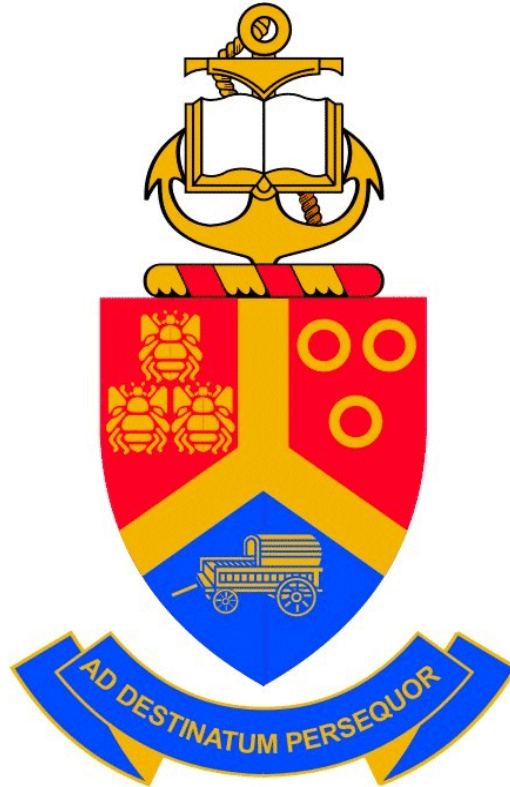


Modification of Functional Groups on the Surface of Carbon Materials

by

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Dissertation presented in partial fulfilment of the requirements for the
degree of

Master of Engineering in Chemical Engineering

Faculty of Engineering, Built Environment and Information Technology

Department of Chemical Engineering

University of Pretoria

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Synopsis

Modification of Functional Groups on the Surface of Carbon Materials

A promising energy harvesting technique involves the use of thermal nanofluids, capable of collecting solar UV/visible radiation and storing it as latent heat in phase change materials (PCM), i.e. molten salts. Carbon-based materials are very interesting candidates for UV/visible light absorption and heat transfer in the nanofluid. The crucial point of the development is the stabilisation of dispersed carbon in a suspension. This work is an investigation on the preparation of stabilized suspensions of carbon black, mesophase carbon beads or exfoliated graphite, in aqueous solutions. To achieve this goal, chemical modifications of the surface functional groups of the carbon grains have been attempted.

Carbon has many allotropes in which it can exist such as diamond, graphite and amorphous carbon. None of these forms a stable suspension in water without a proper surface treatment. The first priority of this study was to identify possible surface treatments that would modify the surface complex on the carbon materials. Once the treatments had been identified, the focus of the study moved to selecting the most effective treatment based on its dispersion properties. The temperature ranges under which the carbon material remained in a suspension were measured. Finally, the effect of the surface area of the treated carbon material on the stability of the carbon material suspension was investigated.

The characterisation techniques that contributed to achieving these objectives were observations with the naked eye, mass spectrometer measurements, thermogravimetric analysis, BET and scanning electron microscope images. The mass spectrometer and scanning electron microscope provided information on the modification of the surface complexes to gain an understanding of the effect of the treatment on the surface of carbon materials. The stability of the carbon and water suspension was measured by using the mass spectrometer and doing a thermogravimetric analysis. The BET results indicated the size of the specific surface area. The size of the surface area could assist in understanding of the stability of the carbon and water suspension.

Following an analysis of the results, the researcher reached the following conclusions: First, acid treatments with a concentration of 1 molar for the duration of a minimum of 4 days modify the surface complexes of the carbon black. Second, the treatment with the most stable dispersion properties is the potassium permanganate and nitric acid treatment, which is the only treatment that formed a stable suspension. Carbon materials with a smaller surface area than the treated carbon black does not form a stable suspension, even though they have similar surface complexes. The stable dispersion remains stable only up to 250 °C. Higher temperatures cause the carbon material to start decomposing, when the carbon surface complexes are broken and released.

Keywords: Stable suspension, Modification, Carbon materials

Acknowledgements

I would like to express my gratitude to:

- my academic supervisor, Dr H Badenhorst, for his guidance, support and discussions during the course of the study;

- fellow students for their assistance on the equipment in the laboratories;

- my parents, Joseph and Mariana, as well as my brother Pieter for support and prayers;

- family and friends for their interest, encouragement and support; and

- Ms P Ahrens who edited the document.

Soli Deo Gloria

Declaration

I, Albert Roberson, declare that the dissertation, which I hereby submit for the degree of MEng: Chemical Engineering at the University of Pretoria, is my own work and has not been submitted for a degree at any other tertiary institution.

Signature: _____

Date: _____

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1. Introduction

Energy and its storage are and will become more important as natural resources become scarcer and are depleted (Lu *et al.*, 2013). Numerous studies have been conducted on the use of carbon material in energy storage (Wen-Xing, 2014). A subdivision of carbon material research is to test energy storage of carbon materials in water combined with other salts (thermal nanofluids). For this research to progress, the carbon material needs to form a stable suspension indefinitely. In this study, carbon black was the resource gatherer utilising the UV light from the sun to heat up, while graphite served as the conductor in the water transferring energy from the carbon black to the salts present in the suspension. The energy stored and released relies on the salts' enthalpy property to crystallise and melt.

The objective of this study was to find the surface treatment that would allow the carbon material to stay in a stable suspension and to determine the best carbon material for this purpose. The study also considered the effect that surface area had on the stability of the suspension.

The materials used in this study were carbon black, mesophase carbon beads and exfoliated graphite, which meant that there were different surface area sizes. The surface treatments comprised various acid treatments, as well as treatment with potassium permanganate together with nitric acid, to interact with the surface groups of the carbon materials.

Surface treatments were followed by the characterisation of the carbon material surface to determine the effect of the treatment on the surface. Characterisation (quantifying the substance properties) was done by using a variety of techniques such as mass spectrometry, thermogravimetric analysis, BET and FESEM.

During the subjection of the carbon materials to heat, the researcher was able to ascertain the temperature at which the carbon material started to decompose with the mass spectrometer and thermogravimetric analysis. This would also be the temperature at which the suspension destabilised.

The effect of the water on the carbon materials was also investigated to see if dispersing them in the water made any difference to their surface groups.

2. Literature

One option to find a new source of energy stood out above the rest, thermal fluids using carbon in a suspension. The energy will be recycling and in addition to that, there will be no by-product to poison or harm the environment. The literature starts with the previous studies on carbon dispersion that inspired this study.

2.1 Thermal Nanofluids

A suspension with small particles with sizes ranging from 1 to 100nm in a solvent media is known as a nanofluid. Nanofluids have been intensely researched due to the enhanced thermal properties and high heat conductivity that these suspensions can sustain.

The improvement of conventional heat transfer fluids has been slow, due to the low heat conductivity, particles settling out of the solvent to the bottom, clogging of flow channels when used in a continues flowing system and increased pressure drops in the fluid pipe lines.

A thermal fluid can be broken into four elements:

- A solvent medium that allows UV light to penetrate the liquid and reach the nanoparticles;
- A particle that can absorb UV light, convert that energy into heat, and emit and scatter the energy throughout the medium;

- Particles that can absorb the heat being emitted from the absorbing particles and transfer the heat quickly to the salt; and
- A salt or material that can store this energy via melting and crystallising.

Once the fluid is done melting and the energy has reached the point of saturation, the energy will then be released when the environment can no longer sustain this heightened state via the crystallisation of the salt, transferring the energy to heat conductive particles. The heat released in this manner can be used as the energy source and then be converted to the state of energy desired (Philip & Shima, 2012).

2.2 Carbon Background

In a solid state, carbon has various forms ranging from diamond structures (different isotope forms) to structures such as graphene, graphite, mesophase carbon beads and activated carbon. The main difference lies in the carbon density inside a unit cell and the sp^2 and sp^3 electron bonds between the carbons. Functional groups also play a role in the properties within each of these different forms of carbon (Bovenkerk *et al.*, 1989). Functional groups are best described as the additional molecule on the skeletal carbon material that changes the property of the material depending on the properties of the functional groups. The different structures are discussed next as they were part of the project.

Graphite is an anisotropic layered structure that has a high thermal conductivity, high mechanical strengths and high resistance to thermal shock. As graphite has a high melting temperature, it is used in many intense heating processes and therefore has become a common material in industry. Graphite also conducts electricity very well in planar orientation, making it ideal for transferring energy in a thermal nanofluid (Chukhrov *et al.*, 1986).

Graphene is a hexagonal sp^2 carbon sheet that can be rolled into a cylinder (nanotube) and multiple sheets on top of one another make graphite. A graphene sheet has two typical edges, namely a zig-zag and an armchair edge configuration (Fujita *et al.*, 1996). Due to the three-dimensional orientations of multiple sheets of graphene, the edges of graphite are more complex and therefore more difficult to characterise. This is a common structure in the research field of nanotechnology.

Expandable graphite is an intercalated graphite layered structure that expands up to 200 times its original size when heated to 230 °C or more. It is used in fire extinguishing as a volume enhancer (foam – low density). Expandable graphite can also help in the characterisation of graphite sheets and in determining the functional groups binding to the edges of graphite (Camino *et al.*, 2001). After expansion through heat and sonification for the separation of the sheets, the resulting material is called exfoliated graphite.

Carbon can take on a semi-crystalline structure, also known as mesophase carbon, where some of the carbons will orientate in a plane, stacked on one

another in sp^2 hybridity to form a crystalline structure with amorphous carbon randomly structured in between the carbon plates. Mesophase carbon display both the properties of graphite and amorphous carbon, favouring the properties of the structure it mostly consists of, usually graphite-like structures (Korai, Mochida & Yoon, 2002).

Carbon black is an amorphous form of carbon with a variety of functional groups on the surface, with carbon as the main element in this substance. Carbon black was first used as a pigment and was easy to produce using the channel process or the oil furnace process in the late 1800s. Carbon black still has many uses, among others to reinforce tyres and in solar panels (Novakov & Rosen, 2013). It is made by heating hydrocarbons with a limited supply of oxygen. Carbon black has a specific surface area of 10 to 50m²/g in general and also remains stable in acid solutions. It absorbs UV very well and disperses the energy in turn as heat.

2.3 Dispersion

Dispersion is a process in which particles go into solution without dissolving in the solvent. This happens when an incompatible particle is mixed with the solvent and no interaction between the particle and the solvent takes place.

A third component can be added to the mixture, also known as the dispersing agent, which can associate with the particle as well as with the solvent. The

dispersing agent has two sides. In most cases it will be a polar side and a non-polar side of a molecule. The polar side carries the charge that will react with the polar substance (it can be the particle or it can be the solvent) and the non-polar side will associate with the non-polar component (Grimme, 2006).

2.3.1 Adsorption

Adsorption can be described as the adhesion of the adsorbate to the surface of the adsorbent. The molecules react with the surface and leave the solution to stack on the surface until a film of the adsorbate molecules forms on the surface. This is caused by a slightly charged surface attracting the molecules that then neutralise the surface and give the surface a lower surface energy.

Van der Waals forces can be the adhesive force keeping the adsorbate on the adsorbent. The adsorbate can act as the dispersing agent and keep the adsorbent stable in the solution (Özacar, 2002). Therefore, adsorption is commonly known to be a temporary bond and the film layer is limited to the concentration of the adsorbate.

2.3.2 Surface Complex

A surface complex is formed when a molecule interacts with the oxygen or hydrogen on the material surface instead of interacting with the material itself. The complex bindings range from binding to one site to up to four sites.

These complexes occur when the material undergoes oxidation and hydrogen and oxygen bind with the material. These sites of oxygen and hydrogen that give the surface a slight charge attract other molecules that then neutralise this charge.

The surface sites enable adsorption that, in turn, can help to disperse the material in a solvent which would otherwise not be possible (Haderlein *et al.*, 2014). The surface complex is a fixed multidimensional group on the surface and similar to a functional group.

2.4 Previous work on Carbon Dispersion

Carbon dispersion has been done before by using a strong oxidising agent and a strong acid, but the only stability noted was tested for only a few days and, therefore, more information was needed. A surfactant can also be used to disperse the carbon material but due to the aim of this project and the desire to suspend the carbon without compromising on the heat conductive properties, the surfactant option was not used for this experiment.

In the study by Kratochvil and Matjevic (1982), carbon powder was dispersed using an ultrasonic bath on the carbon powder in water for 5 min. The additives

were then made up in various concentrations and mixed together with the carbon powder suspension. Triton X-100 was used as the electrolyte/surfactant and proved to sustain the suspension of carbon powder in water for up to a few days.

This method was carefully considered, but, as previously mentioned, the surfactant option might prove to be of no use if the surfactant would hinder the carbon material's heat conductivity and UV adsorption.

The other method previously used seemed to favour the aim of this project and, therefore, it was used as a guideline to doing our own experiment and stability tests.

In Donnet's (1962) study, carbon black was treated with an acid and metal hypochlorite to make it water soluble. It was later found that the carbon black did not dissolve but rather formed a suspension. The idea was to oxidise carbon black and give it hydrophilic functional groups. The patent goes on to say that the carboxylic groups and nitric acid concentrations were varied and the pH was measured, but does not specify how it was done or what equipment was used except for using a BET method to determine the specific area.

The patent also states that the higher the nitric acid concentration, the more carboxylic groups are formed, but oxidation to completion takes longer (Donnet, 1962). From the results, it seems to be a viable method to modify the

surface groups of the carbon materials rather than using a surfactant to disperse the carbon.

A study was done to enhance the thermal conductivity of carbon nanotubes by treating them with polyethylene glycol using a Fischer esterification. Other properties also influenced were viscosity, heat capacity and pressure drop rate, which all seem to favour the goal of having a nanofluid.

Sigma Aldrich supplied 95% polyethylene to be used along with the carbon nanotubes and then sulphuric acid was added to catalyse the reaction and bind the tubes to the polyethylene. After the reaction took place, the compound was then added to water where a suspension formed that could be tested to see if the nanotubes were performing better or worse after the treatment.

The viscosity of the suspension increased as the concentration of the compound increased while the thermal properties also increased. The heat capacity of the fluid also increased dramatically to nearly double the raw material's capacity and the transfer rate of the heat was 20% faster (Atieh *et al.*, 2016). This method could serve only as a last resort as it is financially costly.

Another study on the thermal stability of nanofluids was done testing various carbon nanotube treatments and dispersing them in various base solvents to find the best combination.

The tests were done at 20, 80 and 100°C. They added nitric acid, sulphuric acid or potassium persulphate to the carbon nanotubes. The treatment that received the most attention was the potassium persulphate. The treatment also required that the solvent medium be deionised water. A sonic bath was used on the components and nanotubes to open the surface and give penetration opportunities to the sulphate groups.

Once the mixture started to react, they also added potassium hydroxide until the pH was 13 or higher to saturate the carbon nanotubes. The treatment was successful and the carbon nanotubes were also able to disperse in non-polar solvents (Crisostomo *et al.*, 2016).

2.5 Characterising Methods

Characterisation methods that can aid in the understanding of the solubility when dispersing the various carbon materials are listed below, with an explanation of how each one works and how the various methods were useful to this research.

2.5.1 BET Method

This instrument can measure the adsorption of a gas on a solid material and the specific surface area. It is important to characterise the porous surface area when working with graphite, as this will help with the characterisation of the

functional groups that are bonded to the graphite edge surfaces. Equation 1 and 2 are used to calculate the values and was derived from the BET adsorption isotherm equation:

$$S_{\text{total}} = (V_s \times N \times A_c) / V_m \quad (1)$$

$$\text{and } S_{\text{BET}} = S_{\text{total}} \times \alpha \quad (2)$$

S_{total} represents the total surface area (cm^2), where specific surface area is represented by S_{BET} (cm^2/g), N represents the Avogadro's number (6.023×10^{23}), α the mass of the sample (g), V_m the molar volume of the adsorbate gas (cm^3/mole), A_c represents the samples cross section area (cm^2) and V_s representing the volume of the sample (cm^3).

This means that the measurement is based on the amount of gas that is able to penetrate the substance and go inside the pores to find the total surface area. The mass and density of the sample are recorded beforehand.

The volume necessary for the BET to measure the area is a simple calculation obtained from measuring the volume needed to have no loss in pressure when the gas has finally gone into all the pores.

The BET method used for characterising the surface area was developed by Brunauer, Emmett and Teller and was derived from the Langmuir theory of adsorption (Djordjevic & Tamhina, 2010).

The Langmuir theory of adsorption measures the surface area of the material by using a monolayer of adsorbate gas that forms a film over the surface, the pressure increase that would have taken place in the empty column is calibrated beforehand and the lack of that pressure increase indicates that the gas under vacuum condition is adsorbing to the surface of the material. Pores in the material can form multi-layers of adsorbate gas, while the outer-surface is still a monolayered film, this will result in a much higher specific surface area reading. The BET theory is the multi-layered version that will include the pores and give a more accurate specific surface area value.

Their method combined with nitrogen adsorption isotherms measured at 77 K can accurately determine the surface area of the porous graphite. The BET method uses the amount of gas that can infiltrate the substance, the weight of the sample and the total size of the sample to calculate the surface area.

The pressure inside the chamber is measured as a ratio to the reference pressure. The lower the ratio, the more the gas that is able to infiltrate the substance (Snurr & Walton, 2007). The density of the material must be known before doing the experiment.

2.5.2 Density

The density is defined by the mass of the substance per its volume so that if one substance weighs more than another and both have the same volume, the one with the heavier mass will have the highest density. There are two chambers (reference chamber and sample chamber) being compared to one another throughout the experiment.

A gas pycnometer can measure the volume of powders, granules or crystals placed inside the chamber. Seeing that the mass of the sample is also recorded at the beginning, measuring the volume will indicate the density of the sample. To measure the specific volume, the pycnometer uses Equation 3:

$$V_s = V_c + V_r / (1 - [P_o/P_x]) \quad (3)$$

V_s represents the sample volume, V_c is the empty sample chamber and V_r will be the reference chamber volume (all the volumes are calculated in cm^3). P_o represents the initial pressure while P_x represents the current pressure in time (both recorded in Pa).

As these runs will lead to the V_s value, the rest can then be determined beforehand (Jingjing & Qing, 2012). The pycnometer can measure pores in a solid piece of rock as well and determine the volume of the pores in between powder granules.

2.5.3 Pyrolysis and Mass Spectrometry

The mass spectrometer uses the mass-to-charge property of each element to identify it. Each atom/molecule has its own mass-to-charge ratio, which means that this property can be utilised to identify the elements within a sample after they are introduced into the charged chamber, due to the distance each element travels inside. The mass spectrometer can also identify molecules and not just the atoms.

The sample can be ionised using different voltages at each end and then using a detector at the end of the tube to burn the sample and read the different elements contained in the sample (Glish & Vachet, 2003). The MS can identify the elements or molecules being released under heated conditions.

2.5.4 Thermogravimetric Analysis

The measurement is made by continually measuring the mass of the sample as it is being heated. In cases where combustion is possible, an inert gas flowing through the furnace is needed to inhibit any combustion activities.

The TGA is made up of three different components, namely a scale to weigh the sample, a furnace to heat the sample and gas to flow through the furnace.

The sample decomposes as it is being heated and the energy allows for the sample to decompose while heated (Abbasi & Ebrahimi-Kahrizsangi, 2008). The volatile gases evaporate from the rest of the sample so that only the non-volatile solid is left.

The flow rate and the choice of gas can be set before the runs are done and the ramp rate of the temperature can also be set beforehand. This means that the mass will be the only unknown variable when the run is done.

The balance scale for the thermogravimetric analysis is accurate to a hundred micrograms and is highly sensitive to any change in the weight of the sample.

2.5.5 Field Emission Scanning Electron Microscope

The FESEM can be used to investigate material surfaces and to determine their electric properties.

The microscope uses a tip with a high melting point to increase resistance capability. On the other side of the chamber there is a fluorescent screen with a positive charge, while the sample itself has a negative charge, thereby creating a field emission of electrons near the tip close to the sample.

Black and white patches are detected and sent to the computer to create a picture of the surface. This microscope can take nano-size pictures and aid in characterising surfaces of the coated samples.

The magnification is determined by the tip radius and the distance from the screen to the tip. Other factors that influence magnification to a lesser extent are voltage over the tip or the sample's induced charge (Honkanen, Koivuluoto & Vuoristo, 2009).

3. Experimental

The first objective was to find the treatment that would modify the surface of the carbon black. The first plan was to use different time spans for the acid treatments and to use different concentrations to see what the effect of each concentration was. Nitric acid, sulphuric acid and hydrochloric acid were used.

The treatment with the most stable dispersion would then be used on all three carbon materials, namely carbon black, mesophase carbon beads and exfoliated graphite, carbon black being the amorphous structure, mesophase carbon beads the intermediate material and exfoliated graphite being the crystalline structure.

The mesophase carbon beads and exfoliated graphite would also be observed after the best surface treatment to find out whether they formed a stable suspension when dispersed. The mass spectrometer and TGA would indicate the temperature limit for a stable dispersion. The mass spectrometer would indicate which atoms or molecules get released when heated.

3.1 Carbon Materials Used and Surface Treatment

Three types of carbon (exfoliated graphite, carbon black and mesophase carbon beads) were tested on the mass spectrometer after having been soaked in various acids and bases.

The acid and base treatments are given in Table 7.1 (Appendix A). Acids of different concentrations were chosen to see whether an acid would release different gasses than the untreated carbon. Potassium permanganate in combination with nitric acid was one of the treatments used on the carbon materials.

The acids, graphite and the potassium permanganate were AR grade and supplied by Merck. The mesophase carbon beads were bought from CHNM and the carbon black was bought from Printex. The nitrogen and helium gas were supplied by AFROX. The steel pipes, connections and steel cylinder were bought from Swagelok.

The samples were washed after the treatment and the pH of the filtrate of every batch was measured until a pH of more or less 7 was obtained. A pH of 7 indicated that the samples did not have significant amounts of impurities or acid/base residue. Each sample was then dried under convection conditions at 100 °C.

The carbon materials were treated with potassium permanganate and nitric acid with 5g carbon material, 15g potassium permanganate and 150 ml nitric acid with 50 ml water, and left to react for either 2 days or 4 days. Two samples were made after filtration and washed so that one could be tested right after treatment, while the other was soaked in water for a week and then tested on the mass spectrometer. The prepared samples are listed in Table 3.2 (Appendix A).

3.2 Suspension Stability Tests

Observations were done by placing the sample in water and mixing the sample vigorously before letting it stand in front of a white screen to see whether the sample stayed in solution or agglomerated and settled out. This determined which samples were considered for the rest of the tests.

3.3 Density Tests

First a size volume was chosen on the computer running the machine and then two runs were done with nitrogen gas, one run being done in an empty sample holder and the second run being done with a holder filled with a perfect sphere.

An AccuPyc II 1340 Gas Pycnometer made by Micromeritics was used. The samples were weighed before being placed inside the chamber holder until the holder was filled to over the three-quarter volume mark. The sample was then placed back into the pycnometer. The top of the pycnometer was closed and sealed to make sure that no gas leaked from it. The computer controlled the experiment and let the gas flow in and out of the pycnometer, while sending the data accumulated during the 5 minutes of the experiment to the computer.

3.4 Surface Area Tests (BET)

The sample was dried and a vacuum was created in the sample test tube to remove all residual vapours.

The test tubes were heated while the sample was under a vacuum to make sure that the sample did not contain any water by the time it was used inside the BET. After the sample had gone through the preparation steps, the sample tube was screwed off the gas unit and screwed into the BET, three tubes at a time.

The BET needed nitrogen as an inert gas and cooling source for the test. The computer measured all the parameters such as density and mass before it started analysing the sample by creating a vacuum inside the test tubes and letting each fill with gas again. This continued until 5 distinctive runs had been done and the final result was expressed as an average. The BET model was a TriStar II Surface Area and Porosity and the sample degasser model was a VacPrep 061 Sample Degas System, both made by Micromeritics.

3.5 Field Emission Scanning Electron Microscope

Before treatment and after treatment the carbon materials were observed through the FESEM.

The potassium permanganate with nitric acid treatment was used for the samples. The carbon materials were carbon black, mesophase carbon beads and exfoliated graphite.

Before the sample could be observed under the lenses, the sample needed to be plated and given a charged carbon coating to enhance its electrical conductivity. The coating was a thin layer and would enhance the carbon materials' surface structures on the microscope. Black adhesive tape was used to stick the carbon materials to the plate and the sample was blown afterwards to make sure that the sample would stick to the plate and not separate while under the charged conditions.

When the sample had been plated, the carbon coating process could start. For this process, the tips of two carbon lead pins spun against each other and released a carbon cloud that filled up the chamber and settled on the sample. The sheer force on the tip of the lead pin broke the outer surface on the tip into small particles that were released into the chamber. It was very important that each sample preparation was duplicated exactly so that the results could be compared and relevant.

After the carbon had been puffed into the chamber for 5 minutes, the remainder of the carbon lead pins was used to spark an arc and heat up the carbon so that it could form an electrical conductive film on the sample.

The sample plate itself (with all the samples on top) was kept up straight with a small shifting table inside the chamber for the first coating. Then, after the first coating, the sample plate was angled at 45° to the carbon lead pins and coated again to increase the affectivity of the coating. The angle was also used on the opposite side of the sample to ensure that the entire sample was coated equally.

Once the samples were coated with this charged carbon film, they were placed inside the FESEM. Finding the correct magnification was time consuming with three functions playing a role, namely the distance between the sample and the lens, the high magnification, and the noise eliminator (compensates for dark spots and rough lines on the pictures).

3.6 Thermogravimetric Analysis

The control sample crucible and the sample crucible (both empty) were placed inside the TGA balancing beams. The furnace was closed and the computer calibrated both crucibles. After the calibration had been done the furnace was opened and the sample crucible was placed on the scale which was zeroed.

A sample was now added to the crucible until the sample weighed 2 mg. The crucible was placed back into the TGA. The sample could be tested by heating at 50 °C per minute until the oven reached 1000 °C, while nitrogen gas flowed through to ensure that the sample was heated but did not oxidise inside the hot furnace. The TGA model used in this study was an SDT Q600 made by Advanced Laboratory Solutions.

3.7 Pyrolysis and Mass Spectrometer

When using the mass spectrometer, a tunnel oven was used to heat the sample in 50 °C intervals from 25 °C up to 1025 °C.

Each step depended on the time it took for the sample to stabilise (stop increasing or decreasing) at that specific temperature, which meant that each mass spectrometer run would have an individual experimental duration.

The sample was placed inside a stainless-steel cylinder and connected to a valve to control the flow rate through the cylinder. Helium gas that flowed through the system was the inert carrier. From the helium gas cylinder to the mass spectrometer everything was sealed to prevent any atmospheric contamination. The mass spectrometer model used in this study was a GSD 301 T3 mass spectrometer made by Pfeiffer Vacuum.

The carbon materials were treated with potassium permanganate and nitric acid with 5 g of carbon material, 15 g of potassium permanganate, 150 ml nitric acid and 50 ml water. Two samples were made after having being filtered and washed so that one could be tested right after treatment, and the other be dispersed in water for a week and then tested on the mass spectrometer.




4. Results and Discussions

4.1 Suspension Stability Tests

The observations revealed that almost all the samples precipitated except for those treated with potassium permanganate, and this treatment only showed efficacy when carbon black was treated.

Immediately after the carbon black, mesophase carbon beads and exfoliated graphite were treated and dried, they were placed in water and photos were taken, 1 hour later and 5 hours after having been soaked in water. The results are shown in Table 4.1.

Table 4.1: Observation Summary

	Carbon black	Mesophase carbon beads	Exfoliated graphite
Mixed			

1 hour later



**5 hours
later**



The left-hand side polytop contained the carbon black and the carbon black stayed in solution permanently, while the mesophase carbon beads (middle polytop) settled out after 5 hours. The exfoliated graphite (right-hand side) settled out after 2 hours, similar to the rest of the surface treatments. The carbon black dispersed, but the mesophase carbon beads and graphite did not stay in suspension. The dispersion information indicates that the treatment effects carbon black more than the other carbon materials. More experiments will help to determine why only carbon disperses.

4.2 Density

The results for the pycnometer are shown in Table 4.2.

Table 4.2: Pycnometer results

Sample name	ρ (g/cm ³)
Carbon black treated	2.25
Carbon black untreated	1.87
Mesophase carbon beads treated	2.28
Mesophase carbon beads untreated	1.88
Exfoliated graphite treated	1.17
Exfoliated graphite untreated	0.62

From the results, the density consistently increases after being treated, The exfoliated graphite density can be increased by breaking the flakes into a powder, but for consistency the sample was kept as flakes to represent the sample as it was used. The density should be decreasing after being treated, but it is possible still that the inert gas condensate inside the pores and misleads the reading due to the pycnometer not picking up the pores and open spaces.

4.3 Surface Area Tests

The results for the BET are shown in Table 4.3.

Table 4.3: Results for the BET

Sample name	S_{BET} (cm ² /g)
Carbon black treated	46.90
Carbon black untreated	34.20
Mesophase carbon beads treated	33.05
Mesophase carbon beads untreated	20.36
Exfoliated graphite treated	17.60
Exfoliated graphite untreated	15.97

The carbon black has the biggest specific area size, while exfoliated graphite has the smallest specific area size. This means that the carbon black can react with the treatments much quicker, while the active sites of graphite are being oxidized, but only on the exposed edges of the monolayers. Mesophase carbon beads are found in the middle of the two other samples as they have bigger structures than the carbon black and are stacked a little more compactly, however their structures are still not as big as those of the exfoliated graphite sheets. After treatment, the specific area size increases due to the more compact structure. The exfoliated graphite seems less due to a lack of adsorbate gas being able to penetrate in between the monolayers, using a different adsorbate gas could yield a much higher specific surface area for the exfoliated graphite.

4.4 Field Emission Scanning Electron Microscope

Figure 4.1 shows the results from the FESEM at 25 000 times magnification and Figure 4.2 shows the sample at 175 000 times magnification.

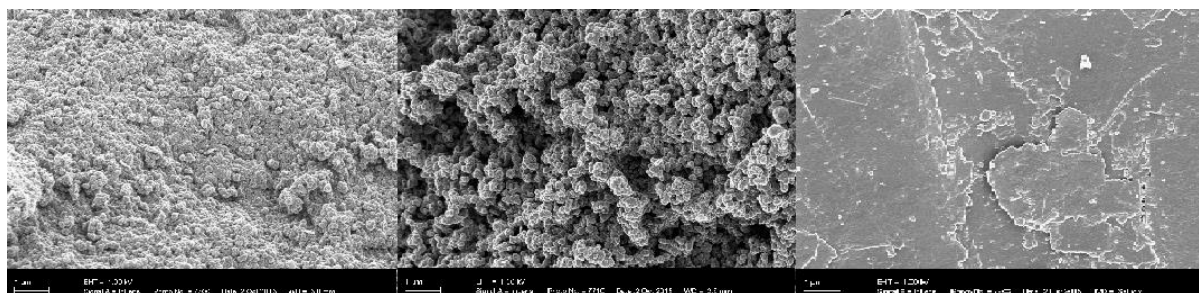


Figure 4.1: Carbon black (left), mesophase carbon beads (middle) and exfoliated graphite (right) results at 25 000 times magnification

The result on the left show the carbon black surface, the middle the mesophase carbon beads and on the right the exfoliated graphite photos taken by the FESEM with a 25 000 times magnification for each sample. Comparison between the materials reveals a minor difference in structure, which will ultimately have a big influence on the reaction and the dispersion capabilities of the material. The same results are shown in Figure 4.2, at 175 000 magnification.

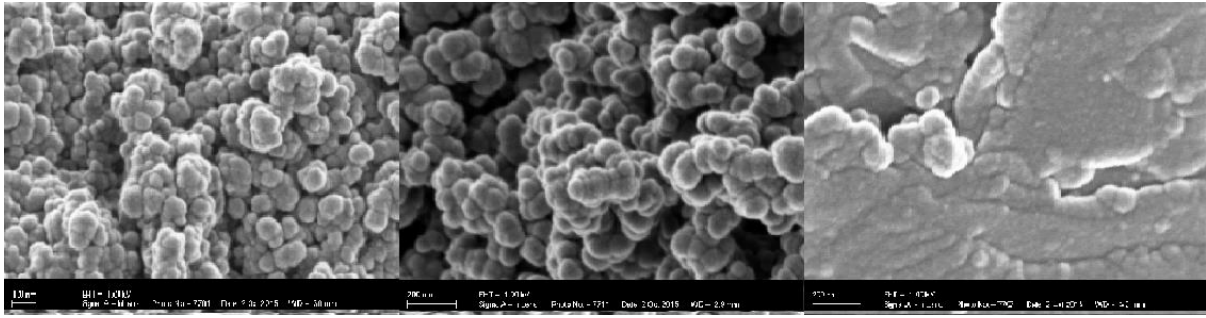


Figure 4.2: Carbon black (left), mesophase carbon beads (middle) and exfoliated graphite (right) at 175 000 times magnification

On left is the carbon black surface, the middle is mesophase carbon beads and on the right the exfoliated graphite. On a small scale like this, the structures of the mesophase carbon beads and the carbon black start to look similar, but the mesophase carbon beads seem to have larger free spaces in the material matrix compared to the carbon black.

4.5 Thermogravimetric Analysis

The results for the carbon black, mesophase carbon beads and exfoliated graphite showed a difference in the sample before and after treatment and different groups were released, as shown in Figure 4.3.

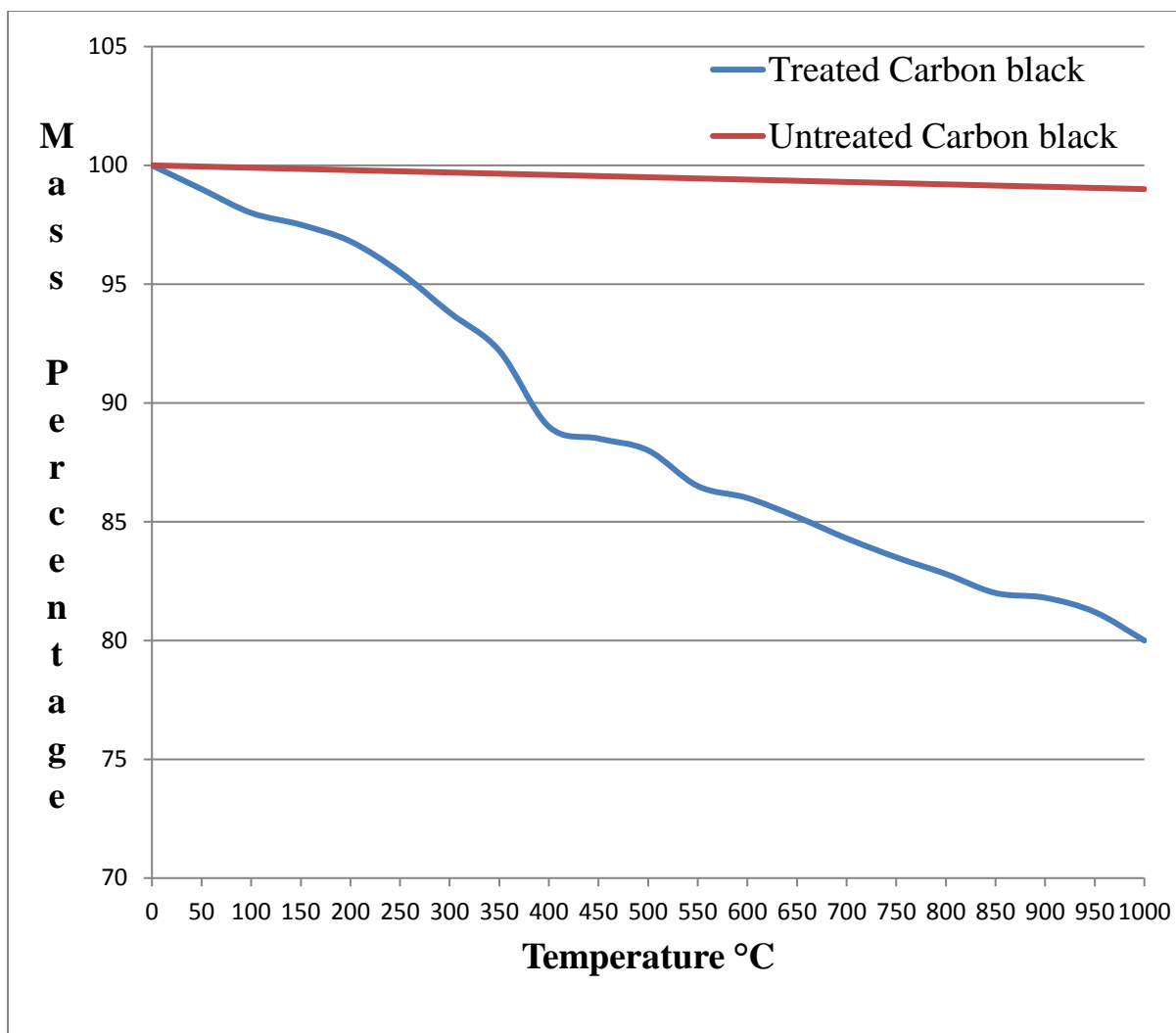


Figure 4.3: Treated and untreated carbon black obtained at a 50°C/min heating rate

Before the treatment there was no decomposition and afterwards the mass loss showed the same tendency as the results from the mass spectrometer, with carbon dioxide being released and nitrogen oxide being released later on. For the treated sample, the mass loss was 20 times higher than for the untreated sample, which means that the treatment caused chemical association between the nitric acid and the carbon material. Water could cause the initial increase in the mass loss rate.

Most of the mass loss can be ascribed to the carbon dioxide being released. Later on, the nitrogen oxide being released also contributes to the mass loss, seeing that, apart from the usual groups before treatment, it is the only additional group that can make up for the entire mass loss. Thus, the results from the mass spectrometer and the TGA together give a better understanding. Though the TGA curve itself runs smooth, the increase of the mass loss rate and decrease at certain temperatures will render more valuable results than simply looking at the mass loss.

Results for the mesophase carbon beads for the TGA are shown in Figures 4.4 for both treated and untreated samples.

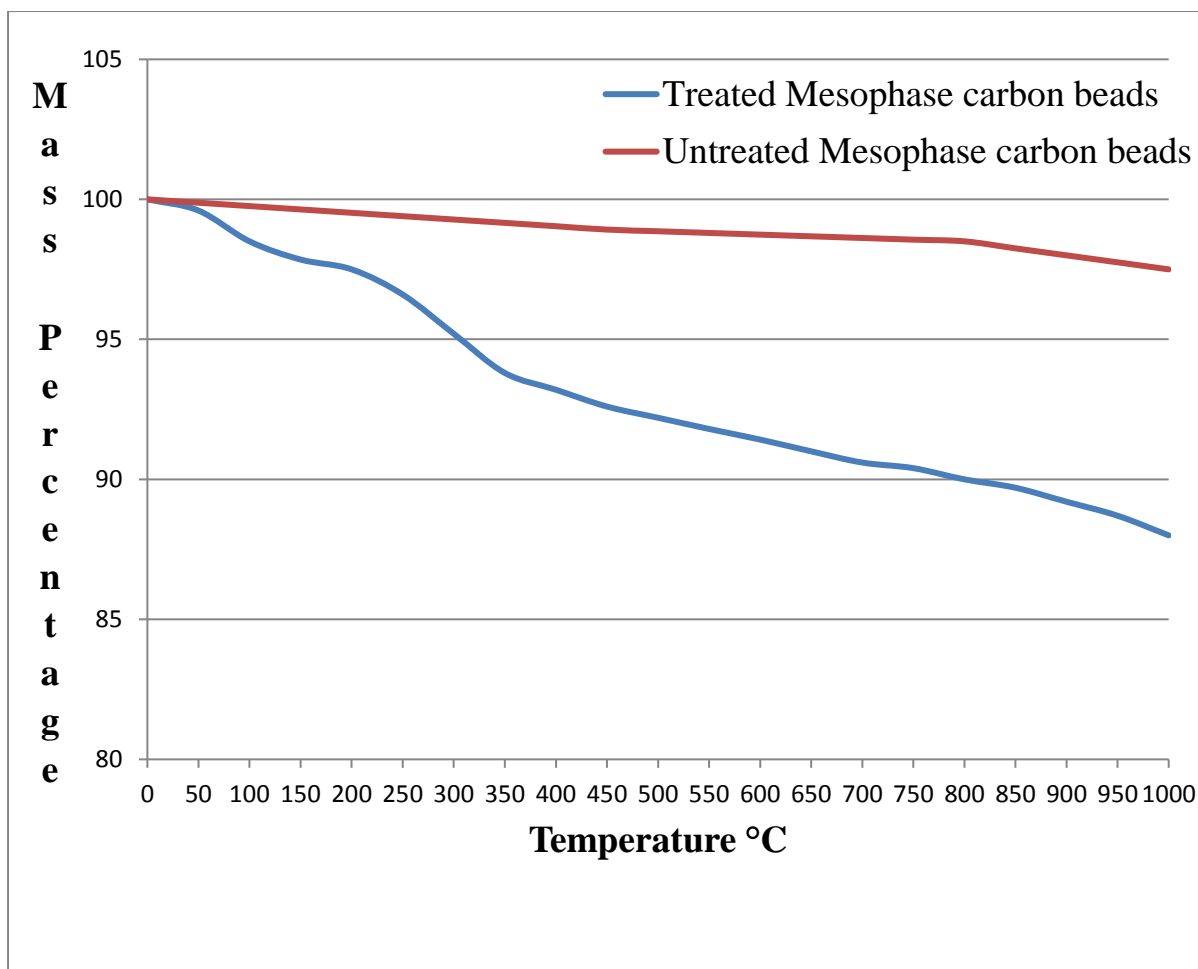


Figure 4.4: Mesophase carbon beads after treatment and before obtained at a 50°C/min heating rate

The results for the TGA indicate that the same decomposition occurs in both, but the treated sample releases four times the amount of the same groups. The temperatures indicate that the mass losses, in both cases, are due to the carbon dioxide being released, with the additional mass loss due to the nitrogen oxide being released from the treated sample. Water could cause the initial increase in the mass loss rate.

The TGA results for the treated and untreated samples of exfoliated graphite are given in Figure 4.5.

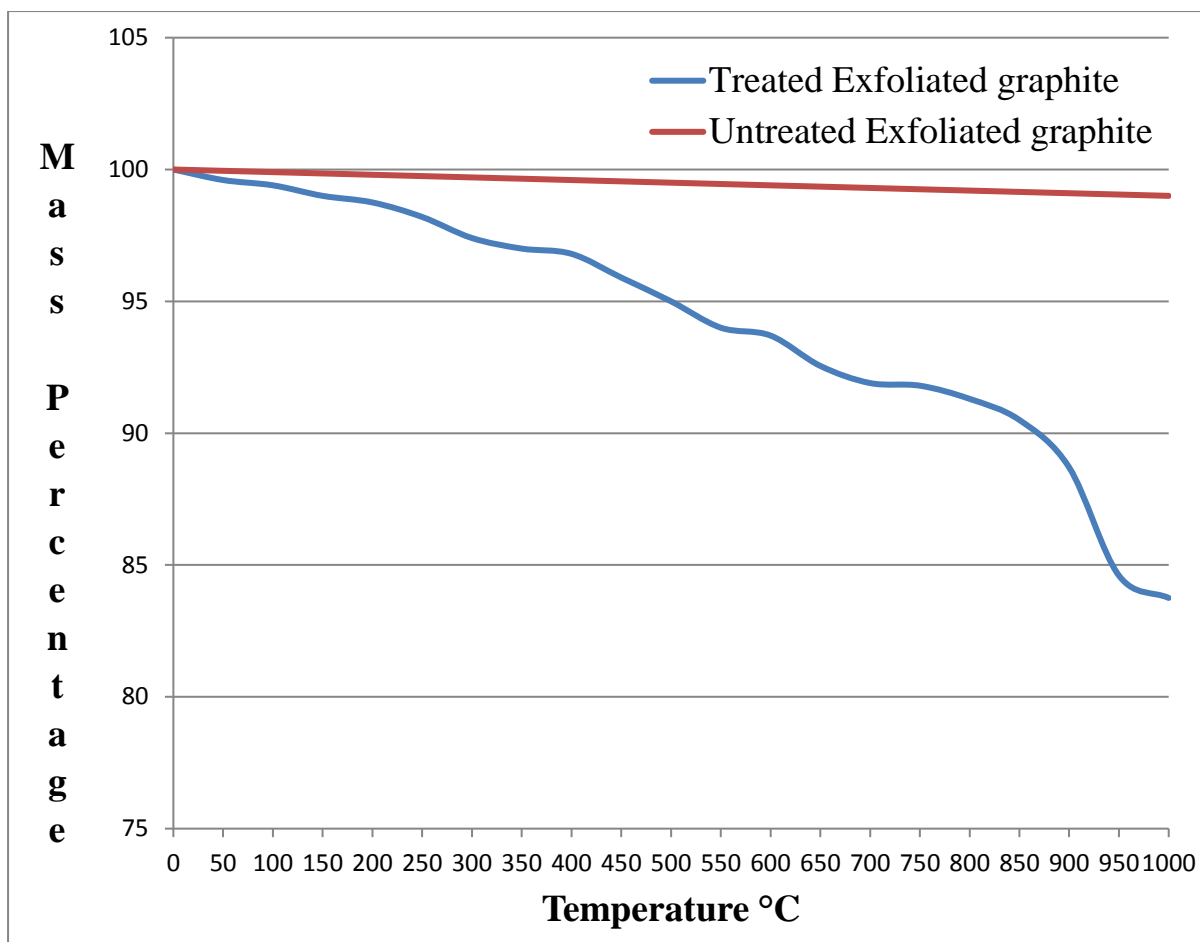


Figure 4.5: Treated and untreated exfoliated graphite obtained at a 50°C/min heating rate

According to the TGA graphs, the same groups are decomposing, but once again, the treated sample shows up to 4 times more decomposition. The samples start decomposing at 250 °C, which is consistent with the MS for the carbon dioxide being released. The sulphur present in both samples causes an additional mass loss throughout the experiment. Water could cause the initial increase in the mass loss rate.

The evolved gasses being released in the TGA graphs are deducted from looking at both the TGA and MS pyrolysis data, but to be sure of the quantity and the molecules being released a larger variance of experiments would be required. Important to consider the mass loss derivative line to observe peaks.

4.6 Pyrolysis and Mass Spectrometry

All the original results for the mass spectrometer are given in Appendix A. The carbon black reference sample is the most common result with the only peaks observed being carbon dioxide. The samples that were soaked for only two days yielded the same results as the hydrochloric acid results. The results are given in Figure 4.6. Water was always present but only with the peroxide groups, were the release of these species significant enough to mention.

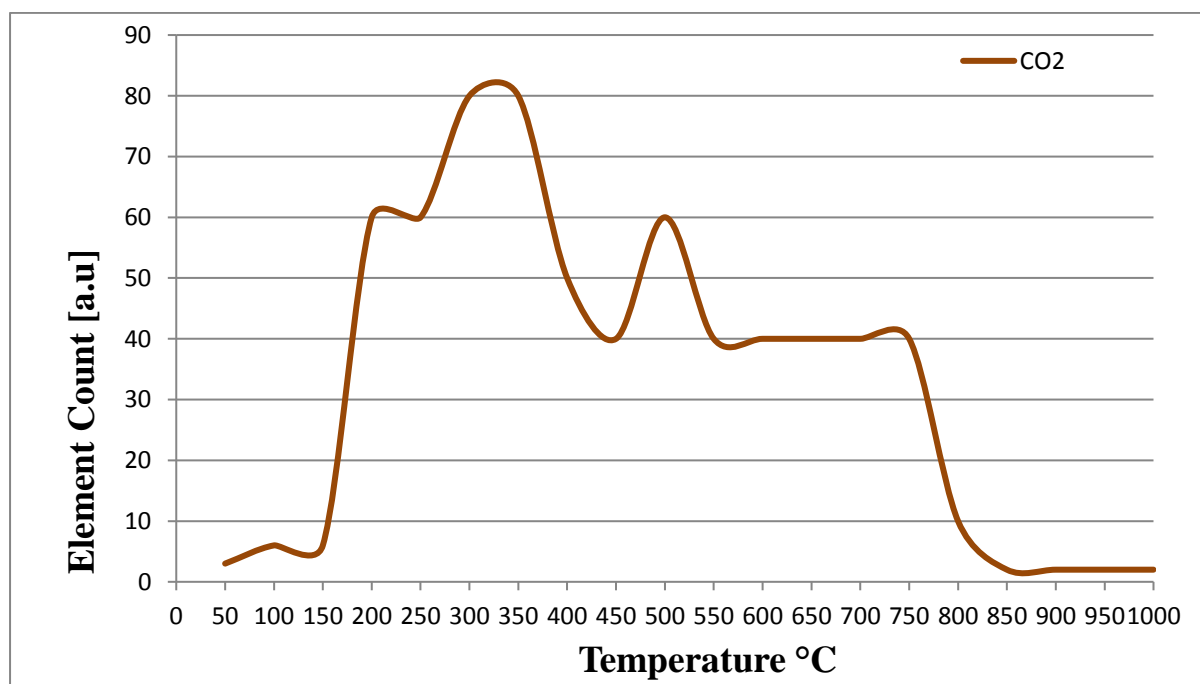


Figure 4.6: Carbon black reference

The line represents carbon dioxide. The water and the helium lines are excluded from the graph so that the scale fits the important result, namely the carbon dioxide line. Helium and water were also present but serve as nothing more than control lines.

The carbon dioxide starts with a small peak at 350 °C. The other lines are of no concern to this study as they are multiples of the original lines and show the same tendencies. This is the result that was obtained with most experiments – no peaks other than carbon dioxide and slight peaks for water and helium.

The results of the samples treated with sulphuric acid are shown in Figure 4.7 (results before being soaked in water) and Figure 4.8 (results after being soaked in water for a week, filtered, washed and dried).

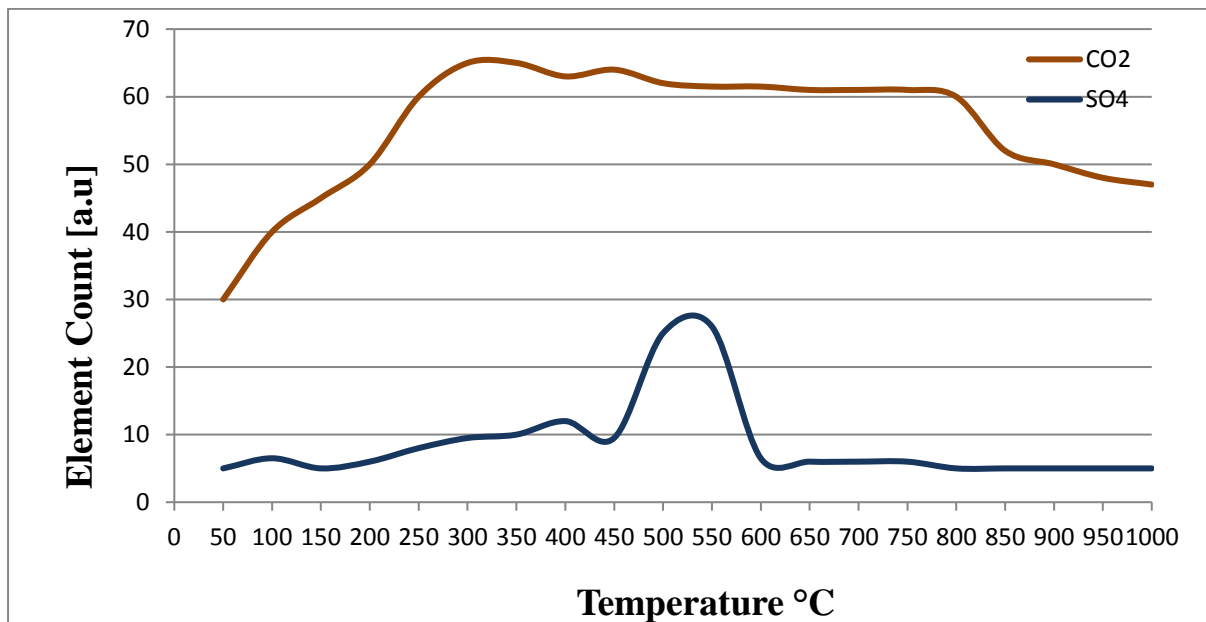


Figure 4.7: Carbon black treated with sulphuric acid

The blue line represents the sulphate groups released by the heat and the brown line is the carbon dioxide group. The results show sulphur groups are released at 455 °C and the carbon dioxide groups at 251 °C. These look like the carbon black reference results except that sulphur groups are also present.

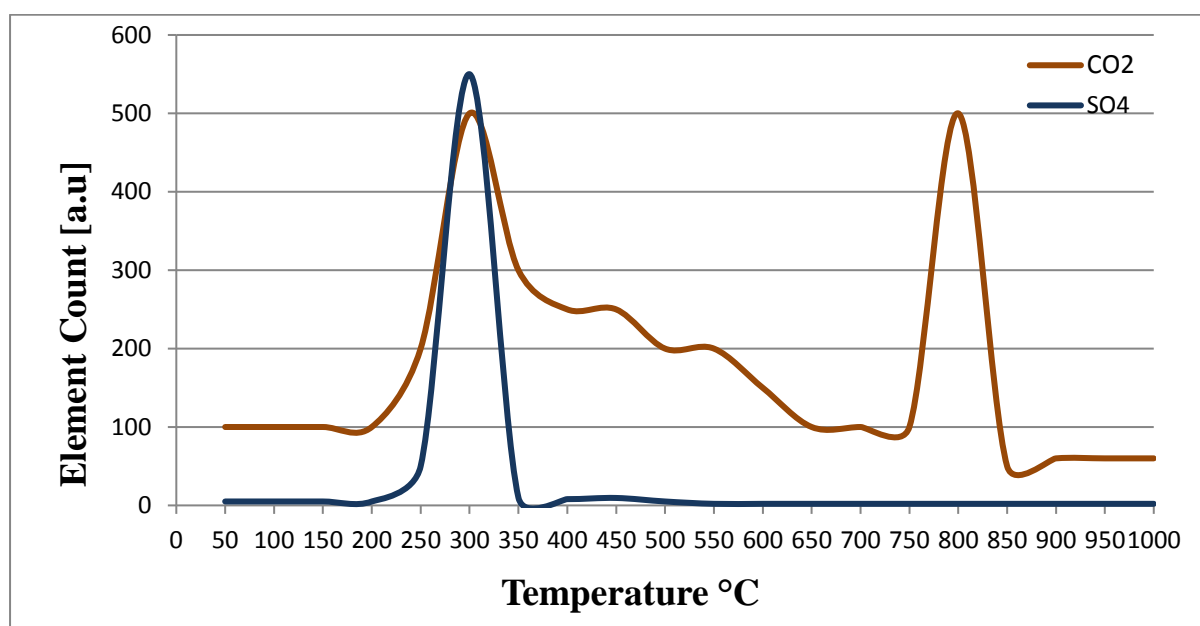


Figure 4.8: Carbon black treated with sulphuric acid and then soaked in water for a week

The results show that the sample did not undergo much change from when it was soaked in water, with the temperatures and functional groups still present and under the same conditions.

The nitric acid samples were tested in the same way as the sulphuric acid samples. One was tested right after treatment and the other after having soaked in water for a week. Figures 4.9 and 4.10 show the results for these mass spectrometer tests.

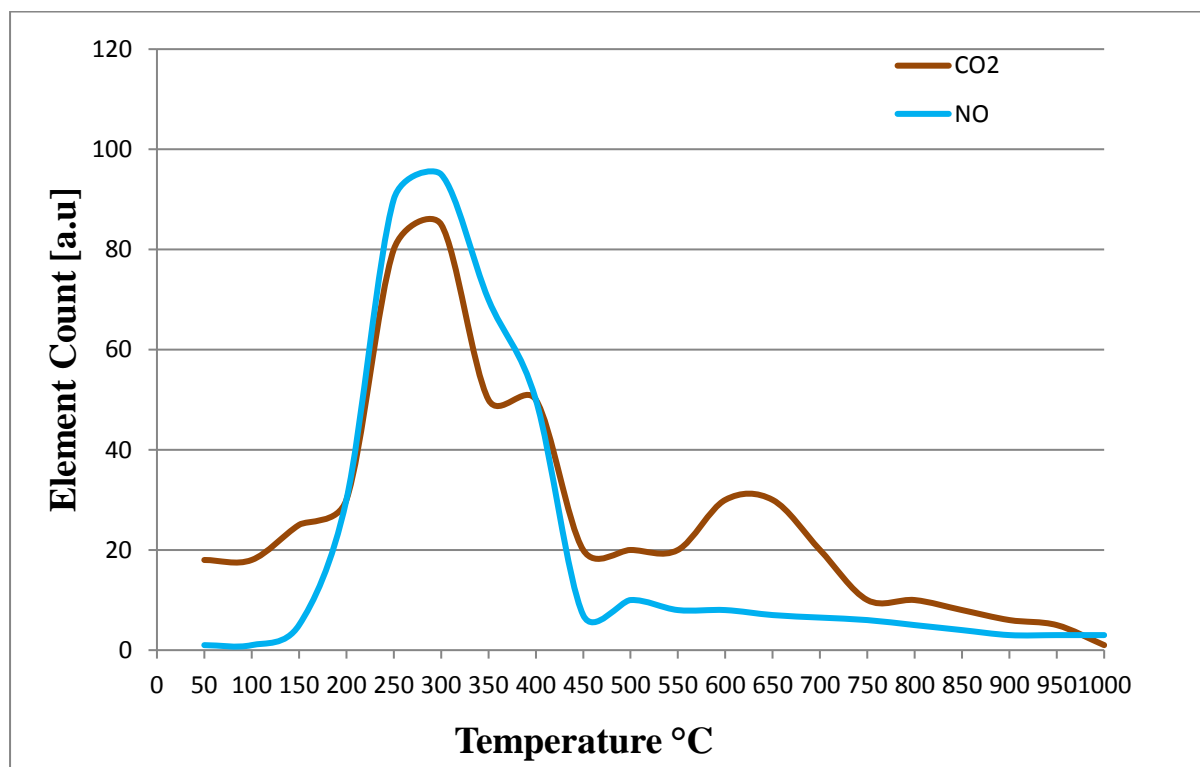


Figure 4.9: Carbon black treated with nitric acid

The result for the samples treated with nitric acid indicated by the blue lines represents the nitrogen oxide groups and the brown lines represent the carbon dioxide groups being released. From these results it can be seen that nitrogen oxide groups are released at 250 °C and carbon black groups at 255 °C. There is water present in carbon black even after having been dried in the oven.

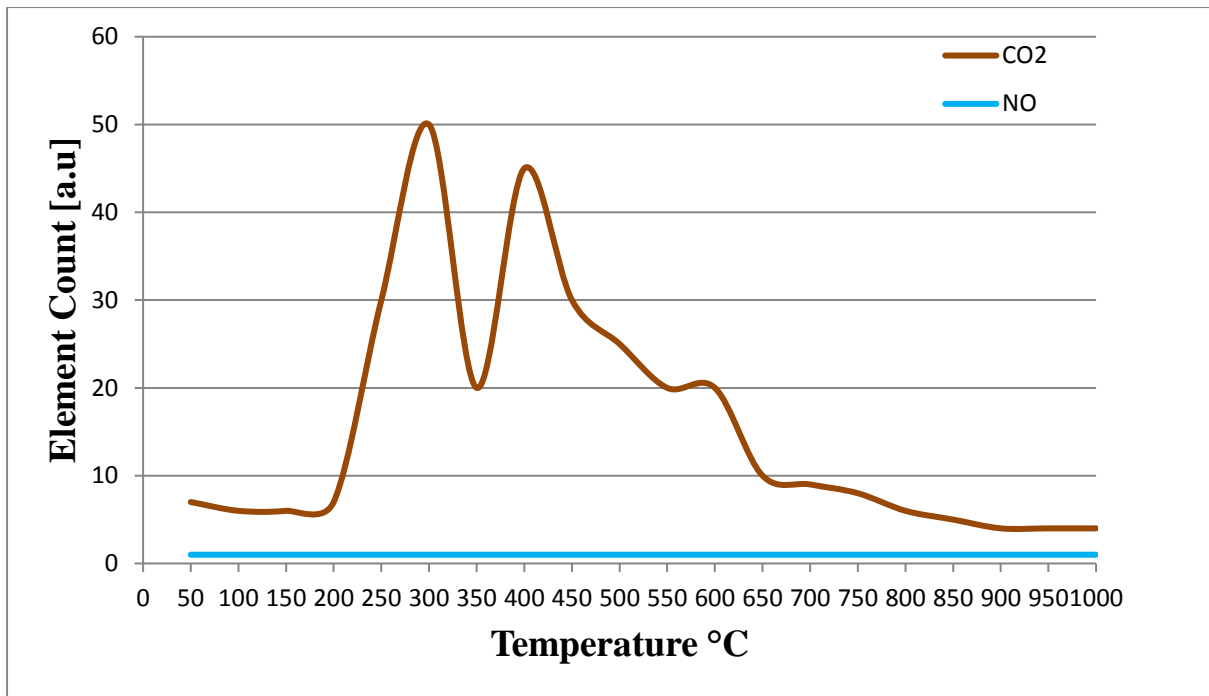


Figure 4.10: Carbon black treated with nitric acid and then soaked in water for a week

The result for the nitric acid sample that was soaked in water for a week differs from before it was soaked in water. Although the carbon dioxide was reduced, it was still present. The nitrogen seems to have disassociated after being soaked in water, which means that it would rather dissolve in the water than to associate with the carbon black.

The results of treatment with hydrogen peroxide are shown in Figure 4.11. The results before soaking the carbon black in water and after soaking were almost exact duplicates on the mass spectrometer.

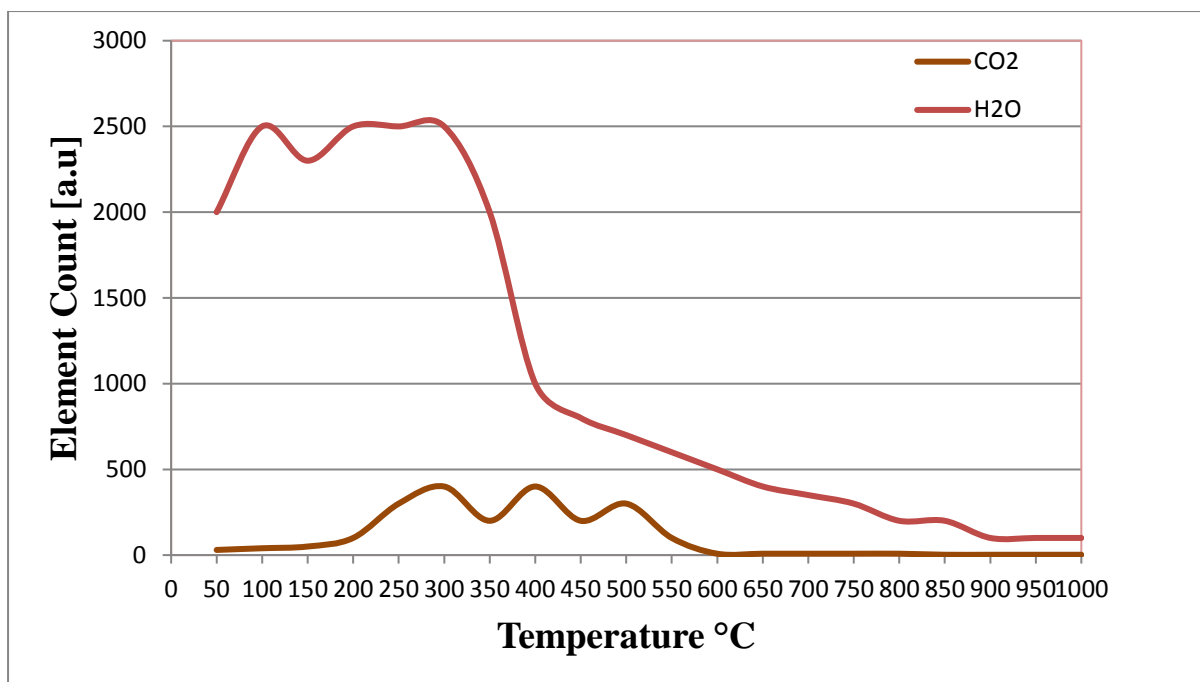


Figure 4.11: Carbon black treated with hydrogen peroxide

The results show that carbon dioxide was released as well as water. Carbon dioxide was released at a temperature of 252 °C and kept on being released up to a temperature of 314 °C. The water was released from 108 °C to 270 °C. This graph was the same for both experiments.

The results of the potassium permanganate treatment are shown in Figures 4.12 and 4.13, with Figure 4.12 showing the results for the carbon black right after treatment and Figure 4.13 showing the results after it had been soaked in water.

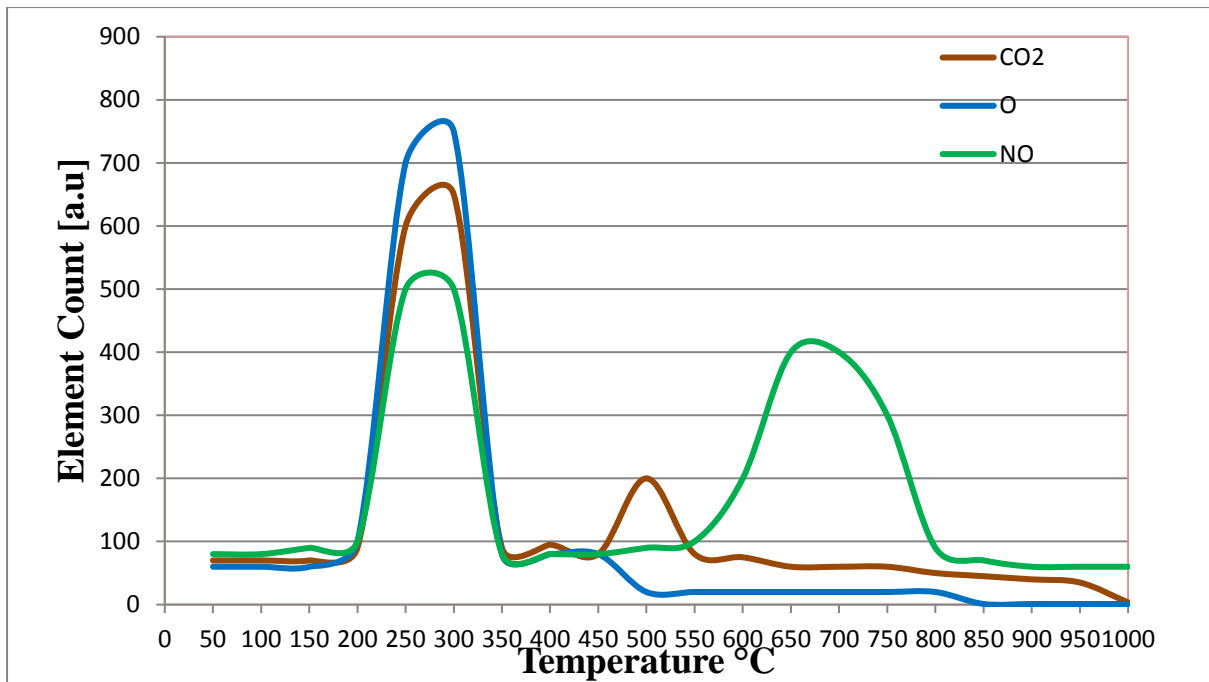


Figure 4.12: Carbon black treated with potassium permanganate and nitric acid

The results for the potassium permanganate sample show carbon dioxide (brown line), nitrogen (light green line) and oxygen (light blue line) being released. The carbon dioxide, nitrogen and oxygen were released at a temperature of 258 °C. Nitrogen then later peaked at 714 °C. Water was released throughout the experiment.

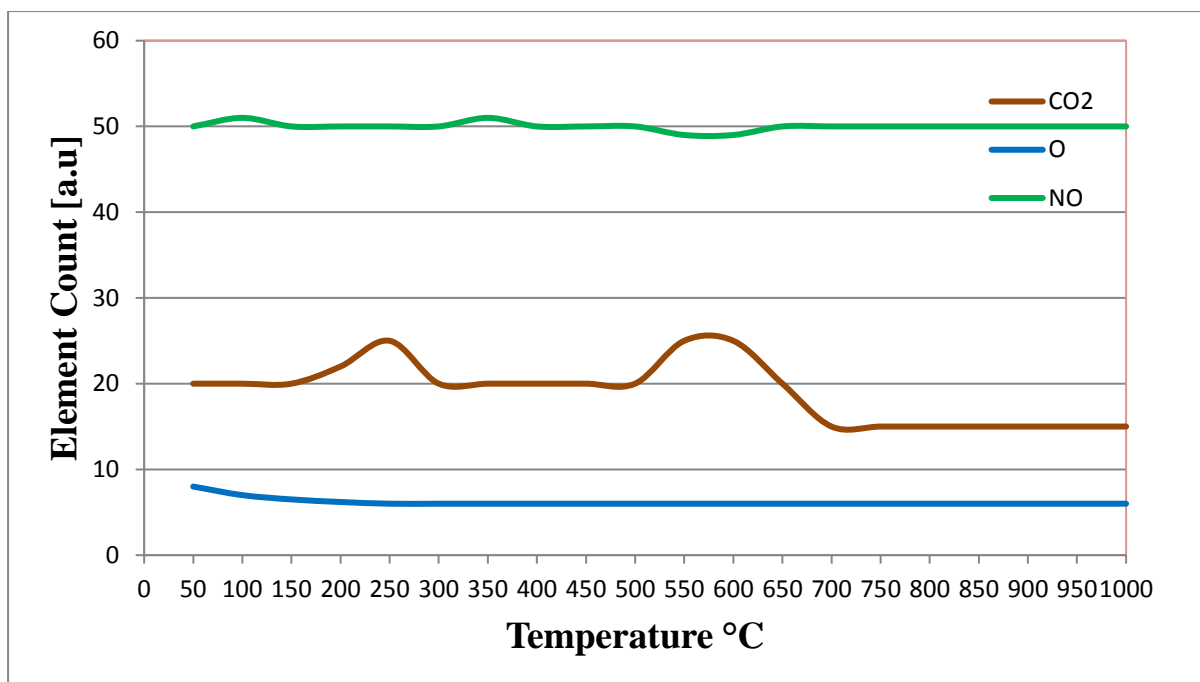


Figure 4.13: Carbon black treated with potassium permanganate and then soaked in water

The results show that carbon dioxide was the only small peak in the experiment (brown line). After the sample had been immersed in water, dried and heated up while running through the mass spectrometer, the results show that only carbon dioxide was released at 255 °C. Neither oxygen nor nitrogen peaks were evident while the mass spectrometer test was done in this result. This indicates that the functional groups formed during the surface treatment reacted while being soaked in the water.

The results for the mesophase carbon beads that were treated with KMnO_4 and nitric acid and the sample that was left to soak in water for a week after the treatment are shown in Figures 4.14 and 4.15.

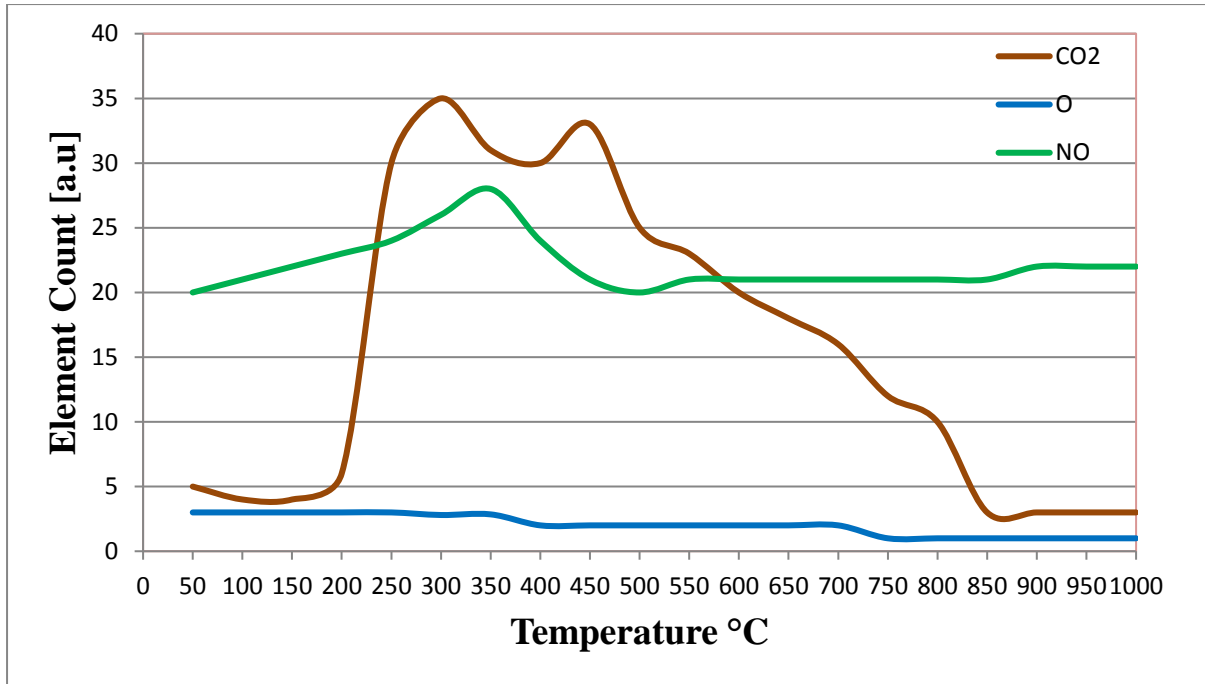


Figure 4.14: Mesophase carbon beads after the potassium permanganate and nitric acid treatment

From the results it can be observed that carbon dioxide (brown line) was released from the sample from 256 °C up to 700 °C and nitrogen oxide (green line) at 260 °C. The oxygen (blue line) peaked at 335 °C and then did not release at all after that. The rest of the lines was constant and did not show relevant peaks.

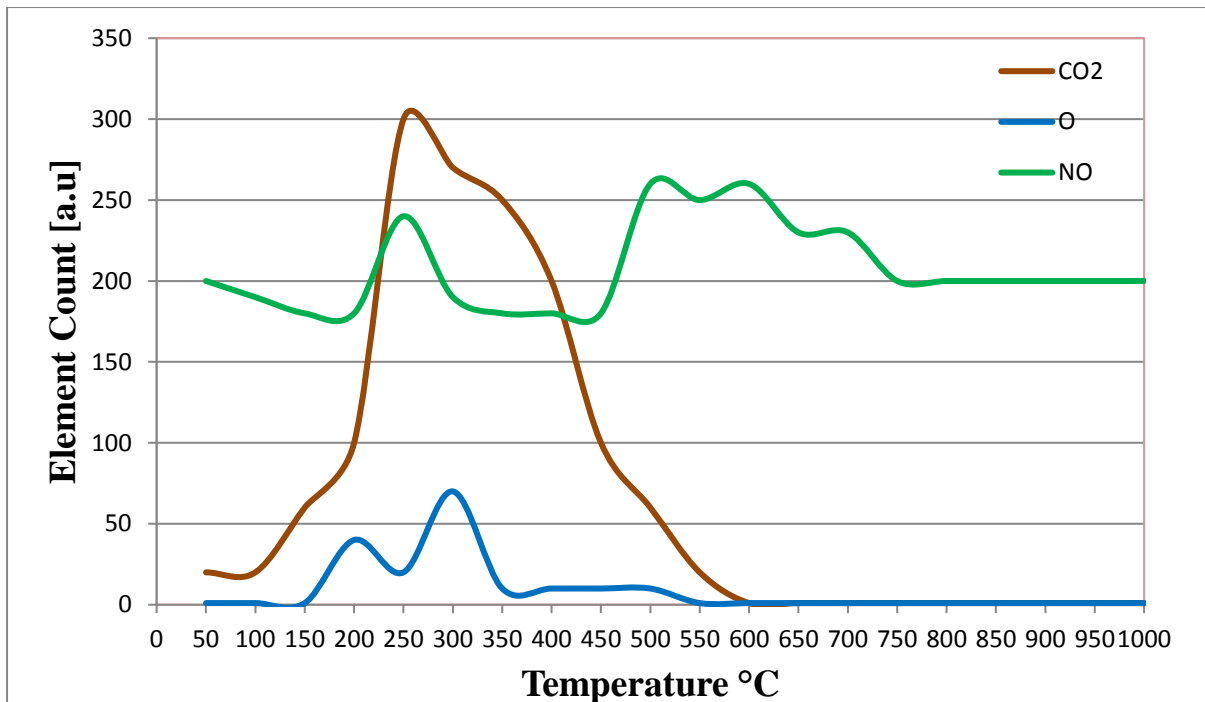


Figure 4.15: Mesophase carbon beads after treatment and soaking in water for a week

The only relevant peak that shows is the carbon dioxide line (brown line) that starts peaking at 249 °C and keeps on releasing until 612 °C. The nitrogen oxide (green line) does make a peak at 554 °C after having been soaked in water and the oxygen only makes a slight peak at 311 °C.

Exfoliated graphite was subjected to the same tests and the results are shown in Figures 4.16 and 4.17.

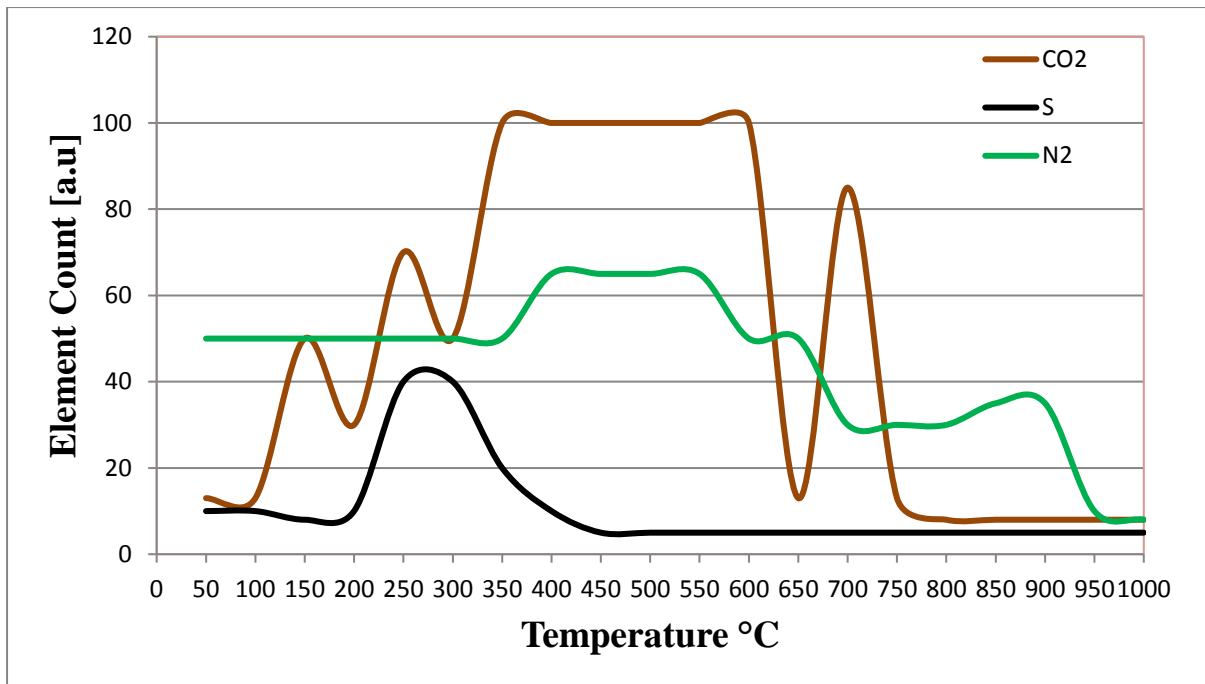


Figure 4.16: Exfoliated graphite directly after treatment

The results show that after the potassium permanganate and nitric acid treatment, three components were released as the sample was heated. Carbon dioxide (brown line) peaks at 281 °C, nitrogen (green line) peaks at 262 °C and sulphate (dark line) is released at 240 °C.

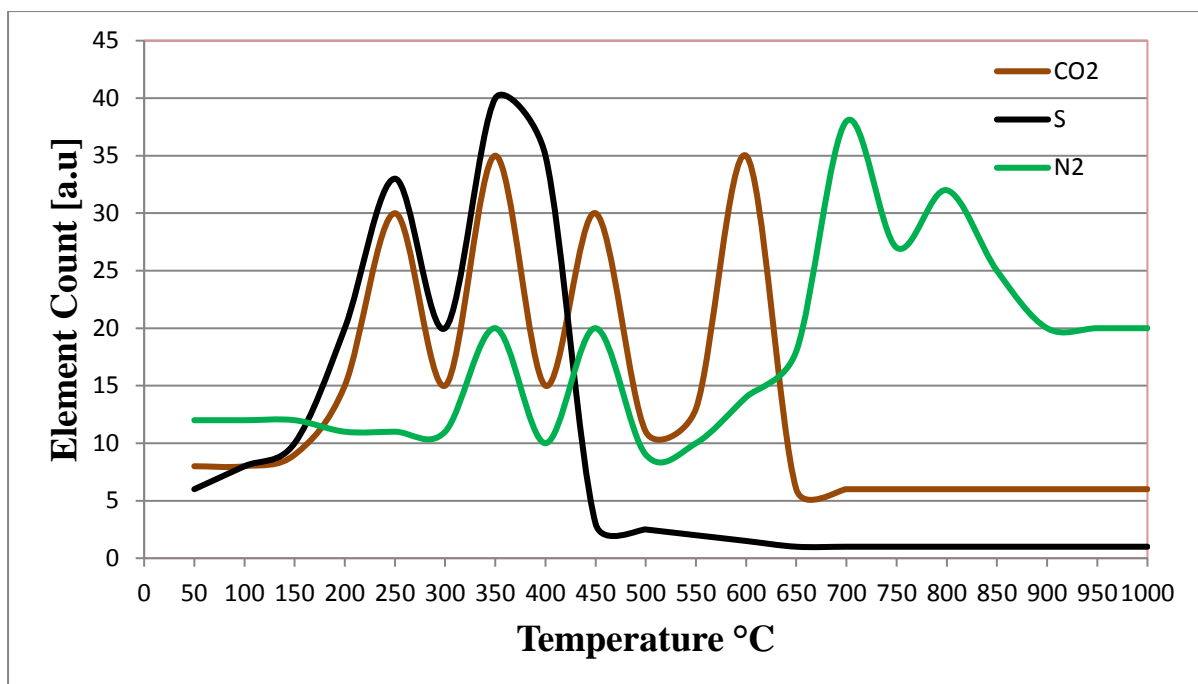


Figure 4.17: Exfoliated graphite after treatment and being soaked in water for a week

The graph results for the exfoliated graphite that was soaked in water looked very confusing initially, but after breaking them down, they actually showed three peaks before stabilising. Carbon dioxide (light brown line) is released at 250 °C, nitrogen (green line) is released at 627 °C and sulphur (dark line) is released early at 206 °C. After being soaked in water the same elements are still present, but the heat at which they are released changed after the soaking.

The results of both the mass spectrometer reading and the thermogravimetric analysis show that carbon dioxide is released from the sample at more or less 250 °C because the oxygen groups are volatile. The nitrogen oxide is released at 550 °C. That implies that the dispersion will be chemically stable up to 250 °C, after which the sample starts decomposing.

Table 4.4: Summary of the mass spectrometer results

	CO ₂	H ₂ O	SO ₄	NO	H	O	N
Carbon Black							
Untreated	√	-	-	-	-	-	-
H ₂ SO ₄ treatment	√	-	√	-	-	-	-
H ₂ SO ₄ treatment & H ₂ O	√	-	√	-	-	-	-
HNO ₃ treatment	√	-	-	√	-	-	-
HNO ₃ treatment & H ₂ O	√	-	-	√	-	-	-
H ₂ O ₂ treatment	√	√	-	-	-	-	-
K ₂ MNO ₄ treatment	√	-	-	√	-	√	-
K ₂ MNO ₄ treatment & H ₂ O	√	-	-	√	-	√	-
Mesophase Carbon Beads							
K ₂ MNO ₄ treatment	√	-	-	√	-	√	-
K ₂ MNO ₄ treatment & H ₂ O	√	-	-	√	-	√	-
Exfoliated Graphite							
K ₂ MNO ₄ treatment	√	-	-	-	-	√	√
K ₂ MNO ₄ treatment & H ₂ O	√	-	-	-	-	√	√

The summary of the mass spectrometer results is shown in Table 4.4 above.

Only using an acid or base with no other reagent revealed a molecular decomposition containing carbon dioxide, water and the particular acid or base group such as sulphate or nitrate, but when the carbon material was treated with the potassium permanganate and nitric acid, an oxygen peak was also present indicating that the carbon material also formed carboxylic-like structures.

From the results, it can also be seen that the oxygen/sulphur fraction of the samples not soaked in water is higher than that of the samples when soaked. This leads to the conclusion that the treated carbon materials do interact with the water and any exposed oxygen or sulphur that is not in a stable bond will then be removed by the water.

5. Conclusions and Recommendations

The study to disperse carbon materials in water to form a foundation on which thermal fluid research can start from, used three types of carbon (carbon black, mesophase carbon beads and exfoliated graphite). The carbon materials were oxidized with strong acid reactions and after the reaction was complete, they were characterized. Characterization consisted of observations with the naked eye, density measurements, specific surface area measurements, FE-SEM, TGA and pyrolysis together with a MS.

From the results of the pyrolysis and mass spectrometer, all the treatments that lasted for four days resulted in atoms or molecules being released that differed from the reference sample. The treatments that only lasted for two days had the same results as the untreated carbon black. The results for the successful treatments are summarised in Table 4.1. The temperatures of each molecule released can be observed in the TGA results as well as a mass loss, starting at the same temperature as the MS molecular identification.

The TGA results confirm that the treatment did in fact modify the carbon material's surface because the treated sample lost more weight than the untreated sample that only lost 1-3% at a time. The carbon dioxide, nitrogen and oxygen were released in much bigger quantities. The additional surface groups made up 15–18% of the total mass of the sample seeing that the untreated sample did not lose that mass. The results from both the TGA and mass spectrometer indicate that there was some form of chemical association when the carbon materials were subjected to the treatments.

The results also indicate a greater loss in mass with carbon black than mesophase carbon beads due to the reaction having more active sites to use on the carbon black. The exfoliated graphite mass loss was between that of the carbon black and mesophase carbon beads due to the additional loss of sulphate groups being released when heated.

As shown in Table 4.2, when observing the samples with the naked eye, the nitrogen surface complex, ketone and carboxylic groups interacted with the water to form a stable suspension. Carbon black seems to have the most of these groups when taking the observations into account.

Graphite immediately starts precipitating while mesophase carbon takes a bit longer, but follow the same pattern by precipitating out eventually. The carbon black was the only sample when treated with potassium permanganate that stayed in a stable suspension.

The mass loss of carbon dioxide and nitrogen oxide when combusting the carbon materials is the biggest with the carbon black, which also has the largest specific surface area according to the BET results.

The surface area also plays a significant role in the dispersion of the sample in water, as a decrease in specific surface area decreases the time the sample stays in a stable suspension.

The surface increases from the smallest specific area size on the exfoliated graphite to the largest specific area size on the carbon black due to their structures and mesophase carbon beads are almost right in the middle of the two.

The carbon black was the only sample that stayed in suspension, which implies that a specific surface area of $46.9 \text{ cm}^2/\text{g}$ or more will have enough surface complex groups to react with the treatment to stay in suspension.

It is recommended that the concentrations of the nitric acid and the potassium permanganate be varied to determine which concentration will give the optimal result for dispersing carbon in water. This should make a contribution to studies on dispersed carbon materials and advance the field of thermal nanofluids.

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7. Appendixes

7.1 Appendix A

Table 7.1: Soaked samples

	Sample Name	Time (days)	H ₂ SO ₄ (M)	HNO ₃ (M)	NaOH (M)	HCl (M)	H ₂ O ₂ (M)
	AR 015	2	1	-	-	-	-
	AR 016	2	0.1	-	-	-	-
	AR 017	4	1	-	-	-	-
	AR 018	4	0.1	-	-	-	-
	AR 019	2	-	1	-	-	-
	AR 020	2	-	0.1	-	-	-
	AR 021	4	-	1	-	-	-
	AR 022	4	-	0.1	-	-	-
	AR 023	2	-	-	1	-	-
Carbon	AR 024	2	-	-	0.1	-	-
Black	AR 025	4	-	-	1	-	-
	AR 026	4	-	-	0.1	-	-
	AR 04	2	-	-	-	1	-
	AR 05	2	-	-	-	0.1	-
	AR 06	4	-	-	-	1	-
	AR 07	4	-	-	-	0.1	-
	AR 08	2	-	-	-	-	1
	AR 09	2	-	-	-	-	0.1
	AR 10	4	-	-	-	-	1
	AR 11	4	-	-	-	-	0.1
Mesophase	AR 027	2	1	-	-	-	-

carbon	AR 028		0.1	-	-	-	-
beads	AR 029	4	1	-	-	-	-
	AR 030		0.1	-	-	-	-
	AR 031	2	-	1	-	-	-
	AR 032		-	0.1	-	-	-
	AR 033	4	-	1	-	-	-
	AR 034		-	0.1	-	-	-
	AR 035	2	-	-	1	-	-
	AR 036		-	-	0.1	-	-
	AR 037	4	-	-	1	-	-
	AR 038		-	-	0.1	-	-
	AR 052	2	-	-	-	1	-
	AR 053		-	-	-	0.1	-
	AR 054	4	-	-	-	1	-
	AR 055		-	-	-	0.1	-
	AR 056	2	-	-	-	-	1
	AR 057		-	-	-	-	0.1
	AR 058	4	-	-	-	-	1
	AR 059		-	-	-	-	0.1
	AR 039	2	1	-	-	-	-
	AR 040		0.1	-	-	-	-
	AR 041	4	1	-	-	-	-
	AR 042		0.1	-	-	-	-
Graphite	AR 043	2	-	1	-	-	-
	AR 045		-	0.1	-	-	-
	AR 046	4	-	1	-	-	-
	AR 047		-	0.1	-	-	-
	AR 048	2	-	-	1	-	-

AR 049		-	-	0.1	-	-
AR 050	4	-	-	1	-	-
AR 051		-	-	0.1	-	-
AR 060	2	-	-	-	1	-
AR 061		-	-	-	0.1	-
AR 062	4	-	-	-	1	-
AR 063		-	-	-	0.1	-
AR 064	2	-	-	-	-	1
AR 065		-	-	-	-	0.1
AR 066	4	-	-	-	-	1
AR 067		-	-	-	-	0.1

Table 7.2: Second group of samples

Sample	Sample Material	Treatment	Time of treatment
AR 113	Carbon black	Potassium permanganate and nitric acid	1 Week
AR 114	Mesophase micro beads	Potassium permanganate and nitric acid	1 Week
AR 115	Graphite	Potassium permanganate and nitric acid	1 Week
AR 116	Carbon black	Same as AR 113-115 but soaking it in water afterwards	2 Weeks
AR 117	Mesophase micro beads	Same as AR 113-115 but soaking it in water afterwards	2 Weeks
AR 118	Graphite	Same as AR 113-115 but soaking it in water afterwards	2 Weeks