

# Structural Evolution of Coal Fines to Graphite Produced by Metal-Assisted Microwave Method

Boitshepo Ivy Marakalala, Willie Nheta, Nomsa Priscilla Baloyi

**Abstract**— The generation of coal fines over the years has increased owing to increased mechanization in mineral processing. Many studies are ongoing to find the best ways to utilize coal fines to make them marketable. Coal can be used to produce synthetic graphite using high-temperature treatment; however, the process is expensive due to the use of high temperatures above 2800°C. Metal-assisted microwave offers a greater alternative coupled with catalysts such as ferric oxide and ferric chloride that allows for graphitization at lower temperatures. A coal graphitization experiment was conducted on coal fines obtained from a colliery plant in Botswana. The aim of the study was to investigate the structural evolution of the coal sample during the catalytic graphitization process and to study how the synthesized graphite compares with market graphite. The metal-assisted microwave method was employed whilst meeting the necessary graphitization requirements; use of high temperature from copper foil sparks, a catalyst, and operate in a reducing environment (Ar/H<sub>2</sub>).

**Keywords**— Synthetic graphite, structural evolution, metal-assisted microwave, catalytic graphitization.

## I. INTRODUCTION

Coal fines are coal particles of small size, usually below 3mm [1], [2]. These are mostly dislodged from coal seams during processing or transportation. Given the frailty of coal, mechanization has increased the production of fines during coal handling, and they are cumbersome to manage. It has been reported that millions of tons of coal fines (<3mm) are generated during processing annually [1]. This has led to the stockpiling of these fines in landfills or underground as they fail to participate in various industrial productions as sources of fuel since they do not meet the requirements of various industrial uses [3]. These stockpiles pose a health hazard to the communities living near these coal plants as they cause air,

land and water pollution from effluents that seep to the ground during rains and end up contaminating underground water sources [4]. The stockpiles have ultra fines and dust that can be carried by the wind to nearby homesteads causing various diseases including black lung, cardiopulmonary, hypertension, chronic obstructive pulmonary disease (COPD), and kidney diseases [5]. Studies have found that these health conditions are found in higher-than-normal rates in people whose communities are around coal mines [6]. The utilization of these fines will add value to them as well as reduce environmental pollution.

Coal provides approximately 40% of the world's electricity, and Botswana has coal reserves of around 212 billion tons [4]. Coal plants in Botswana have stockpiles of coal owing to years of mining with no market value. Converting coal material to higher value material is currently of high interest [7], [8]. Coal is made up of various organic and inorganic impurities in both their stable and volatile states [9]. Given its complexity, the transformation of coal into products such as graphite, graphene and liquid fuel is not a trivial task. Researchers have proposed different techniques such as briquetting, pyrolysis and gasification [4], [10], [11]. These techniques produce end products such as coal briquettes, char, tar and pyrolytic gases that can help create cheaper fuels to be used in various industries [12], [13].

Coal is an abundant and cheap natural source of carbon, which can also be used to effectively generate graphite [14]. Natural graphite has finite reserves, and its extraction process is of environmental concern due to pollution [5]. Previous research on the use of coal fines has shown potential in using this material for production of graphite adoptable for usage in various industries such as anode material for lithium-ion batteries, water treatment, refractories, electronics, fuel cells etc. [2]– [4]. Given the heterogeneity of coal, intensive studies are necessary to accommodate different coal ranks. Most studies have been made on the use of anthracite as it has a higher carbon content, is a cleaner coal and graphitizes at a lower temperature when compared to other coal ranks [8]– [10]. Bituminous and sub-bituminous coals can also be used for synthesizing graphite. A study by [11] successfully prepared graphite anode material using bituminous coal with good electrochemical properties using a graphite furnace.

The major factors affecting the degree of coal graphitization are high temperatures, the use of a catalyst and, a reducing

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environment [9]. Coal fines are normally treated with a heat range of 2500°C - 3000°C as the graphitization transition process involves the orderly transformation of unstable carbons thermodynamically from disordered structures to graphite crystals by thermal activation. At this processing condition, impurities are removed, resulting in high quality graphite [7], [12]. A study by [5] showed that the microstructural development of graphite increases with an increase in graphitization temperature. Coal graphitization using a furnace requires a high temperature of above 2600°C as it has a significant effect on graphitization. In a study by [6], graphite of highly ordered layered structure and well-developed mesopores was prepared at a temperature of 2800°C after preliminary carbonization. Microwave treatment can be used for graphitization, given that all the necessary conditions for graphitization are met [9]. In some cases, preliminary carbonization is done using an inert medium such as nitrogen or argon before coal graphitization [9]. During microwave treatment, sparks of temperature above 1000°C are created by fork-shaped metal foil when it is irradiated within seconds. The sparks that are induced are a novel approach to the creation of high temperatures that are necessary for graphitization. Metals with higher melting points can even be used to create higher temperatures [9].

Graphitization requires high temperatures to overcome the high graphitization enthalpy of graphite. This energy barrier is one of the major obstacles that hinders graphitization [26]. A solution to overcome this is the use of additives that can help facilitate the graphitization process at lower temperatures [24]. Catalytic graphitization is mostly done to allow graphitization at low temperatures. A catalyst is used to enhance the crystallization of carbon. Catalysts are divided into the following three categories: elemental substances (Fe, Ni, Ti, and V); compounds ( $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{MnO}_2$ ) and alloys (Fe-Si and P-Ni) [13]. In a study carried out by [11], synthetic graphite was produced using industrial silicon powder as a catalyst, and graphite material with a stable structure and good electrochemical performance was obtained. The catalyst of 5% silicon at 2800°C had a higher degree of graphitization when compared to the ones of 10 and 15%.

## II. MATERIALS AND METHODS

### A. Materials

The sample used was obtained from a coal mine in Palapye, Botswana. Proximate analysis of the coal was done following the ASTM D3176 standard method, and the results are present in Table 1. The sample had low moisture content, medium ash, volatile matter, and fixed carbon content. The coal sample was ball milled (dry) for 10 minutes for size reduction. The sample was further pulverized to obtain coal powder, which was carbonized at 1000°C for 2 hours in a tube furnace with nitrogen flow at a heating rate of 10°C/min. The carbonized coal was treated with different wt.% of  $\text{Fe}_2\text{O}_3$  catalysts of 5, 10 and 15% before graphitization. Copper foil (99%) of 25µm was cut to a fork-like shape using scissors and used during the

graphitization process. The microwave irradiation induced sparking of the copper foil that produces temperatures above 1000°C.

TABLE I  
PROXIMATE ANALYSIS RESULTS

Moisture	Ash	Volatile Matter	Fixed Carbon
3,52%	17,73%	28%	50,75%

### B. Microwave graphitization procedure

A catalyzed (wt.5%) coal sample of 10g was placed inside a crucible. Copper foil cut into fork-like shape was immersed in the coal. The coal covered 2/3 of the foil, while the top was exposed to microwave irradiation. During the microwave graphitization process, the copper foil created sparks due to microwave irradiation. The experiment was run at varying times of 5 to 20 minutes until the induced sparks from the copper foil stopped. The flowchart of this experiment is shown in Fig. 1. This procedure was followed to treat other catalyzed coal samples. Iron in the samples after treatment was washed out using nitric acid (55%), and the acid was washed out using deionized water until the pH was at 7 and dried.

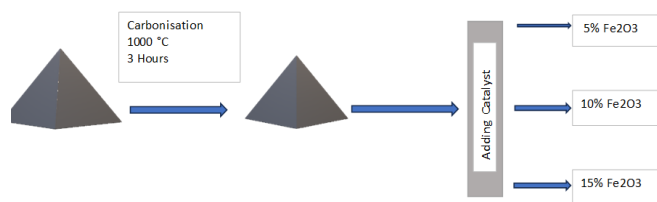


Fig. 1 Coal graphitization process

### C. Structural Characterization

The chemical structural characteristics of synthesized graphite were analyzed using Raman spectroscopy and Fourier-transform infrared spectroscopy. For comparison purposes, raw coal, a carbonized sample before adding the catalyst, and pure graphite were analyzed. Raman spectroscopy is a non-destructive chemical analysis technique that provides information on the chemical structure, phase, crystallinity, and molecular interactions [14]. The samples for both FTIR and Raman analysis were prepared by mixing them with a pestle and mortar for homogeneity and placed them in a sample holder before placing them in the analysis machines. The peaks of the obtained results were fitted using Gaussian with Origin 2023b software. The sample powders were placed in a pellet for SEM analysis and analyzed.

## III. RESULTS AND DISCUSSION

### A. Crystallographic Analysis

For the study of chemical structural changes during the graphitization process, Raman spectroscopy was used, as it gives information on the crystallinity and graphitization degree of carbon materials [8]. Coal is a polycrystalline structure that has both disordered short-range and long-range

chains [9]. The sensitivity of the Raman signal to short-range disorder allows it to effectively study the development from amorphous coal structure to crystalline graphitic structure [3], [5]. The Raman spectrum has first order and second order spectra. The most observed bands for first order in this study were D1 ( $-1350\text{cm}^{-1}$ ) and G ( $-1580\text{cm}^{-1}$ ) and the second order 2D band ( $-2700\text{cm}^{-1}$ ). In amorphous carbons, additional peaks may appear that are on a first-order spectrum, such as  $1618\text{ cm}^{-1}$  (D2),  $1527\text{ cm}^{-1}$  (D3), and  $1148\text{ cm}^{-1}$  (D4) [2]. Different bands give information on the chemical composition and the structure of the sample [10]. The characteristic peak D1 band, which is  $1350\text{cm}^{-1}$  or lower, gives an indication of the presence of disordered amorphous carbon in the sample. It also indicates the presence of aromatic clusters containing more than six rings [12], [14]. The D2 and D3 bands represent defects in the graphitic structure and the presence of amorphous carbons of composition  $\text{sp}^2$  and  $\text{sp}^3$  hybridization bonding [3]. The presence of the D3 band may be caused by the presence of functional groups that consist of oxygen, and this is normally observed in poorly ordered carbon structures. The G band has a characteristic peak around  $1585\text{cm}^{-1}$  which indicates the presence of more graphitic or crystalline carbon.

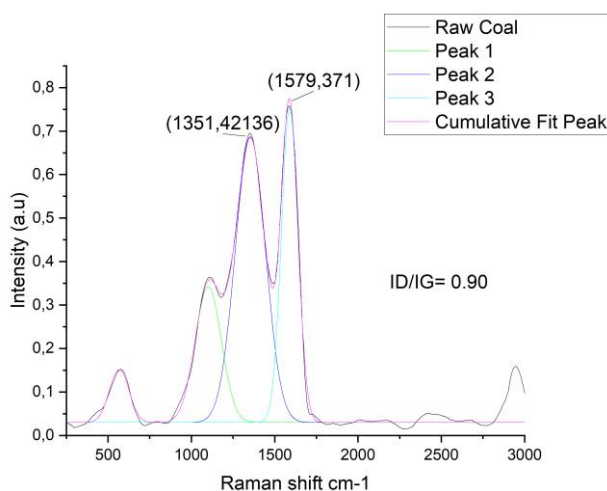


Fig.2 Raman Spectra of raw coal

Fig. 2 shows the results obtained for the raw coal sample (RC), where two prominent peaks of the D band ( $1349\text{ cm}^{-1}$ ) and ( $1599\text{ cm}^{-1}$ ) were observed. This shows the presence of disordered  $\text{sp}^2$  carbons in the sample and the presence of graphitic carbon (G band). The crystallinity of the sample is calculated using the peak intensities of D and G as  $R=I_D/I_G$ . The calculated R for raw coal was 1.1, and this value indicates that the amorphous structure dominates the structure of coal, hence the low graphitization. The R value is inversely proportional to the degree of graphitization, and a low value of R indicates highly ordered structure and a higher graphitization degree [6], [11]. The 2D peak was not observed from raw coal as expected, signifying the absence of graphitic long-range order material. Raw coal exhibits a strong D band, which indicates the existence of structural imperfections [8],

[2]. Fig. 3 shows the Raman spectra of pure graphite (PG), raw irradiated coal (RIC), carbonized coal with no  $\text{Fe}_2\text{O}_3$  catalyst (CI-0%), 5% of  $\text{Fe}_2\text{O}_3$  by wt% (CI-5%) and 15% of  $\text{Fe}_2\text{O}_3$  by wt% (CI-15%).

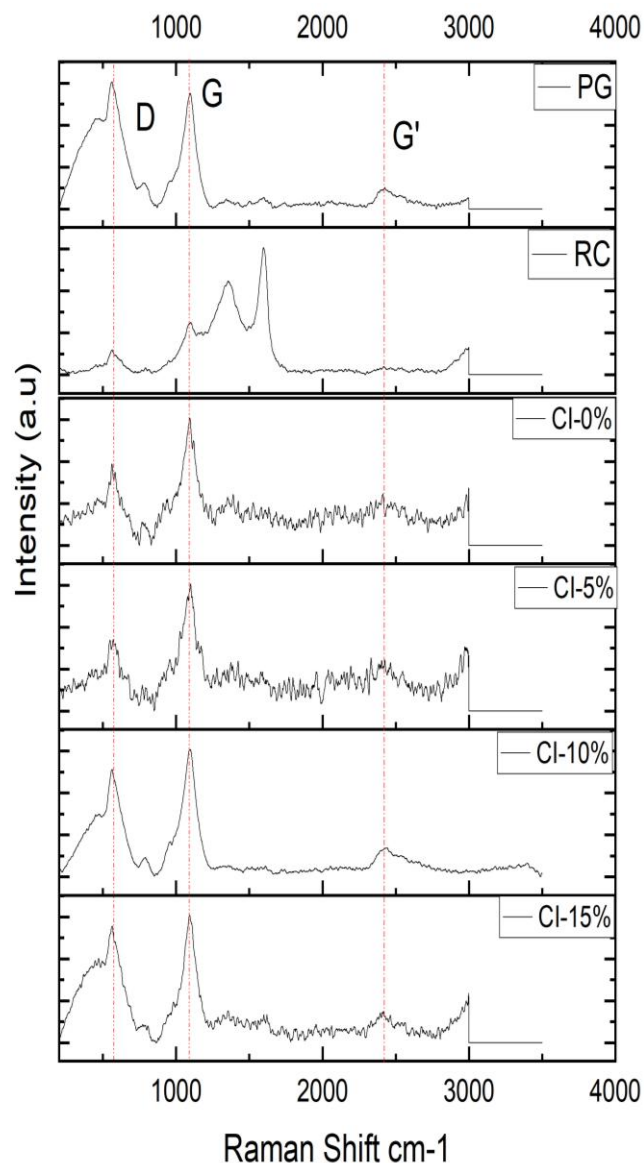


Fig.3 Raman spectrum of Pure graphite (PG), raw coal (RC), raw irradiated coal (RIC), carbonized coal irradiated coal at different catalyst wt%, CI-0%, CI-5%, and CI-15%

Peak fitting was done on the obtained spectra, and the Raman parameters that were automatically generated are shown in Table 2.  $L_a$  and ID/IG were calculated. The decrease in the D band can be observed when comparing the spectrum of irradiated carbonized coal with no catalyst and that with 5% of the catalyst in Fig. 3. The calculated R for CI-0% was 0.64, and that for CI-5% was 0.54. The decrease in the R intensity ratio indicates the development of more stable order and an increase in graphitization. A high degree of graphitization and the formation of a more ordered graphite structure are associated with a lower ID/IG value and a stronger G band

[5]–[7]. This shows that the addition of a catalyst has contributed to graphitization. For samples with long-range order, additional peaks in the second order can also be observed at approximately  $2450\text{ cm}^{-1}$  and  $2700\text{ cm}^{-1}$ , which indicates the presence of a highly ordered graphitic lattice in the material [1], [7]. The D1 band corresponds to the double carbon atom bond in the molecular structure, while the G band corresponds to the CC vibration between aromatic rings. As the G band becomes sharper, the D band decreases with an increase in catalyst, except for CI-15%. [12] stated that even if the presence of  $\text{Fe}_2\text{O}_3$  has a positive effect on the orientation of carbon to graphitic carbon, the graphitization degree does not increase significantly at  $\text{Fe}_2\text{O}_3$  above 15%.

TABLE II  
PARAMETERS FROM RAMAN SPECTROSCOPY

Sample	Peak	Position ( $\text{cm}^{-1}$ )	Intensity	FWHM	ID/IG	La
Raw coal	D	1351,86	0,685	214,69		
	G	1446,12	0,791	116,21	0,90	33,34
Pure Graphite	D	570,78	0,326	160,29		
	G	1087,61	0,763	138,27		
	G'	2456,04	0,141	195,74	0,43	16,45
Carbonised Coal	D	787,77	0,585	236,26		
	G	1104,97	0,679	120,41		
	G'	2442,27	0,057	144,74	0,86	33,17
CI-0%	D	587,27	0,344	146,25		
	G	1105	0,513	132,41		
	G'	2380	0,275	801,89	0,67	25,82
CI-5%	D	576,57	0,383	120,44		
	G	1048,79	0,732	170,57		
	G'	2380	0,261	351,13	0,52	20,14
CI-10%	D	571,74	0,498	168,72		
	G	1045	0,653	158,64		
	G'	2512,78	0,138	1383,63	0,76	29,36
CI-15%	D	576,09	0,686	153,08		
	G	1091,47	0,804	129,85		
	G'	2469,09	0,204	245,31	0,85	32,85

### B. FTIR-Infrared Spectroscopy Analysis

The surface chemical properties of samples can be determined using the FTIR method, which gives information on the functional groups that exist in the sample [14]. Fig. 4 shows the FTIR spectrum of all samples after subtracting the base line using Origin software, and the peaks were fitted using Gaussian. All the samples have similar absorption bands of aromatic structure ( $700\text{--}900\text{ cm}^{-1}$ ), oxygen-containing structure ( $1000\text{--}1800\text{ cm}^{-1}$ ), aliphatic chains ( $2800\text{--}3000\text{ cm}^{-1}$ ), and hydroxyl structure ( $3000\text{--}3600\text{ cm}^{-1}$ ) with varying intensities [5], [6]. The first dominating peaks identified are those of the O-H stretching vibration, which is located around  $3400\text{ cm}^{-1}$ . This wide peak indicates the presence of  $\text{H}_2\text{O}$  in the sample and will not be considered for discussion as it was interfered with absorbed moisture and the technique used in sample preparation before analysis. The other weak signal peaks at  $2925\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  were detected in some of the samples, which are ascribed to aliphatic  $-\text{CH}_2$  and  $-\text{CH}_3$ ,

respectively. These peaks appear stronger in raw coal samples and gradually decrease with graphitization. The declining peaks indicate graphitization with dehydrogenation and depolymerization, implying a decrease in aliphatic hydrocarbons [13]. The peak at  $1635\text{ cm}^{-1}$  is attributed to the C=C bond, an aromatic group in the benzene 6 ring. It can be observed that this peak intensity shows a decrease, indicating an increased concentration of the C=C bonds during graphitization. This trend is due to dehydrogenation effected by high thermal energy that causes the breaking down of C-H bonds. Hydrogen is removed as a gaseous by-product.

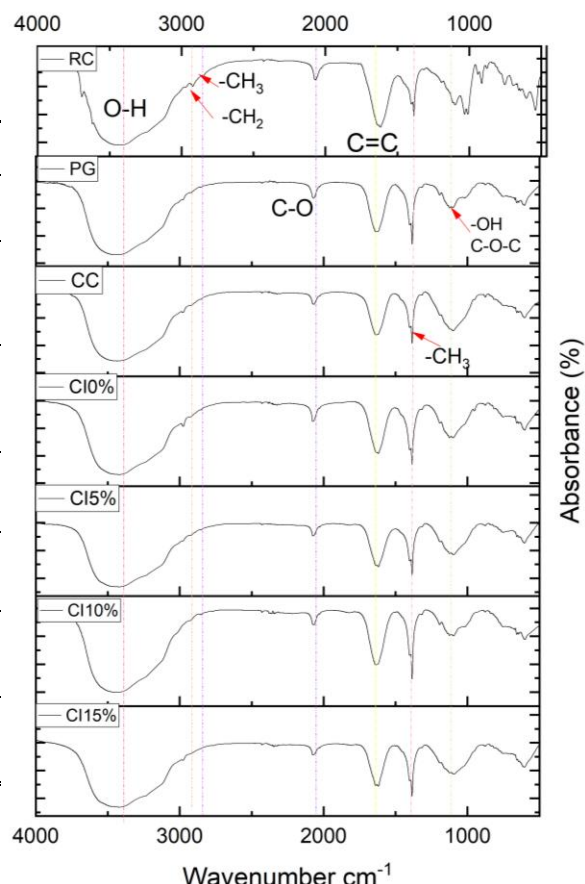


Fig.4 FTIR spectra of samples with denoted functional groups

The oxygen-containing group exists from  $1400\text{--}1000\text{ cm}^{-1}$ , where a peak of C-O is evident at  $1385\text{ cm}^{-1}$ . Fig. 5 shows the decrease in the intensity of these peaks with graphitization; therefore, oxygen-containing functional groups engage in the process of aromatic ring condensation. The peaks at  $900\text{--}700\text{ cm}^{-1}$  fall under the fingerprint of the FTIR spectrum [4]. The peaks in this region are not normally considered, but they do indicate the presence of aromatic bonds of C-H and phenolic deformation of C-O-C [1]. These are caused by deformation vibrations of  $-\text{CH}$  outside the aromatic rings and the presence of mineral matter. The overlap of peaks in this region makes it hard to distinguish the substances.

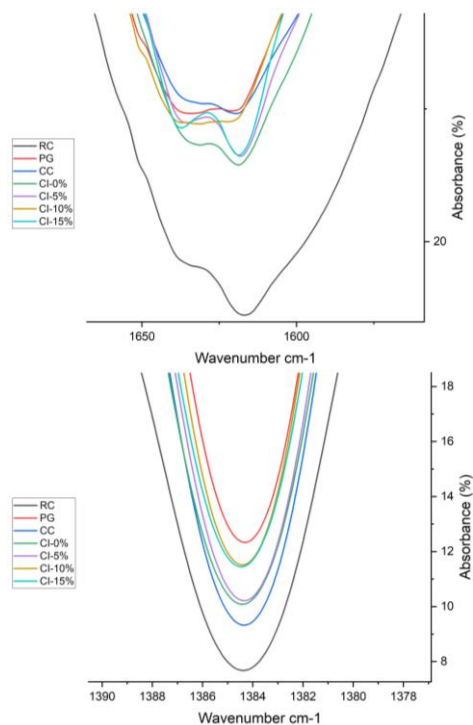


Fig.5 The FTIR peaks of C=C ( $1650\text{-}1600\text{cm}^{-1}$ ) and -CH ( $1390\text{-}1380\text{cm}^{-1}$ )

### C. Morphological Analysis

SEM was used to examine the samples' morphology and surface structure. The examination of a raw coal sample illustrating an amorphous structure is shown in the micrographs in Fig. 6. It is evident that stacked lamellar structures have developed on the surfaces of irradiated coal samples with the help of the catalyst. A characteristic amorphous structure with the emergence of tiny flaky structures on the particle surface is seen in Fig 6(a). Fig 6 (b) and (c) demonstrate a stronger development of flaky structures with an increase in catalyst. The fact that there were more graphite flakes in the samples suggests that the catalyst did, in fact, encourage graphitization. The surface morphology has changed, suggesting that there has been development.

### D. Effect of Catalyst in Graphitization

Coal graphitization was aided by the application of  $\text{Fe}_2\text{O}_3$  as a catalyst during microwave treatment. At temperatures higher than its melting point ( $1538^\circ\text{C}$ ), the elemental volatilization process of Fe occurs in  $\text{Fe}_2\text{O}_3$ . This reaction is caused by microwave-induced sparking in copper foil. Fe has a high activity and readily interacts with carbon to generate the intermediate compound  $\text{Fe}_x\text{C}_y$ , which recomposes to graphitizable carbon, hence this reduction process affects graphitization [6]. This carbon will further transform into crystalline graphite when exposed to the high temperature caused by the sparking. Next, 55% nitric acid was used to leach off the remaining Fe. According to the FTIR data, as graphitization occurs, the concentration of C=C bonds rises. Cu foil's high temperature causes a decrease in hydroxyl and oxygen-bearing structures.

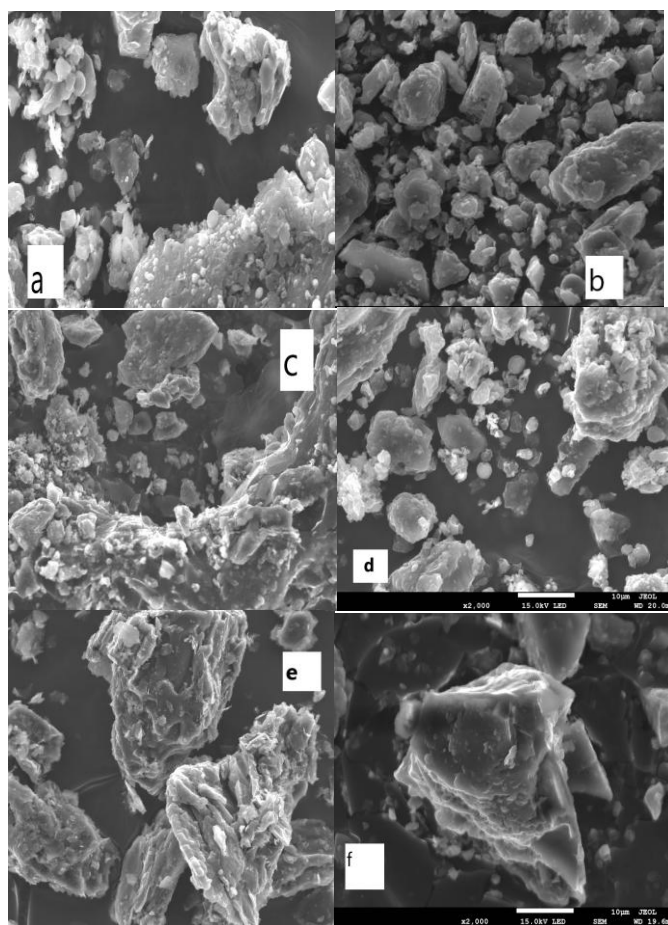


Fig.6 Shows the morphology of samples a (CI-0%), b (CI-5%), c (CI-10%), d (CI-15%), e (graphite) and f (raw coal)

## IV. CONCLUSION

This work examined the structural transformation of coal into graphite using a metal-assisted microwave technique. The effect of  $\text{Fe}_2\text{O}_3$  on graphitization was studied by its usage as a catalyst; Raman spectroscopy, FTIR, and SEM were utilized to examine the samples. When the microwave ignited the Cu foil, the heat produced by the copper foil caused a change in the coal's structure. At 10 weight percent of catalyst, well-developed graphite with structural properties resembling those of the graphite employed as a comparative was obtained. The oxygen-bearing structures and hydroxyl structures were among the functional groups that had decreased, according to the FTIR and Raman. The resulting material is an amorphous graphite, the application of which can be further investigated in many sectors.

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