2O_3%	Al_2O_3%	CaO%	MgO%	Others
A	94.8057	2.9566	0.3584	1.3997	0.1906	0.1389	0.1501
B	98.7931	0.6384	0.1551	0.3218	0.0339	0.0231	0.0346
C	99.7669	0.0721	0.0526	0.0886	0.0126	0.0033	0.0039
D	99.9621	0.0298	0.0012	0.0027	0.0015	0.0009	0.0018

According to the results from Table 1, the main impurities in the graphite raw material A were SiO_2, Fe_2O_3, Al_2O_3, and other oxides. The carbon content of the graphite sample B after the alkali fusion treatment was 98.7931%; there are still many impurities in the graphite, presenting that the impurities cannot be removed by only a one-step alkali fusion treatment. The purity does not meet the standards of the high-purity graphite, which has a carbon content of more than 99%. Under the optimal acid leaching process conditions, the carbon content of the graphite sample C reached 99.7669%. After acid leaching, each element decreases with acid leaching and water leaching. The purity of graphite has been greatly improved, but it still has not reached the pre-set target (99.95%). The carbon content of the graphite sample D was obtained after introducing additives using a two-step method under optimal acid leaching conditions. By adding ascorbic acid during the acid leaching process and EDTA during XRD, the water washing process, the content of various metal elements in the graphite sample were significantly reduced, and the carbon content of the graphite reached 99.9621%. It was proved that the two-step method of introducing additives had a significant effect on the graphite purification [19].

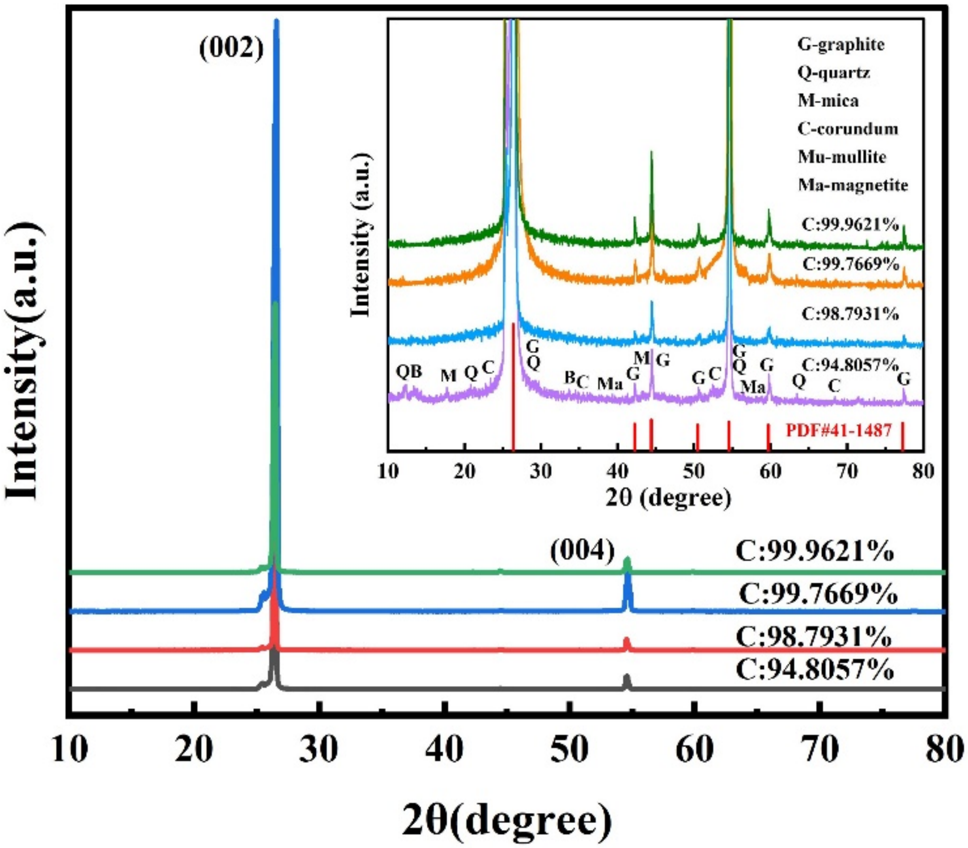

Figure 1. The XRD patterns of the graphite samples in four stages.

Figure 1 exhibits the XRD patterns of the graphite samples in four stages, confirming that the structure of the graphite is maintained well after treatments. The graphite's crystalline structure serves as the foundational basis for its excellent performance characteristics [20]. In the process of graphite purification, it is essential to strive for the preservation of the integrity of the graphite structure. As depicted in Figure 1, which illustrates the XRD patterns of the graphite raw material and graphite after acid leaching, these patterns offer valuable insights. In the pattern of the raw material, the higher the intensity of graphite diffraction peaks indicated a larger graphite content, and a well-defined crystallinity. After alkali treatment, alkali fusion, and acid leaching, the number of impurity peaks gradually decreased, while the graphite diffraction peaks were still strong. This result indicates that the acid leaching process has a relatively minimal impact on the graphite microcrystalline structure. Therefore, the basic structure of graphite remains basically intact during this purification process, and its excellent properties can be maintained, while the impurities are removed. This method ensures the integrity of the purified graphite, giving it the properties of an indispensable material in a variety of industrial applications. The results of the XRD patterns demonstrate that the purification process effectively removes the impurities without damaging the underlying graphite structure [21].

Figure 2 (a, b) showed the SEM images of the graphite raw materials, presenting that the large-scale graphite had an obvious lamellar structure. Additionally, there were many white spots on the surface of graphite; these were the impurity components in graphite. Figure 2 (c, d) showed the SEM images of graphite after the only one-step alkali fusion. It could be seen that there were still many white spots on the surface of graphite after the alkali fusion treatment; these were the salt compounds remaining in graphite after the reaction of the impurities in graphite and sodium hydroxide. Moreover, the fixed carbon content of graphite was only 98.79%, demonstrating that the further acid-leaching treatment was needed for the graphite purification [22].

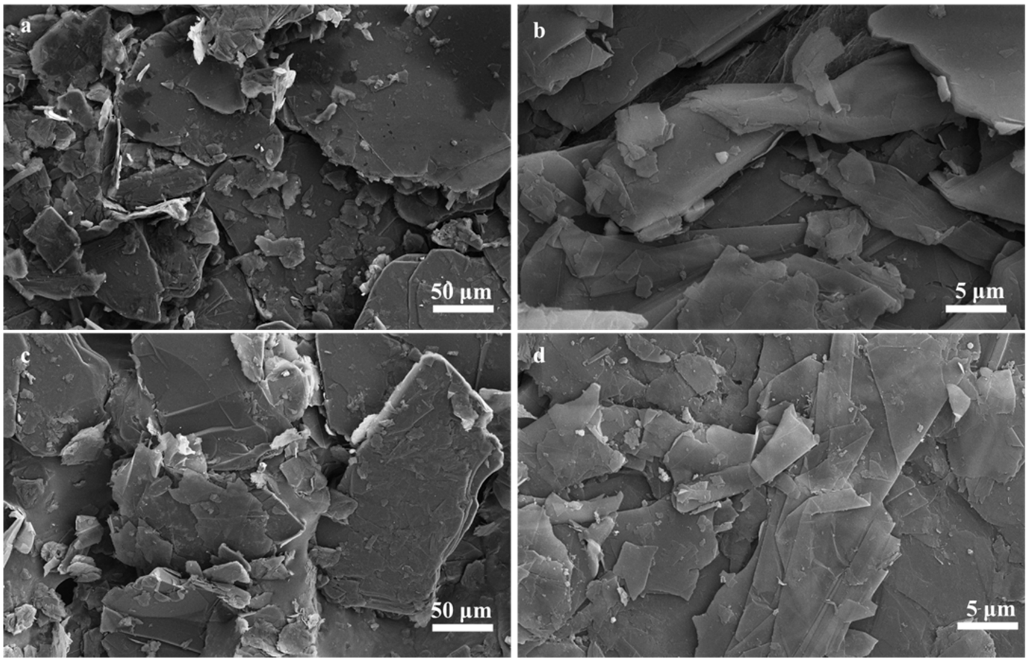

Figure 2. (a, b) The SEM images of the graphite raw materials. (c, d) The SEM images of graphite after alkali fusion.

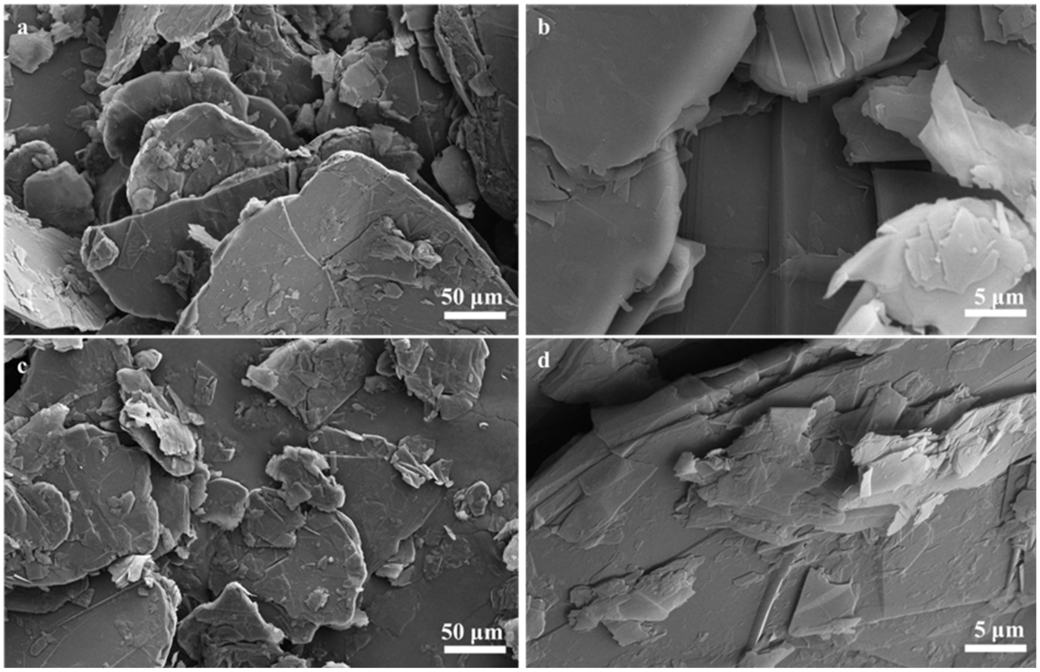

Figure 3. (a, b) The SEM images of graphite after the alkali fusion-acid leaching. (c, d) The SEM image of graphite after a two-step process, aided by the introduction of additives in the alkaline acid method.

Figure 3 (a, b) showed that the SEM images of graphite under the optimal conditions of alkali fusing and acid leaching process. Compared with Figure 2, the white spots on the surface of graphite after acid leaching were significantly reduced, and the purity of graphite was significantly improved. Figure 3 (c, d) showed the SEM image of graphite after purification by the two-step auxilium-assisted alkaline acid method, and the white spots on the surface of the graphite almost disappeared completely. These results proved that the graphite was efficiently purified, and in accordance with the fixed carbon content. Moreover, the microstructure of graphite treated by this method was still lamellar, indicating that the basic structure of graphite was not destroyed.

3.2. Selection of optimal conditions for acid leaching

Since the acid leaching process would be affected by many factors, a variety of parameter ranges were designed to determine the best optimization conditions. The specific values are shown in Table 2, and the detailed are described in the test method section. Different concentrations of acid solution were mixed with graphite at a set solid-liquid ratio (1:20). The experiment was conducted at 80 °C for 80 min. Based on the results, the influence of the acid leaching concentration in the acid leaching step on the graphite purification was determined, and shown in Figure 4(a). When the acid concentration was less than 1.5 mol/L, the graphite purification effect was better with the increasing acid concentrations. The optimized purification effect of graphite was 99.45% with the concentration of 1.5 mol/L. When the concentration of the acid solution was larger than 1.5 mol/L, the fixed carbon content of the purified product showed a downward trend with the increase of the acid concentrations. When the concentration of the acid solution was more than 2.5 mol/L, the fixed carbon content of the purified product decreased slowly, and the increase of concentration had a little effect on the fixed carbon content of graphite. As the acid concentration increases, the metal precipitates generated during alkali fusion react with the acid. The precipitate can dissolve in the water and filter out, so the fixed carbon content increased gradually. However, when the concentration of hydrochloric acid increased, there was a downward trend due to its volatile character. Hence, the high concentration could reduce the amount of reaction between the acid and the metal ions, causing harm to the environment. Moreover, the excess acid would react with sodium silicate with the increasing acid content, which was not completely removed during the alkali leaching process[23]. This could result in the formation of the polycrystalline silicic acid, which tended to agglomerate. From an industrial perspective, the high concentration of hydrochloric acid could accelerate the corrosion of the equipment, and also increase the amount of waste liquid treatment. Therefore, 1.5 mol/L was used as the acid leaching concentration through the above results.

Table 2. Factors of optimal conditions.

Factors	1	2	3	4	5	6
Concentration /(mol/L)	0.5	1	**1.5**	2	2.5	3
Temperature/°C	35	50	**65**	80	95	
Time/min	40	**60**	80	100	120	
Liquid-to-solid ratio	1:10	1:15	**1:20**	1:25	1:30	

The acid solution with a concentration of 1.5 mol/L hydrochloric acid was mixed with graphite at a set of solid-liquid ratio of 1:20. Then the reactions were carried out for 80 min at various temperatures (35 °C, 50 °C, 65 °C, 80 °C, and 95 °C). Subsequently, the influence of the acid-leaching temperature on the graphite purification in the acid-leaching step was determined, and shown in Figure 4(b). With the increasing acid-leaching reaction temperatures, the fixed carbon content of graphite increased firstly, and then decreased. When the temperature was 65 °C, the fixed carbon content of graphite was the highest of 99.64%, indicating the purification effect. When the temperature was lower than 65 °C, the fixed carbon content of graphite increased with the increasing temperature, which resulted from the inorganic reaction between hydrochloric acid and the impurities. The reaction rate accelerated as the temperature increased. The higher temperature was beneficial to optimize the purification effect, and improved the reaction efficiency. In Figure 4(b), when the temperature was higher than 65 °C, further increasing the reaction. The temperature could not improve the purity of graphite, and was not conducive to the removal of the impurities. This is because the reaction that occured during the acid leaching process was a reaction between the acid and metal hydroxide, which was a typical exothermic reaction. According to the principle of thermodynamics, increasing the temperature could reduce the equilibrium constant of the reaction, and promoted the reverse reaction, hindering the removal of heterogeneous reactions [24]. Moreover, as the acid leaching temperature further increased, the dehydration of silicic acid in the solution led to an increase in the formation of the rate of the silicic acid colloid groups. The increase in the insoluble silica gel and the system viscosity not only produced a new insoluble matter, but also affected the removal of the soluble salt impurities during the subsequent washing processes. After the temperature reached 65 °C, the temperature continued to increase, which increased unnecessary reaction, energy consumption, and affected the acid leaching efficiency, reducing the purity of the graphite obtained by acid leaching. Therefore, 65 °C was selected as the optimal reaction temperature for the acid leaching step.

Graphite was mixed with a 1.5 mol/L hydrochloric acid solution at a fixed ratio. Then the reaction was performed at 65 °C for the corresponding times (40 min, 60 min, 80 min, 100 min, and 120 min). The influence of the acid-leaching time on the graphite purification in the acid-leaching step was determined, and the results were shown in Figure 4(c). When the acid leaching time was less than 60 minutes, the fixed carbon of the graphite samples increased with the increase in the acid leaching time. After more than 60 minutes, the fixed carbon first remained stable, and then decreased slightly. When the acid leaching time was prolonged within a certain range, the contact time between hydrochloric acid and the metal precipitate was more sufficient, which was conducive to the complete reaction, so the fixed carbon was increased, and the reaction effect was better. However, the acid leaching time is too long, and the reaction in the acid solution was completed; blindly prolonging the reaction time would make the water leaching process residue of the metasilicic acid slowly deposited down, forming a multi-molecule silicic acid colloid that was not easy to remove, affecting the purification effect. The excessive increase in the reaction time would make the equipment immersed in a strong acid solution for a longer time, resulting in a serious corrosion of the equipment, and would also prolong the production cycle, and reduce the utilization rate of the equipment [25]. Increasing the acid-leaching reaction time could improve the purification effect, but the purification effect of graphite could be improved infinitely. Considering the purification effect and the production cost, the acid leaching time was determined to be 60 minutes, and the fixed carbon content was 99.77%.

When other conditions were determined, the purification effect could be further explored by changing the solid-liquid ratio. According to the results, the effect of the liquid-solid ratio in the acid-leaching step on the graphite purification was determined, and the experimental data and rules were shown in Figure 4(d). The results showed that the fixed carbon content of graphite after acid leaching increased first, and then flattened with the increasing ratio of acid to graphite. When the liquid-to-solid ratio was lower than 20:1, as the acid ratio increased, the dispersion effect of graphite in the acid solution was better. The leaching reaction was more complete, so the fixed carbon content also increased, and the graphite purity increased. However, when the liquid-to-solid ratio exceeded 20:1, the amount of acid reacting with graphite reached the maximum, and the improvement in the graphite purity was negligible. Further increasing the proportion of acid would only cause a waste of resources, and was not conducive to the subsequent water washing, and would further intensify the corrosion of the equipment. Therefore, after a comprehensive consideration, the liquid-solid ratio of the acid to graphite was determined to be 20:1.

3.3. Simulation of orthogonal experiment by response surface method

The simulation modelling was based on single-factor experiments. The simulation parameters are shown in Table 3, with a single-factor value as the independent variable, and the fixed carbon content as the evaluation indicator. According to the data in Table 4, a quadratic polynomial regression model for fixed carbon content was obtained by the Design-Expert 8.0 software [25].

$$Y = 99.75 + 0.044A - 0.097B + 0.11C + 0.029D + 0.035AB + 0.045AC - 0.0025AD + 0.078BC - 0.0075BD + 0.012CD - 0.34A^2 - 0.27B^2 - 0.17C^2 - 0.038D^2$$

where, Y is the fixed carbon content, A is the hydrochloric acid concentration, B is the temperature, C is the time, and D is the liquid-solid ratio.

According to the results of the analysis of variance (Table 4), the $P < 0.001$ of the regression model indicates that the regression model is highly significant; the $P > 0.05$ of the model mismatch term indicates that the model mismatch is not significant, and the regression model has a good fit. Thus the above 4 factors have a significant impact on the fixed carbon content from the P value; the order of influence on fixed carbon content is time, temperature, acid concentration, and the liquid-solid ratio.

$P < 0.05$ in the regression model of the fixed carbon content indicates that the interaction of the four regression terms is significant in the regression model. The determination coefficient R^2 and correction determination coefficient are close to 1, indicating that the fixed carbon content fitting the regression model has a high reliability.

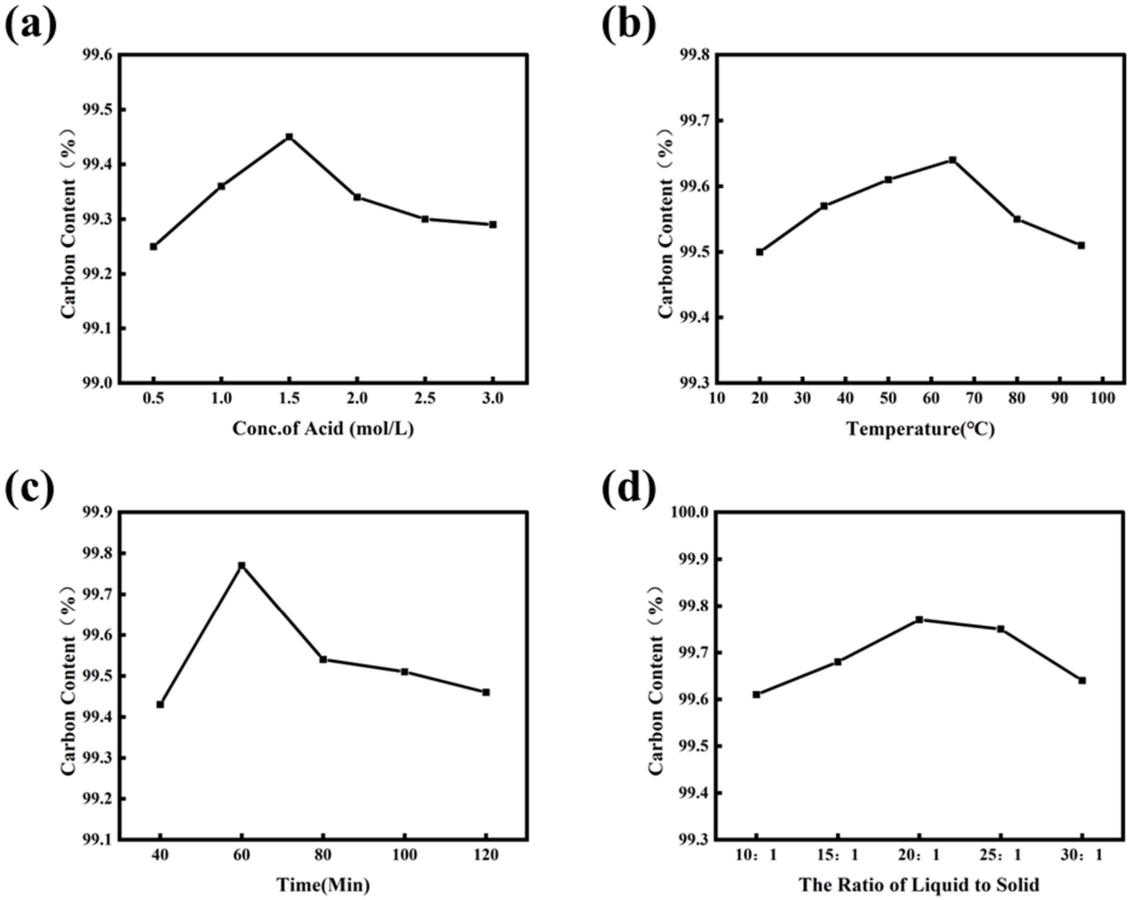

Figure 4. (a) Effect of the acid solution concentration on carbon content fixed in graphite. (b) Effect of the acid leaching temperature on the carbon content fixed in graphite. (c) Effect of the acid leaching time on the carbon content fixed by graphite. (d) Effect of the ratio of liquid to solid on the carbon content fixed in graphite.

According to the results of the regression model, the Design-Expert 8.0 software was used to draw the 3D response surface diagram of the interaction effects of each factor. The response surface of the cone diameter and the depth of embedment to the effective depth are shown in Figure 5 (a). When the acid concentration decreased from 2.5 mol/L to 0.5 mol/L; the fixed carbon content first increased, and then decreased with the increase in the temperature. When the temperature changed from low to high, the fixed carbon content increased first, and then decreased with the increase in the acid concentration. As shown in the response surface (Figure 5(b)) of time and the acid concentration to a fixed carbon content, when the temperature was from 40 °C to 80 °C, the higher the acid concentration used, the fixed carbon content of graphite first increased, and then decreased. As shown in Figure 5(c), when the decrease in the liquid-solid ratio, the graphite purity increases first, and then decreases with the acid concentration, and the curve amplitude before and after the peak is the same. As shown in Figure 5(d), when the time was shortened from 80 min to 40 min; the purity of graphite showed a trend of first increasing, and then the decreasing with the temperature. When the fixed carbon content began to decrease, the higher the temperature, the greater the decrease. As shown in Figure 5(e), when the liquid-solid ratio decreased, the purity of graphite increased, and then decreased with the temperature, and the higher the temperature, the greater the reduction of the graphite purity [26]. As shown in Figure 5(f), with the decrease in the liquid-solid ratio and the increase of time, the fixed carbon content of graphite first increased, and then slowly declined after reaching the peak value.

For the regression model of the ffixed carbon content, the optimization function in the Design-Expert 8.0 software was applied, taking the maximum fixed carbon content as the condition. The optimal parameters of the graphite purification were the hydrochloric acid concentration of 1.58 mol/L, the temperature of 66.96 °C, the time of 66.23 min, the liquid-solid ratio of 24.47:1, and the maximum fixed carbon content of graphite was 99.78%. To verify the above simulation parameters, experiments were carried out under these parameters. Taking 5 points in the test process; the results (Table 5) showed that the average content of fixed carbon in graphite was approximately 99.77%, which was in a good agreement with the simulation result.

Table 3. Factors and levels in the design of Box-Behnken experiments.

Levels	Concentration of (A)/(mol/L)	Temperature (B) /°C	Time (°C)/min	Liquid-to-solid ratio (D)
-1	0.5	50	40	10
0	1	65	60	20
1	1.5	80	80	30

Table 4. Design and results of the orthogonal test.

	Concentration of (A)/(mol/L)	Temperature (B)/	Time (C)/min	Liquid-to-solid ratio (D)	Fixed carbon content/%
1	0.5	50	60	20	99.19
2	2.5	50	60	20	99.23
3	0.5	80	60	20	98.95
4	2.5	80	60	20	99.13
5	1.5	65	40	10	99.36
6	1.5	65	80	10	99.58
7	1.5	65	40	30	99.43
8	1.5	65	80	30	99.70
9	0.5	65	60	10	99.36
10	2.5	65	60	10	99.42
11	0.5	65	60	30	99.40
12	2.5	65	60	30	99.45
13	1.5	65	60	20	99.42
14	1.5	50	40	20	99.06
15	1.5	80	40	20	99.46
16	1.5	50	80	20	99.41
17	0.5	80	80	20	99.11
18	2.5	65	40	20	99.12
19	0.5	65	40	20	99.24
20	2.5	65	80	20	99.43
21	1.5	65	80	10	99.50
22	1.5	50	60	10	99.31
23	1.5	80	60	30	99.56
24	1.5	50	60	30	99.34
25	1.5	80	60	20	99.72
26	1.5	65	60	20	99.77
27	1.5	65	60	20	99.73
28	1.5	65	60	20	99.77
29	1.5	65	60	20	99.75

Table 5. ANOVA of the quadratic polynomial model for a fixed carbon content.

Source	Sum of squares	df	Mean square	F-value	P
Model	1.42	14	0.10	68.47	< 0.0001
A	0.023	1	0.023	15.83	0.0014
B	0.11	1	0.11	75.82	< 0.0001
C	0.15	1	0.15	98.18	< 0.0001
D	0.010	1	0.010	6.90	0.0199
AB	4.900E-003	1	4.900E-003	3.31	0.0902
AC	8.100E-003	1	8.100E-003	5.48	0.0346
AD	2.500E-005	1	2.500E-005	0.017	0.8984
BC	0.024	1	0.024	16.24	0.0012
BD	2.250E-004	1	2.250E-004	0.15	0.7024
CD	6.250E-004	1	6.250E-004	0.42	0.5262
A^2	0.73	1	0.73	492.95	<0.0001
B^2	0.47	1	0.47	317.37	<0.0001
C^2	0.20	1	0.20	132.79	<0.0001
D^2	9.244E-003	1	9.244E-003	6.25	0.0255
Residual	0.021	14	1.479E-003		
Lack of fit	0.019	10	1.863E-003	3.58	0.1152
Pure error	2.080E-003	4	5.200E-004		
Cor Total	1.44	28			

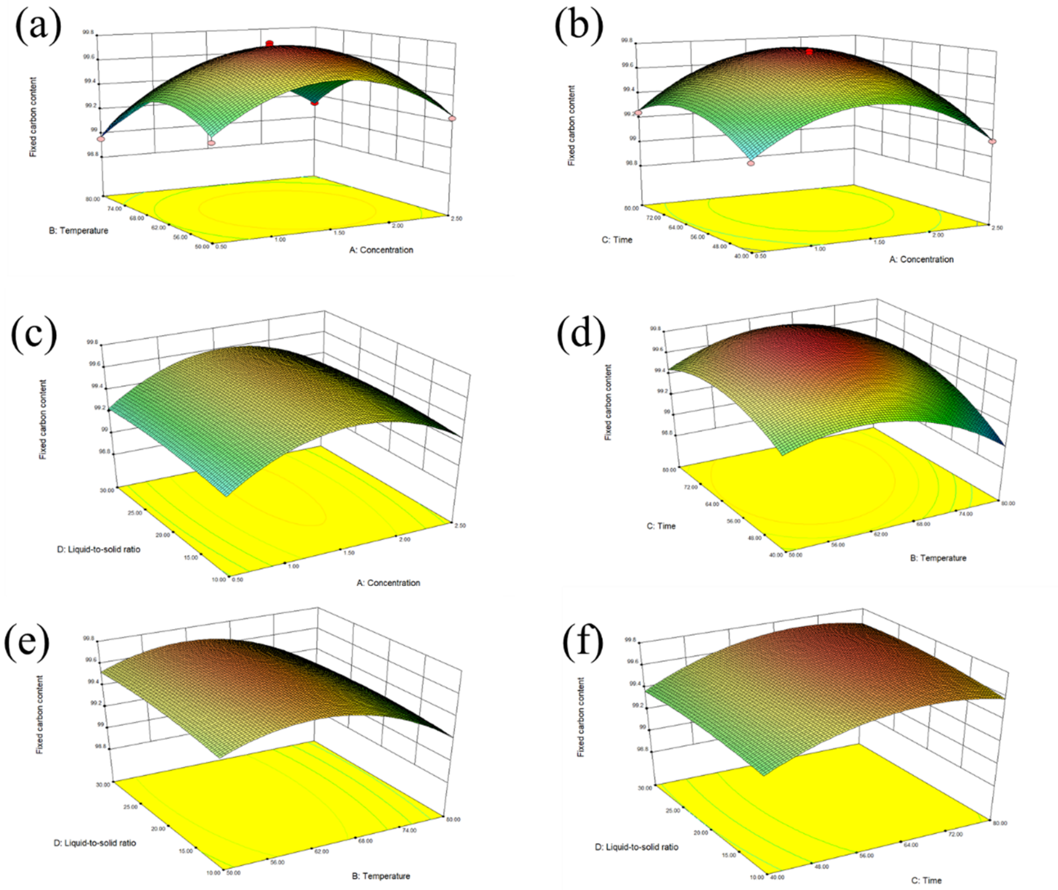

Figure 5. (a) Interaction effect of the response surface of A and B. (b) Interaction effect of the response surface of A and C (c) Interaction effect of the response surface of A and D. (d) Interaction effect of response surface of C and B. (e) Interaction effect of the response surface of D and B. (f) Interaction effect of the response of the surface of D and C.

Table 6. Repeated experimental data.

Frequency	Fixed carbon content/%
1	99.77
2	99.78
3	99.76
4	99.77
5	99.78
Mean	99.77

3.4. Selection of additives

Based on the above experiments, the best process for purifying graphite by the alkaline-acid method during acid leaching was explored. Mix the acid solution with a concentration of 1.5 mol/L hydrochloric acid and graphite according to the set of solid-liquid ratio, and then react at 65 °C for 60 minutes. This process could increase the graphite purity to 99.77%. In the above experiment, the impurities in the graphite could fully react with the acid by improving the process conditions to generate chloride, which improved solubility in water. However, the purity of graphite was still lower than the expected standards. During the process, the metal ions were hydrolyzed to form gel groups during the subsequent washing process. These gel groups still retained in the graphite in other forms, resulting in a poor impurity removal effect. Therefore, the following experiments explored the possibility of introducing additives to further optimize the graphite purification process.

Iron existed in a solution in the form of ferrous and ferric ions. The hydrolysis of the iron ions yielded iron hydroxide with a Ksp of 4.0×10^{-38}, while the hydrolysis of ferrous ions yielded ferrous hydroxide with a Ksp of 8×10^{-16}. Therefore, the difference between these results depended on the different pH conditions for a complete hydrolysis and precipitation. The requirement of not hydrolyzing the iron ions to precipitate was pH < 2; ferrous ion did not hydrolytic precipitation; it requires a solution pH < 6, indicating that the iron ions only existed in a solution of high acidity. With the progress of the washing step in the acid-leaching process, the pH in the solution was difficult to maintain in a state of high acidity. The hydrolysis of the iron ions to form precipitates that would affect the removal of the iron elements. The presence of a reducing agent in the solution could reduce the iron ions to ferrous ions; the acidity requirements in the solution would be reduced, and the stability would be greatly enhanced [26]. The ascorbic acid (vitamin C) crystalline powder is a high-quality reducing agent, which is commonly used in laboratories. It is easily soluble in water, and has a strong reducing power. The addition of ascorbic acid could help the iron compounds to be fully washed away during water washing, thereby improving the purity of graphite.

The disodium of EDTA was considered to be one of the strongest chelators. Disodium EDTA is a colorless and water-soluble organic compound. As a polydentate ligand, EDTA disodium had six coordination sites, which could stably coordinate with the metal ions to form a complex. It showed a strong stability and selectivity, and was widely used in the fields of medicine and environmental protection. Especially, the EDTA sodium salt could be used as a complexing agent, and can complex almost all the metal ions into stable complexes that are not easily decomposed. This can prevent the metal ions from hydrolyzing into the water-insoluble substances, effectively improving the water leaching properties [27]. After reacting with acid, the impurities in graphite could be removed, and the purification effect was improved. Both auxiliaries can help reduce the energy consumption and costs, so the used locations of the two single auxiliaries were experimentally explored, and the used locations and dosages of the auxiliaries were determined through data analysis (Figure 6).

Several of the columns in Figure 6 (a) are a-graphite purification without additive. b- addition of ascorbic acid during acid leaching. c- addition of ascorbic acid during water leaching. d- addition of EDTA during acid leaching. e- addition of EDTA during water leaching. In Figure 6 (a), the introduction of ascorbic acid and EDTA could effectively improve the purity of graphite. However, adding ascorbic acid as a reducing agent only could affect the iron content in graphite, while EDTA could coordinate a variety of the metal ions into stable complexes. Hence, the overall effect of EDTA was better than ascorbic acid. The purity of the graphite-added ascorbic acid in water leaching was lower than that in acid leaching because some iron ions had been hydrolyzed, resulting in an insufficient action of the reducing agent to completely reduce the iron ions to ferrous ions. Adding EDTA during acid leaching could increase the complexing time of the metal ions, and avoid hydrolysis of the metal ions to form gel deposition during acid leaching, and the subsequent suction filtration. Adding the EDTA sodium salt as an auxiliary agent during the acid leaching process was the best method among these sets of single auxiliary experiments. The graphite purity could be increased from 99.77% to 99.91%, but was still lower than the target of the 99.95% graphite purity. Therefore, the way of introducing dual additives during the acid leaching process was further explored. The results were shown in Figure 6 (b).

Several of the columns in Figure 6 (b) are a- graphite purification without additives. b- addition of mixed additives during acid leaching. c- addition of mixed additives during water leaching. d- addition of EDTA during acid leaching followed by ascorbic acid during water leaching. e- addition of ascorbic acid during acid leaching followed by EDTA during water leaching. In Figure 6 (b), the effect of adding two additives at the same time on further improving the purity of graphite was negligible; even a lower than the single additive was used because ascorbic acid and disodium EDTA could form the EDTA-VC complex with a 1:1 molar ratio. Furthermore, this complex was stable, and protected ascorbic acid from the oxidative damage. This consumed the amount of EDTA, and reduced the required reducing properties of ascorbic acid. This method of adding two additives in one step did not make any sense for the graphite purification. The results showed that adding ascorbic acid to acid leaching, and the EDTA sodium salt to water leaching were better than the other methods, and could successfully increase the graphite purity to 99.96%. This addition method first converted Fe^{3+} into Fe^{2+}, and reduced the hydrolysis of the iron ions. The subsequent addition of EDTA could coordinate a variety of ions including the ferrous ions into stable complexes that were easily soluble in water. The effects and advantages of the two additives could be exerted at the same time to minimize the hydrolysis of the metal ions. This further optimized the graphite purification effect, and improved the subsequent graphite washing efficiency. Adding in steps also avoided the negative effects caused by the reaction of the two additives, which is an effective method. Furthermore, the exact value of the appropriate amount of additives through the control variable method was explored.

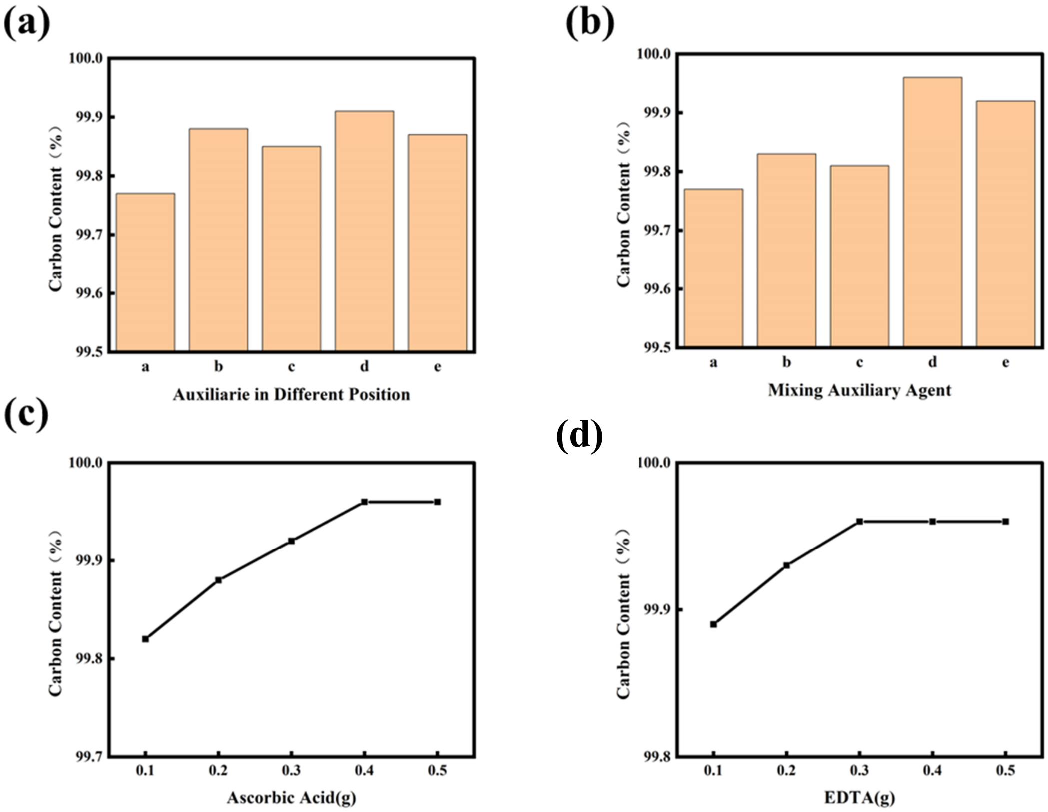

Figure 6. (a) Effect of the single additives on the fixed carbon content of graphite (b) Effect of two additives on the fixed carbon content of graphite. (c) Effect of the amount of ascorbic acid on the carbon content fixed in graphite. (d) Effect of the amount of EDTA on the carbon content fixed in graphite.

The above experiments were conducted under fixed alkali leaching conditions, and the optimal process conditions for acid leaching were also determined. In this experiment, under certain water immersion conditions, the amount of ascorbic acid added during the acid leaching process of 1.2 g, the alkali fused graphite was tested, as shown in Fig 6 (c). The results show that as the amount of additives increased, the fixed carbon content of graphite also increased. When 0.4 g of ascorbic acid was added, the fixed carbon content curve of graphite appeared as a plateau, indicating that increasing the amount of the agent would not continue to improve the purification effect of graphite [28]. Therefore, 0.4 g of ascorbic acid was selected as the optimal dosage for the first step of the two-step introduction of additives. After determining that the amount of additive introduced in acid leaching was 0.4 g; the impact of the amount of EDTA on the graphite purification was further explored through experiments. The amount of EDTA added to the aqueous immersion solution was tested with other condition constants (Figure 6(d)).

The results showed that when the amount of EDTA was lower than 0.3 g, the fixed carbon content of graphite increased with the increase in the additive mass. However, when the dosage was larger than 0.3 g, the fixed carbon content of graphite presented a negligible change, indicating that 0.3 g of EDTA was the optimized content to coordinate to the impurities in the solution. Continuing to enhance the dosage of EDTA would lead to the waste of medicines, and increased costs. Hence, the optimal conditions were adding 0.4 g ascorbic acid during the acid leaching process, and adding 0.3 g ascorbic acid during the water leaching process. The fixed carbon content of the graphite obtained by this process reached larger than 99.96%.

4. Conclusions

In summary, through the control variable method experiment and the Box-Behnken experiment, the best process conditions for the purification of acid-leaching graphite were explored. The control variable method experiments confirmed that the fixed carbon content of graphite could reach 99.77% when the liquid-solid ratio of the acid solution to graphite was controlled to be 20:1. The additives of ascorbic acid and EDTA could improve the purity of graphite. The two-step method of adding ascorbic acid (0.4 g) during the acid leaching process and adding EDTA (0.3 g) during the water leaching process had the best effect. The fixed carbon content of graphite could reach 99.96%, reaching the expected graphite purity target. The characterization results proved the fundamental structure of graphite remained largely intact during this purification process. At last, the Box-Behnken experiment was scientifically verified by both the single-factor and multi-factor experiments. As a result, presenting that the two-step assisted acid leaching method explored in this work was an effective method. It was an effective new process to further improve the purity of graphite based on the traditional alkali-acid method.

Acknowledgments

This work was supported by the Key Research and Development Project of the Heilongjiang Province (2023ZXJ05A01); the Key Program of the Jixi Natural Science Foundation (JKZT2022R01; JKZT2022R03), Research Project of Heilongjiang Transportation Investment Group Co., Ltd. (JT-1000000-ZC-FW2022-0086).

Conflict of Interest

The authors declare no potential conflict of interest.

References

[1]. Cheng, Q.; Marchetti, B.; Chen, X.; Xu, S.; Zhou, X.-D., (2022). Separation, purification, regeneration and utilization of graphite recovered from spent lithium-ion batteries - A review. *Journal of Environmental Chemical Engineering 10* (2), 107312.

[2]. Deng, J.; Gu, Z.; Wu, L.; Zhang, Y.; Tong, Y.; Meng, F.; Sun, L.; Zhang, H.; Liu, H., (2023). Efficient purification of graphite industry wastewater by a combined neutralization-coagulation-flocculation process strategy: Performance of flocculant combinations and defluoridation mechanism. *Separation and Purification Technology 326*, 124771.

[3]. Jara, A. D.; Kim, J. Y., (2020). Chemical purification processes of the natural crystalline flake graphite for Li-ion Battery anodes. *Materials Today Communications 25*, 101437.

[4]. Liu, Y.; Fu, Y.; Zheng, L.; Wang, M.; Wang, Z.; Yang, S.; Liu, J.; Gong, X., (2023). Leaching characteristics and solidification strategy of heavy metals in solid waste from natural graphite purification. *Environmental Science and Pollution Research 30* (11), 30892-30904.

[5]. Qian, Y.; Xiaochen, Z.; Kan, K., (2024). Research progress on purification of natural flake graphite. *China Mining Magazine 33* (7), 254-260.

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

[7]. Zhang, Y.; Chen, Z.; Xie, K.; Chen, X.; Hu, Y.; Ma, W., (2023). Purification of Waste Graphite from Crucibles Used in Photovoltaic Crystallization by an Alkali-Acid Method. *Metals 13* (7), 1180.

[8]. Al-Sairafi, F. A.; Jiang, C.; Zhong, Z.; Saleh, B., (2022). Study on purification of flake graphite by heat activation and hydrofluoric acid. *Advances in Materials and Processing Technologies 8* (4), 4564-4578.

[9]. Liu, Y.; Tong, Z.; Ni, M.; Ren, X.; Bu, X.; Shao, H.; Chehreh Chelgani, S., (2023). Leaching kinetics of impurity removal from aphanitic graphite by HCl leaching. *Separation Science and Technology 58* (8), 1502-1515.

[10]. Chen, Y.-L.; Chiang, W.-P.; Lin, C.-H.; Wu, I.-M.; Chang, J.-E., (2024). Recovery and purification of kish graphite from steelmaking dust by using acid leaching with physical auxiliary methods. *Sustainable Environment Research 34* (1), 26.

[11]. Shen, K.; Chen, X.; Shen, W.; Huang, Z.-H.; Liu, B.; Kang, F., (2021). Thermal and gas purification of natural graphite for nuclear applications. *Carbon 173*, 769-781.

[12]. Lv, Y.; Liu, Y.; Ma, B.; Wang, C.; Qiu, Z.; Chen, Y., (2023). Emission reduction treatment of chlorine-containing waste gas during the chlorination roasting process of lepidolite: thermodynamic analysis and mechanism investigation. *Separation and Purification Technology 315*, 123686.

[13]. Xiyue, Z.; Hongjuan, S.; Tongjiang, P.; Li, Z.; Bo, L., (2024). Purification mechanism of microcrystalline graphite and dissolution of non-carbon impurity during alkali autoclave-acid leaching. *Physics and Chemistry of Minerals 51* (3), 25.

[14]. Xie, W.; Wang, Z.; Kuang, J.; Xu, H.; Yi, S.; Deng, Y.; Cao, T.; Guo, Z., (2016). Fixed carbon content and reaction mechanism of natural microcrystalline graphite purified by hydrochloric acid and sodium fluoride. *International Journal of Mineral Processing 155*, 45-54.

[15]. Jara, A. D.; Betemariam, A.; Woldetinsae, G.; Kim, J. Y., (2019). Purification, application and current market trend of natural graphite: A review. *International Journal of Mining Science and Technology 29* (5), 671-689.

[16]. Wang, H.; Feng, Q.; Tang, X.; Liu, K., (2016). Preparation of high-purity graphite from a fine microcrystalline graphite concentrate: Effect of alkali roasting pre-treatment and acid leaching process. *Separation Science and Technology 51* (14), 2465-2472.

[17]. Yu, K.; Ahn, K. H.; Song, C. K.; Aregay, M. G.; Yoon, T. J.; Lee, Y.-W., (2022). Purification of synthetic diamond and graphite mixtures in catalytic supercritical water oxidation processes. *Diamond and Related Materials 129*, 109371.

[18]. Bao, C.; Shi, K.; Xu, P.; Yang, L.; Chen, H.; Dai, Y.; Liu, H., (2021). Purification effect of the methods used for the preparation of the ultra-high purity graphite. *Diamond and Related Materials 120*, 108704.

[19]. Zhao, S.; Cheng, S.; Xing, B.; Ma, M.; Shi, C.; Cheng, G.; Meng, W.; Zhang, C., (2022). High efficiency purification of natural flake graphite by flotation combined with alkali-melting acid leaching: application in energy storage. *Journal of Materials Research and Technology 21*, 4212-4223.

[20]. Sybir, A.; Fedorov, S.; Hubynskyi, M.; Hubynskyi, S.; Koval, S.; Sukhyy, K.; Foris, S., (2020). Thermal purification of natural graphite by means of high-speed heating. *Voprosy Khimii i Khimicheskoi Tekhnologii 3*, 178-182.

[21]. Duan, S.; Wu, X.; Min, X.; Huang, Z.; Yue, T.; Yue, W.; Fang, M.; Liu, Y., (2019). Effect of purity and proportion of microcrystalline graphite ore on the electrical, mechanical and tribological performance of copper-carbon composites. *Materials Research Express 6* (12), 125604.

[22]. Chen, Q.; Li, Y. In *Study on Purification and Modification Processing Technology of Microcrystalline Graphite*, IOP Conference Series: Earth and Environmental Science, IOP Publishing: 2021; p 012040.

[23]. Kaitano, H. V.; Mudono, S., (2023). Investigating on a Process Method of Beneficiating and Increasing the Graphite Purity to 99% Grade. *Journal of Analytical Sciences, Methods and Instrumentation 13* (04), 39-52.

[24]. Guo, H. F.; Chao, B.; Zhao, Z. Q.; Nan, D. In *Research on Purification Technology of Ultra-Large Flake Graphite Based on Alkali-Acid Method*, Materials Science Forum, Trans Tech Publ: 2021; pp 104-113.

[25]. Lu, X.; Forssberg, E., (2002). Preparation of high-purity and low-sulphur graphite from Woxna fine graphite concentrate by alkali roasting. *Minerals engineering 15* (10), 755-757.

[26]. Shen, K.; Cao, X.; Huang, Z.-H.; Shen, W.; Kang, F., (2021). Microstructure and thermal expansion behavior of natural microcrystalline graphite. *Carbon 177*, 90-96.

[27]. Amaraweera, T.; Balasooriya, N.; Wijayasinghe, H.; Attanayake, A.; Dissanayake, M., (2013). Purity enhancement of Sri Lankan vein graphite for lithium-ion rechargeable battery anode. *Proceedings to 29th Technical Sessions of Geological Society of Sri Lanka 101*, 104.

[28]. Chen, Z.; Ren, Z.; Zheng, R.; Gao, H.; Ni, B.-J., (2022). Migration behavior of impurities during the purification of waste graphite powders. *Journal of Environmental Management 315*, 115150.

خالص‌سازی گرافیت پولکی طبیعی با روش اسیدشویی با استفاده از روش دو مرحله‌ای معرفی مواد افزودنی

جیای لی[۱،۲]، جینگ ژائو[۱،۲]*، زبین وانگ[۱،۲]، هوان لیو[۱،۲]، چینگ ون[۱،۲]، جین لینگ یین[۱،۲]، زی لی[۳]، یانگ لی[۳]، و گویلینگ وانگ[۱،۲]

۱ آزمایشگاه کلیدی مواد فوق سبک و فناوری سطح وزارت آموزش، دانشکده علم مواد و مهندسی شیمی، دانشگاه مهندسی هاربین، هاربین ۱۵۰۰۰۱، جمهوری خلق چین، گوئیلینگ وانگ، جینگ ژائو

شرکت فناوری مواد کربنی هایلونگجیانگ هاچوان، مرکز ملی نظارت و بازرسی کیفیت محصولات گرافیتی، شماره ۸۸ جاده کانگشین، منطقه جیگوان، شهر جیشی، استان هایلونگجیانگ، ۱۵۸۱۰۰، جمهوری خلق چین

گروه سرمایه‌گذاری حمل‌ونقل هایلونگجیانگ، شماره ۸۹۹، جاده نوآوری سوم، منطقه سونگبی، هاربین، استان هایلونگجیانگ، ۱۵۰۰۲۵، جمهوری خلق چین

ارسال ۲۰۲۴/۰۳/۰۸، پذیرش ۲۰۲۴/۱۱/۰۸

* نویسنده مسئول مکاتبات: zhtdzhn@hrbeu.edu.cn

چکیده:

گرافیت سنتی دارای مسائل ایمنی و زیست محیطی است که با تصفیه فلوئور مرتبط است. برای پرداختن به این مسائل، یک فرآیند خالص سازی گرافیت با صرفه جویی در انرژی و کارآمد را می توان از طریق روش اسیدشویی با افزودنی های کامپوزیت بررسی کرد. فرآیند لیچینگ اسیدی با استفاده از روش متغیر کنترل‌شده از جمله تأثیر زمان و دمای خیساندن بر فرآیند خالص‌سازی گرافیت با جزئیات مورد مطالعه و بهینه‌سازی قرار گرفت. سپس از روش سطح پاسخ برای شبیه سازی آزمایش متعامد تصفیه گرافیت برای تأیید صحت آزمایش تک عاملی استفاده شد. خلوص و میکرومورفولوژی نمونه های گرافیت در هر مرحله مشخص و آزمایش شد. نتایج تجربی نشان داد که نسبت مایع به جامد بهینه محلول اسید و گرافیت ۲۰:۱ است که می تواند محتوای کربن ثابت را به ۹۹.۷۷ درصد برساند. بر اساس این شرایط فرآیند بهینه، انواع افزودن بیشتر مورد بررسی قرار گرفت. نتایج تجربی نشان داد که بهترین افزودنی اسید اسکوربیک و EDTA بود که می‌توانست محتوای ناخالصی‌های مختلف در ماده خام گرافیت را بدون از بین بردن ریزساختار گرافیت کاهش دهد. با بهره مندی از افزودن افزودنی های ترکیبی در فرآیند دو مرحله ای، تقریباً تمام یون های فلزی از گرافیت شسته شدند. پس از شستشوی اسید و آب، محتوای کربن ثابت گرافیت می تواند به ۹۹.۹۶٪ برسد. پارامترهای فرآیند ارائه شده در این مقاله به صورت علمی توسط آزمایش‌های تک عاملی و چند عاملی تأیید شد و افزودنی‌های ابتکاری و مؤثر در مراحل مختلف معرفی شدند تا خلوص گرافیت را از ۹۹.۹ درصد عبور دهند که دستیابی به آن توسط روش سنتی دشوار بود. روش.

کلمات کلیدی: گرافیت، تصفیه، فرآیند اسید قلیایی، روش سطح پاسخ، عامل کمکی.