NOVEL APPROACH FOR SYNTHESIZING GRAPHENE OXIDE FOR POTENTIAL WATER PURIFICATION

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CERTIFICATE

This is to certify that work in this thesis has been completed by **Mr. Muhammad Aiesh Ghayoor**, **Mr. Abdullah Afzal,** and **Mr. Muhammad Shahzaib** under the supervision of **Prof. Dr. Muhammad Shahid** and at the School of Chemical and Materials Engineering (SCME), National University of Science and Technology, H-12, Islamabad, Pakistan.

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DEDICATION

This thesis is a testament to the unwavering support and contributions of our parents, teachers, and friends. We are forever grateful for your belief in us and the roles you have played in making this achievement possible.

DECLARATION

We, **Muhammad Aiesh Ghayoor, Abdullah Afzal and Muhammad Shahzaib** declare that this thesis titled**, "Novel Approach for Synthesizing Graphene Oxide for Potential Water Purification**" is our original work completed as a prerequisite for the fulfilments of our bachelor's degree in Metallurgy and Materials Engineering. Under the supervision of **Prof. Dr. M. Shahid**, we conducted the research, analyzed the data, and formulated the conclusions with no plagiarism. All sources used have been appropriatelycited, and ethical guidelines have been followed. This work is submitted to the Department of Materials Engineering SCME as a requirement for the completion of our bachelor degree program.

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ABSTRACT

Following research investigates the potential of carbon derived from sweet limetta and orange peels for synthesis of graphene and its potential application in water purification membranes. Green-sourced carbon, due to its environmental sustainability, abundance, and porosity, is being increasingly explored for these purposes. A combination of oxidation, reduction processes, and exfoliation processes will be employed to produce the green derived graphene derivative. Subsequently, porous graphene oxide will be synthesized and reduced to form graphene oxide coatings, facilitating the development of environmentally friendly products. Characterization techniques such as Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction analysis (XRD) will be utilized to establish a correlation between the layered porous structure of the graphene nano- sheets and the water purification effectiveness of the carbon. A direct link is intended to create between the layered graphene structure and the advanced separation of toxic metal ions, ensuring sustainability and reduction in carbon footprint

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CHAPTER 1

1.1 INTRODUCTION

Carbon is essential to all known life forms, from the human body to trees to biomass to the atmosphere. It has excellent chemical stability, biocompatibility, electrical and mechanical properties, making it versatile. It can be extracted from organic wastes anything that contains carbon in the environment. It can be used for further applications, water filtration, purification, electrical and other substances, making it a valuable resource in many fields. Furthermore, its derivatives, i.e., Graphene, CNT, Graphene Quantum Dots and Fullerenes provide further improved utilities in these various applications.

Graphene Nanosheets, due to their large surface area, superior inter-layer spacing, and excellent chemical stability, are a promising candidate for removing contaminants from water for filtration.

1.2 Background

Water scarcity is becoming an increasingly grave issue for the world community. Plenty of reports and surveys are available which predict the condition to worsen over the years.If the current climate change situation continues, shortage of water would cause displacement of more than 24 million people in arid and semi-arid areas of the world by 2030. According to a report by the Global Water Institute, about 7 billion people will face water stress by the middle of this century . A lot of research is being carried out to address this problem with minimal cost and maximum efficiency. Shannon el al have reviewed some of the new methods being developed to disinfect and decontaminate water supply. One type of these methods, which have gained tremendous popularity in recent years, is the reverse osmosis using membrane technology. In the membrane assisted filtration processes, including nanofiltration, microfiltration and ultrafiltration, pressure is applied to solution at one end of the membrane which drives the separation of permeate and retentate. Currently, polymer, ceramic and metallic filters are available commercially with varying pore sizes and pore densities corresponding to the specific type of particles to be filtered. Ceramic filters, additionally coated in solution of silver nanoparticles, have been used to filter microorganisms such as virus, bacteria and protozoan. Polymer membranes have been utilized to clean biological and arsenic contaminations. Metallic iron is used for household water treatment using mechanisms of co-precipitation and adsorption. Ceramics membranes have good mechanical properties, longer lifetime and thermal stability but are brittle and expensive to produce. Though easy to fabricate through inexpensive processes and mechanically flexible, polymer membranes suffer from problems likes poor chemical stability and shorter lifetime due to fouling. The new class of carbon materials such as carbon nanotubes and graphene show prospect of providing an ideal nanofilter by incorporating good mechanical properties, thermal and chemical stability and economical processing. Despite remarkable water permeation properties of aligned CNT membranes, the difficulty to produce them at large scale eliminate them for further investigation in this discussion. Graphene, a single layer of hexagonal array of carbon atoms bonded via sp2 hybridization, offers outstanding properties. In particular, graphene oxide (GO), which can be produced in large scale by chemically converting graphite or graphene, has shown ability to be deposited as a highly ordered films on microporous substrates. GO films exhibit 2D 6 nanochannels present between two adjacent graphene sheets which were tested for nanofiltration of water. The corrugation of GO sheets in aqueous solution causes the specific surface area of the 2D nanochannels to increase which enhances permeation of water while rejecting organic dyes and nanoparticles to pass through. The functional groups in GO provide enough space between two graphene layers to allow water molecule to pass through. Additionally, frictionless flow is offered to water molecules by the pristine graphitic areas which enhance water permeation. The subnanochannels between graphene sheets behave as sieves allowing water molecules to pass through while retaining solute molecules with sizes greater than the size of subnanochannels. Consequently, the water permeation can be increased considerably by tuning the size of the subnanochannels. Despite of all the advantages of GO in nanofiltration of water, GO membranes still have some shortcomings which must be addressed before properly utilizing them commercially. When exposed to aqueous media, GO membranes tend to disintegrate due to electrostatic interactions between the graphene sheets as well as interaction of functional groups on graphene sheets with the water molecules. A solution to this is forming cross-linking between adjacent graphene sheets using multivalent cationic metal reagents. But this cross-linking causes the permeation of water to decrease due to narrowing of 2D nanochannels. Hence, it is important to reach a compromise between stability of GO membranes in aqueous medium and the permeation of water. One solution is the reduction of GO to reduced graphene oxide (rGO) using organic acids such as tannic acid and theanine amino acid which act as reducing agents forming cross-linking between graphene sheets as well as maintaining enough interlayer distance between them so that permeation is not compromised. Additionally, this reduction increases the fraction of pristine graphitic regions by removing oxygen functional groups, thereby, enhancing permeation of water. The presence of these acids in green extracts has been reported and investigated using green tea extracts for reduction of GO. In this research, we study the ability of green extracts,which contain organic reducing acids, to reduce GO to rGO for use in nanofiltration membranes. Subsequently, we investigate in detail the relation of reduction to permeationof water and rejection of solute contaminants. Additionally, we optimize the thickness of deposited GO or rGO sheets to achieve maximum permeation without compromising rejection ability. In our investigation, we use citrus limetta and orange peels for the reduction of GO. The results shows a direct reduction of graphene without using a chemical reduction process. The reported method is highly economical as it avoids use ofexpensive acids and reducing agents. Moreover, the process of reduction is green and sustainable as naturally available organic resources are used.

1.3 Problem Statement

“The Rising Threat of Carbonaceous Bio-Waste to Environment and the need to replace non-sustainable source with organic source for use in water purification.”

1.3.1 Problem Description

Natural resources like graphite, hard carbon and bio-based materials are the primary source of carbon for graphene development and water filtration]. Due to overconsumption, population growth, and unsustainable development practices, natural resources started to deplete. This led to a severe problem due to increasing demand. So, researchers began to make efforts to recycle. Though easy to fabricate through inexpensive processes and mechanically flexible, polymer membranes suffer from problems like poor chemical stability and shorter lifetime due to fouling. The new class of carbon materials such as carbon nanotubes (CNTs) and graphene show prospect of providing an ideal nano filter by incorporating good mechanical properties, thermal and chemical stability and economical processing. This issue led to a feasible and economical alternative to develop techniques that can use biomass for graphene development which can be used in nanofiltration and membranes.

1.4 Purpose

Our project aims to offer a practical solution for clean water availability, specifically addressing the global water and biomass waste challenges with a focus on Pakistan. We are developing graphene nano sheets using renewable energy sources and inexpensive biomass materials that are abundantly available. These graphene-based membranes are designed to have a higher rejection capability compared to current technologies, allowing them to meet the growing filtration needs more effectively. Additionally, the biomass materials used can be easily recycled, ensuring a sustainable and eco- friendly approach to water filtration.

1.5 Scope

This project's scope covers the application of fabricating a cheap graphene-based membrane using biomass-derived nanosheets as filtration materials. Achieving this milestone through renewable resources decreases the carbon footprint and creates sustainable utility for biomass waste by using it for water purification.

1.6 Project Objectives

The objectives of our project are as follows:

1.6.1 Recycling bio-waste to achieve carbon precursor as a replacement of conventional graphite

The first part of our project aims to recycle biomass waste to compare the conventional unsustainable graphite powder for synthesis of graphene. Pakistan is an agrarian economy, which means that a large proportion of its primary industries are based on producing agricultural products. Consequently, biomass waste is also produced in bulk. This waste includes nut shells, fruit seeds, wheat straw, citrus(orange peel), bagasse, and corncobs. All these materials are produced as waste from the agriculture industry in about 121 million tons annually. Farmers previously burned the biowaste or used it to fire homemade stoves for cooking food—the conventional methods of burning and utilization of biowaste are a hazard to the environment and health. Therefore, a better utility must be sought to use this waste. Due to limited research in this area in Pakistan to utilize agricultural waste, we have not been able to deduce greener routes to make use of this valuable resource. Active research is being undertaken in the rest of the world to utilize agricultural waste as a cheaper and efficient carbon source for graphene production through modified hummers method. We aim to achieve the same with our project.

1.6.2 Synthesizing nano-sheets of graphene derivatives from a sustainable green source.

The method used to derive graphene from biomass has multiple routes, which involve modified hummers method, ultrasonication, and cleaving. To reduce graphene oxide, it is essential to develop a reduction route that is cleaner and free of toxic chemicals in the process. For this, we will are using green organic extracts such as date seeds and green tea leaves which have natural reduction capability. This allows us to introduce a novel reduction process for graphene for water purification.

CHAPTER 2

2.1 LITERATURE REVIEW

2.1.1 Wastewater Treatment

Water is the most crucial and necessary component on the planet for living things to function properly. Unfortunately, the quality of our water resources is constantly diminishing because of population increase, industry, civilization, residential and agricultural activities, and other geological and environmental changes. As a result, water contamination has become a severe concern in the current situation, impacting all living things, households, fishing, transportation, and other commercial operations. The government, scientists, and academicians are concerned and serious about this matter. Thousands of organic, inorganic, and biological pollutants have been identified as water contaminants. Some of them have substantial side effects and toxicities, with a few being deadly and carcinogenic.[11]

The world is experiencing a drinking water crisis. The limited availability of fresh water makes Pakistan more vulnerable to the water crisis. Wastewater treatment and recycling could alleviate some of the pressure on freshwater sources. This has compelled the researchers to employ cost-effective and efficient wastewater treatment technology. Adsorption, membrane filtration, and reverse osmosis are some of the techniques used to prepare wastewater for further use. Adsorption with activated carbon is regarded as one of the most efficient and cost-effective techniques.

The cited article discussed various aspects of water treatment by adsorptionusing nano adsorbents. High cost of coal-based activated carbon has stimulated the search for the cheapest alternatives. Low-cost activated carbon has been the focus of research inrecent years. Agricultural waste, such as coconut shells, orange and banana peels, is receiving a lot of attention these days. Hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch are the fundamental components of agricultural waste materials. They contain a variety of functional groups that can adsorb various pollutants. The use of waste as a cheap adsorbent has two advantages: first, it recycles waste material, and second, it is economical. Agriculture-derived activated carbon has already been shown to be an effective adsorbent for a variety of pollutants. [11,40]

2.1.2 rGO membrane

Graphene-based membranes, made of 2D graphene oxide (GO) or reduced graphene oxide (rGO) nanosheets, are currently gaining popularity in liquid and gas separation. These membranes' nanochannels, which are formed between 2D GO or rGO nanosheets, permit gases and ions smaller than the openings to pass through while blocking all other larger species. In dry state, GO membranes with a void spacing of ≈0.3 nm across GO nanosheets are not permeable to most gases (e.g., He), but water vapor aligned in a monolayer may pass through freely, making it an ideal membrane for separation and selective removal of water. However, when GO membranes are placed in aqueous solution, the hydration effect increases the spacing between GO nanosheets to ≈0.9 nm, which not only destabilizes the membranes but also decreases the selectivity as small, hydrated ions (e.g., K+, Mg2+, AsO43−) can pass through the enlarged nanochannels. In contrast, rGO membranes, which have a similar layered structure to GO membranes, are more stable in water because they can maintain tight interlayer spacing due to a substantially lower number of hydrated functional groups. [1,6,32]

The figure shows the performance of an ultrathin rGO membrane compared to commercial membrane and rGO membrane shows high water flux than commercial membrane which make it ideal for water purification purposes.

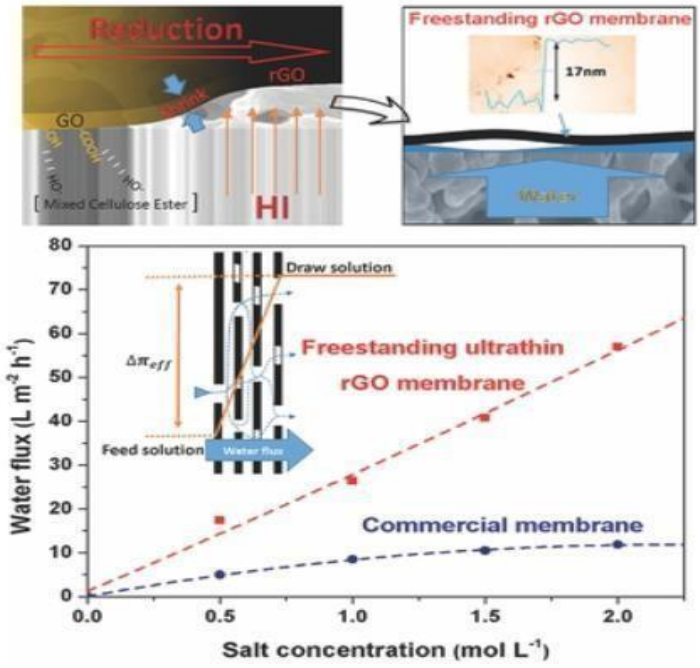


Fig 2.1.2 Freestanding ultrathin rGO membranes.[1]

2.1.3 Reduced Graphene Oxide

The Reduced graphene oxide has honeycomb like cage structures, with various functional groups, which makes it an efficient adsorbent for removal of metals in aqueous solution. Authors have also reported on the efficient removal of Zn2+, Ni2+, and Pb2+ by reduced graphene oxide owing to their reactive polar functional groups like -COOH, –OH and –NH2. From literature morphological appearance of synthesized orange extracted reduced graphene oxide (o-RGO) is notably smaller than graphene oxide hence providing additional reactive sites for adsorption ultimately enhancing the ion removal capacity of o-RGO. Also, one of the notable characteristics of o-RGO is the closely packed array sheets which contrast with the broad layered sheets as depicted by graphene oxide. The above two characteristics of o-RGO set the foundations for the fact that o-RGO is a more efficient choice than graphene oxide for water purification purposes. [2,4]

Among the preparation methods is the utilization of organic extract synthesis to improve adsorption performance. For example, Citrus sinensis peel investigations revealed that it removed more Cu2+ metal than wood sawdust. Similar research on the selective removal of five different heavy metals using modified orange peel demonstrated that orange peel works well in binary systems as an efficient adsorbent. Furthermore, the green synthesis of reduced graphene oxide has the potential to remove dyes from wastewater. The green synthesis of reduced graphene oxide adsorbents with strawberry extracts also demonstrated substantial benefits for supercapacitors and photocatalytic uses.[2]

However, structural defects pose a major obstacle in the synthesis of reduced graphene oxide because they interfere with the reaction system. Nonetheless, it is known that a well-reduced graphene oxide material has a large surface area and better crystallinity. The synthesis can be carried out using thermal heating, which improves crystallinity and reduces defects. Similarly, researchers used a thermal reduction technique to create grape-assisted reduced graphene oxide, and the adsorbent improved in adsorption capacity for the removal of organic dyes. Additionally, orange peel extracts are known to form organic protective layers over surfaces by means of a physical adsorption process. This interaction is associated with R-COO- functional groups on the surface by physisorption.

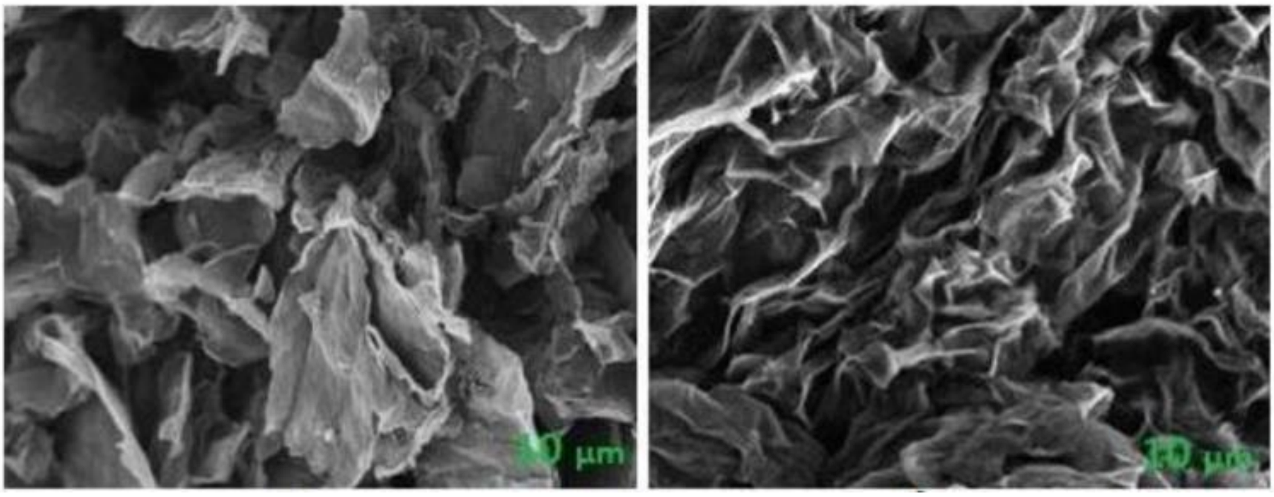


Fig 2.1.3 SEM images for GO (Left) and (b) o-rGO (Right)

In the picture, the o-rGO sheets represent a densely packed array of sheets, whereas GO represents wide layered sheets. The morphological appearance of o-rGO was much smaller than that of GO, resulting in more reactive sites for adsorption. However, because of its huge size, GO accommodates less reactive sites. Also, the high size of GO showed the existence of coarse particles, whereas o-rGO was finely dispersed following thermal reduction.

Hence the SEM results give us the motivation that rGO is best for water purification compared to GO based on the results provided in literature. [2,4,11,14,30]

2.1.4 Activated Carbon

Activated carbon is a special kind of carbon that has a high surface reactivity. This means that it can react easily with other substances on its surface. This property comes from activating the surface of the original material. The more the surface is activated, the more reactive it becomes, because it creates more surface area through pores. The structure of activated carbon is not regular but made of many imperfect layers of carbon atoms connected by groups of carbon and hydrogen atoms. Activated carbon can be used for adsorption in many situations, such as filtering water and capturing gases.

The world is experiencing a drinking water problem. The limited availability of fresh water makes the world increasingly vulnerable to the water crisis. Wastewater treatment and recycling might alleviate some of the burden on freshwater sources. This has compelled the researchers to employ cost-effective and efficient wastewater treatment technologies.

Adsorption, membrane filtration, and reverse osmosis are some of the procedures used to prepare wastewater for future use. Adsorption using activated carbon is regarded as one of the most efficient and cost-effective procedures. A review work [3] explored many elements of water treatment using adsorption with nano adsorbents.

The high cost of coal-based activated carbon has prompted the search for cheaper alternatives. In recent years, researchers have focused on low-cost activated carbon. Agricultural trash such as coconut shell, orange and banana peels are receiving a lot of attention these days. The basic components of agricultural waste materials are hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, which contain a variety of functional groups with potential sorption capacity for various pollutants. The use of trash as a low-cost adsorbent has two advantages: first, it recycles waste material, and second, it is cost-effective.

It has already been demonstrated that agricultural activated carbon is an effective absorber for different contaminants. After comparing the chemical oxygen demand (COD) reduction efficiency of acid-activated pecan shell-based granular activated carbon to the adsorption efficiency of commercial carbon, researchers concluded that acid-activated pecan shell-based carbons had higher adsorption for organic matter as measured by COD. The specific characteristics of activated carbon are determined not only by the raw material, but also by the activation process, which can be carried out physically. Activated carbon made at a lower temperature of carbonization showed superior properties than activated carbon prepared at a higher temperature of carbonization. Phosphoric acid improves the porous structure, resulting in a large surface and high total pore volume of carbons. As a result, chemical activation influences the adsorption of activated carbon and its ability based on changes in surface area, density, pH, and conductivity. [3]

2.1.5 Preparation of activated carbon

Raw materials (coconut shells, banana peels, and orange peels) were gathered from the market; 250 g of each was taken, chopped into smaller pieces, and washed with tap water. Each material was burned at a different temperature, depending on its properties and quantity. [3,5]

Each material was placed in a metal container, which was then placed in a muffle furnace, each containing material at a predetermined temperature and time; coconut shell was burned at 300 °C for 1 hour, while banana and orange peels were burned separately at 200 °C for 1 hour. The temperature gradually raised to the desired level at a rate of 20 °C per minute. After taking out the samples from the furnace, the samples were cooled for 30 min at room temperature, washed with distilled water; to remove dust and impurities, and dried in the oven at 105 °C for 1 h. The samples were then crushed into powder with a mortar before being sieved to get rid of larger particles. For acid activation, three 500 ml beakers were used for the three materials. The milled coconut shells, orange peels, and banana peels were separately added to the 100 ml of concentrated phosphoric acid (H3PO4) in a 500 ml beaker, for 24 h. The soaked shells and peels were burned for the carbonization process at the same temperature and duration as before. After that, the samples were once more immersed in 100 ml of distilled water containing 1 gm of sodium bicarbonate for a full day to eliminate any remaining phosphoric acid. After that,samples were individually cleaned four to five times in distilled water until their pH levelswere neutral. The washed samples were dried at $110^{o}C$.[3]

2.1.6 Physical Properties of OPAC (Orange Peel activated carbon)

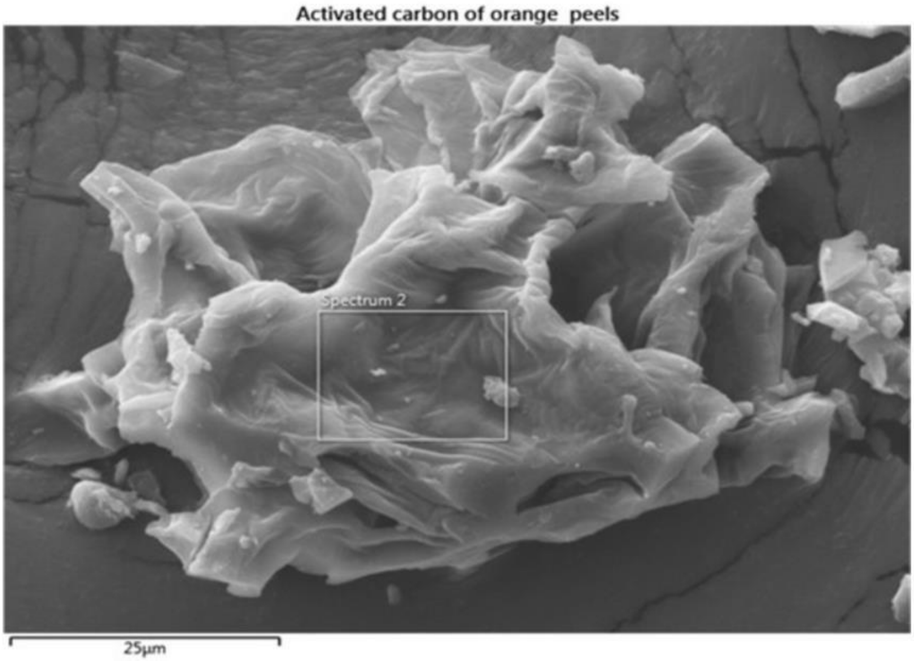

Activated carbon of orange peels

Fig 2.1.6(a) Scanning electron microscopic analysis of activated carbon made from orange peels.[3]

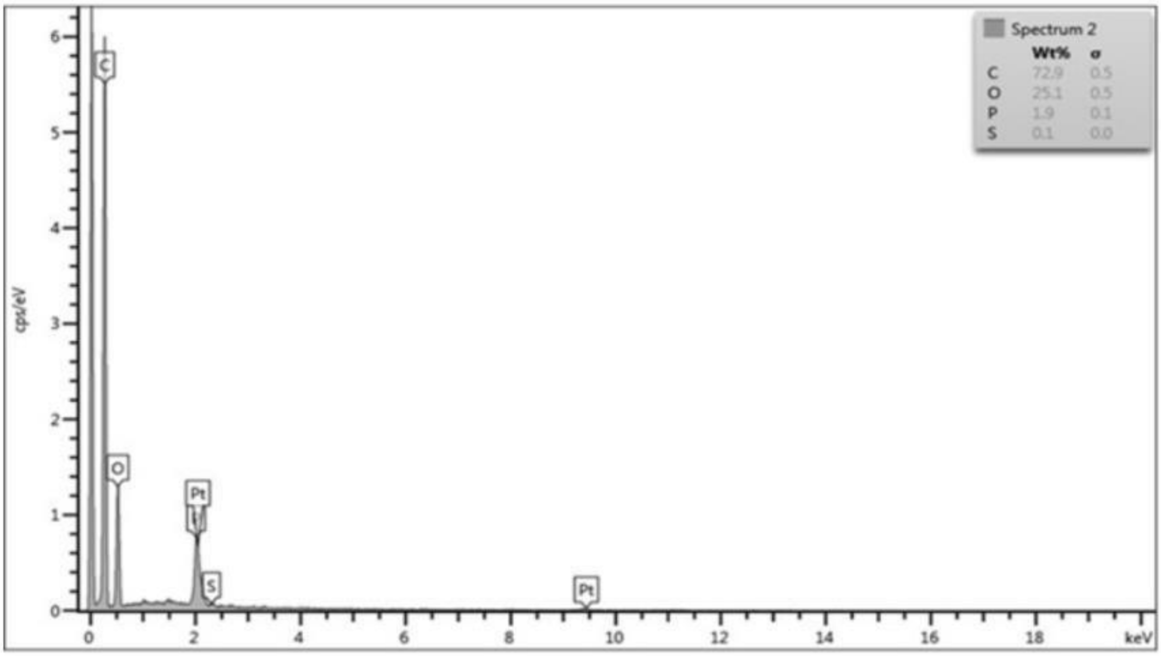


Fig 2.1.6(b) Different elements observed by scanning electron microscopic analysis of activated carbon made from orange peels.[3]

As illustrated in Fig. 2.1.6(a), the surface is smooth, and there is a channel-like wall on the raw material's surface, as well as pores of various sizes and shapes with variable grain sizes in the surface area. Figure 2.1.6(b) depicts the occurrence of several components containing a high percentage of carbon (72.9%). The exterior surface contains a crack and many grain particles with uneven and heterogeneous surface morphology and a well-defined porosity structure. This leads to improved pollutant adsorption.

2.1.7 Pollution Removal Efficiency of activated carbon

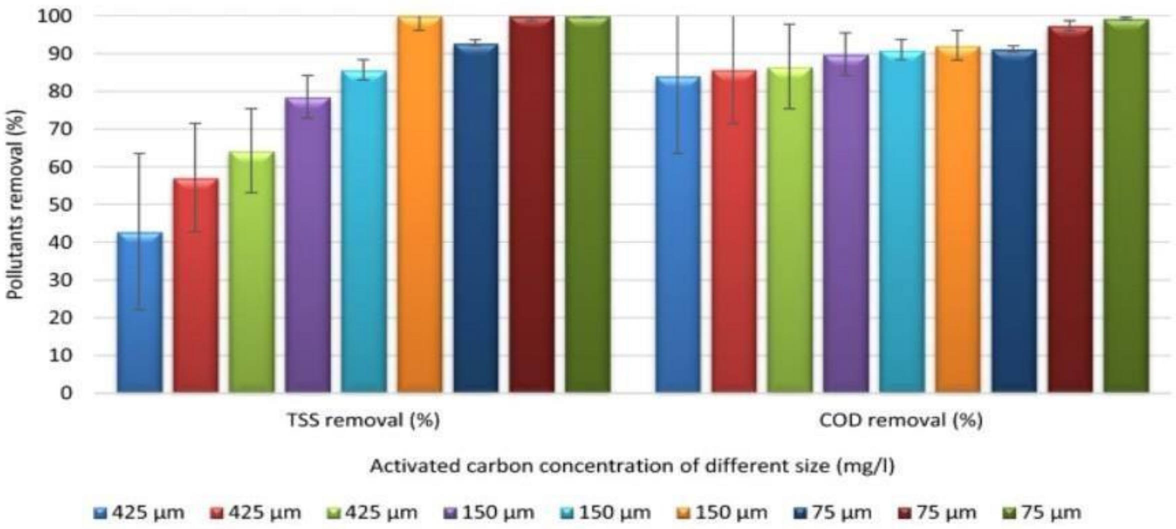


Fig 2.1.7 Effect of orange peels activated carbon concentration and size on removal efficiency of different pollutant.[3]

Figure 2.1.7 shows the results of total suspended solids (TSS) and chemical oxygen demand (COD) removal using activated carbon produced from orange peels (OPAC) at various sizes and concentrations. The results reveal that pH 7-7.5 provided the optimum absorption in all concentrations and sizes. Furthermore, the proportion of TSS and COD removed increases with the mass of activated carbon in all sizes of each material.

Among all the tested materials, activated carbon generated from orange peels outperformed the others, presumably due to the creation of more C-O and C=O functional groups. The use of low-cost organic materials to manufacture activated carbon for wastewater treatment will be an alternative to the more expensive approach, and using organic waste to make low-cost activated carbon may reduce the amount of organic waste in landfills.

2.2 METHODS

2.2.1 Thermal Decomposition

Thermal decomposition is a chemical process in which a substance breaks when heated. In our case, the compound that undergoes thermal decomposition is graphene oxide (GO), which is obtained from graphite by oxidation and exfoliation. The GO is mixed with orange extract and heated at 200 degrees Celsius for 2 hours. This removes oxygen-containing functional groups from graphene oxide. The reason for removing oxygen is that orange extract acts as a reducing agent, donating electrons to graphene oxide and facilitating its reduction. This environmentally friendly method not only emphasizes sustainability, but it also offers a green choice for obtaining RGO to be used in water purification applications [4].

The orange peels were repeatedly cleaned with tap water to remove grit and dust from its surface. It was then cut open to extract the seedlings. A blender was used to smash around 40 g of the entire orange (without the seeds) and transfer it to a round bottom flask containing 50 mL of de-ionized water. The mixture was heated in a water bath for 20 minutes before equilibrating at room temperature. The colored solution was then filtered to get the extract.

3 g of graphite, 18 g of $KMnO4$ Wt. equivalent, and 360/40 mL of $H2SO4/H3PO4$ were thoroughly mixed with continuous stirring. The combination was filtered to produce graphene oxide, and the filtrate was rinsed with deionized water to a pH of 7.0. To make the orange-assisted reduced graphene oxide (o-rGO), 90 mg of GO was mixed into 140 mL

of extract and vigorously agitated to evenly distribute the GO. Adding 400 µl of aqueous NH3 to the reaction mixture changed the hue. The reaction mix was kept at 318-323 K in a water condenser for time intervals of 1.0, 2.0, 3.0, and 4.0 hours.

After these heating cycles, the o-rGO was filtered and dried at a constant temperature of 353 K to yield about. This method was performed three times to get a weighted o-rGO sample of about 500 mg[4].

2.2.2 Tour Method:

To begin the GO synthesis, 30 ml of concentrated sulfuric acid and 3.3 ml of concentrated ortho-phosphoric acid were mixed. The purpose of adding orthophosphoric acid is to facilitate the insertion of the oxidation solution. After stirring the previously mentioned acid mixture for 30 minutes, 1 g of graphite powder was slowly added. The mixture was then treated with 6 g of potassium permanganate, and the temperature was kept below 20 °C. The colour of the resulting mixture turned from purple to muddy green. Then, the mixture was stirred for 2 h at 35 °C. The resulting mixture was diluted with 100 cc of water and stirred for 30 minutes using a magnetic stirrer. After that, a dark brown suspension was formed. To halt the reaction, 100 ml of distilled water (D.I.) and 10 ml of hydrogen peroxide (to remove the excess potassium permanganate) were used. As a result, the color of the solution turned from dark brown to golden yellow. After being allowed to develop for an entire night, the resultant sample was centrifuged and cleaned with distilled water to neutralize its pH. After that, the sample was dried for 24 hours at 70 °C in an oven.[9]

The purpose of H2O2 was to reduce residual KMnO4 to soluble manganese sulfate (MnSO4) in an acidic medium, as described in the following reaction:

$$\begin{aligned}&2KMnO_4 + 5H_2O_2 + 3H_2SO_4\\&\quad\longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O\ (\text{steam}) + 5O_2\end{aligned}$$

Graphene oxide was reduced with ascorbic acid as a reducing agent. 400 mg of GO powder was distributed in 400 mL of distilled water (0.1 mg per mL). After adding 4g of ascorbic acid (AA) to the solution, mix it with a magnetic stirrer for 30 minutes at 60°C. The reduced product was then centrifuged at 4000 r/s for 40 minutes to remove the supernatant. To oxidize the remaining ascorbic acid, 30 wt.% H2O2 was added to the black paste and stirred at 60°C for 30 minutes. After stirring, the black product was centrifuged at 4000 r/s, washed with ethanol and distilled water three times, and dried at 120°C for 24 hours.

The preparation process of reduced graphene oxide (rGO) consists of three steps: oxidation or intercalation, exfoliation, and reduction [8].

a) Graphite oxide (GTO) was created by oxidizing graphite powder with potassium permanganate and H2SO4/H3PO4 (9:1) (v/v) at 50°C for 12 hours in a water bath. H2SO4 is the most often used intercalating agent.

b) Exfoliation involves dispersing oxidized graphite into distilled water to create single-layer graphene oxide (GO), which is then heated at 60°C with a magnetic stirrer for 12 hours in a water bath. The black paste was recovered using filtering and centrifugation, then dried at 60°C for 24 hours.

c) Reduction is the final stage in synthesizing reduced graphene oxide (rGO). In this stage, the GO from stage (ii) was distributed and ascorbic acid was added as the reducing agent, followed by heating at 60°C for 30 minutes. The reduced product was obtained using filtering and centrifugation. The black result was cleaned with ethanol and distilled water three times before centrifugation. It was then dried in an oven at 120°C for 24 hours.

2.2.3 Hydrothermal Reduction

This method involved ultrasonically sonicating 200 mg of synthesized GO for 30 minutes in 20 ml of DI water. The GO mixture was sonicated, and then 50 ml of lemon peel extract was added for reduction. The mixture was then stirred for 20 minutes to achieve homogeneity. This solution was reduced by heating it to 180 °C for six hours in a hydrothermal autoclave. The resultant black rGO product then became settled at the autoclave's bottom. After this washing was done with DI water several times to remove unwanted impurities. Then the sample (Black Powder) was dried at 70 °C for 8 h [9].

2.2.4 Modified Hummer Method

The most essential and extensively used technique for GO synthesis was established by Hummers and Offeman. This approach has three distinct benefits over previous strategies. First, the reaction is completed in a few hours; second, potassium chlorate can be substituted with potassium permanganate for a safer reaction; and third, the use of sodium nitrate avoids acid mist generation. However, the approach is not without flaws, as hazardous gases such as nitrogen dioxide and dinitrogen tetroxide are generated during the oxidation process. [11]

Furthermore, salt and nitrate ions are difficult to remove from the wastewater generated during the process of synthesis and purification of graphene oxide.

By adding more potassium permanganate and eliminating sodium nitrate, the Hummers method has been improved in previous research, allowing the reaction to be completed in a single mixture. This modification introduces phosphoric acid into the reaction system while also improving reaction performance and lowering the release of harmful gases. According to earlier studies, the Hummers method's sulfuric and nitric acid mixture functions as a "chemical scissors" for graphene planes, facilitating the oxidation solution's penetration.

On the other hand, potassium permanganate can achieve complete graphite intercalation, resulting in graphite bisulfate. This interaction ensures that potassium permanganate penetrates the graphene layers and oxidizes graphite. As a result, potassium permanganate replaces the function of sodium nitrate, making it unnecessary for the reaction. In our experiment, we used a simple synthesis route to produce GO via a low-cost and environmentally friendly modified Hummer's method. Furthermore, the synthesis route is highly reproducible in terms of producing graphene oxide, which is then reduced to RGO for use in various applications.

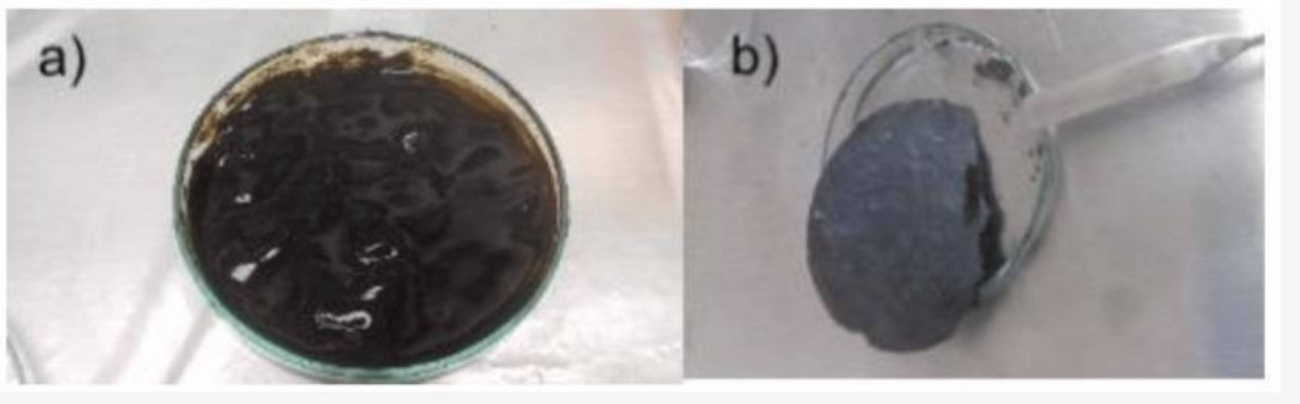


Figure 2.2.4(a) GO synthesis by the Hummers method: (a) after washing, (b) after drying.

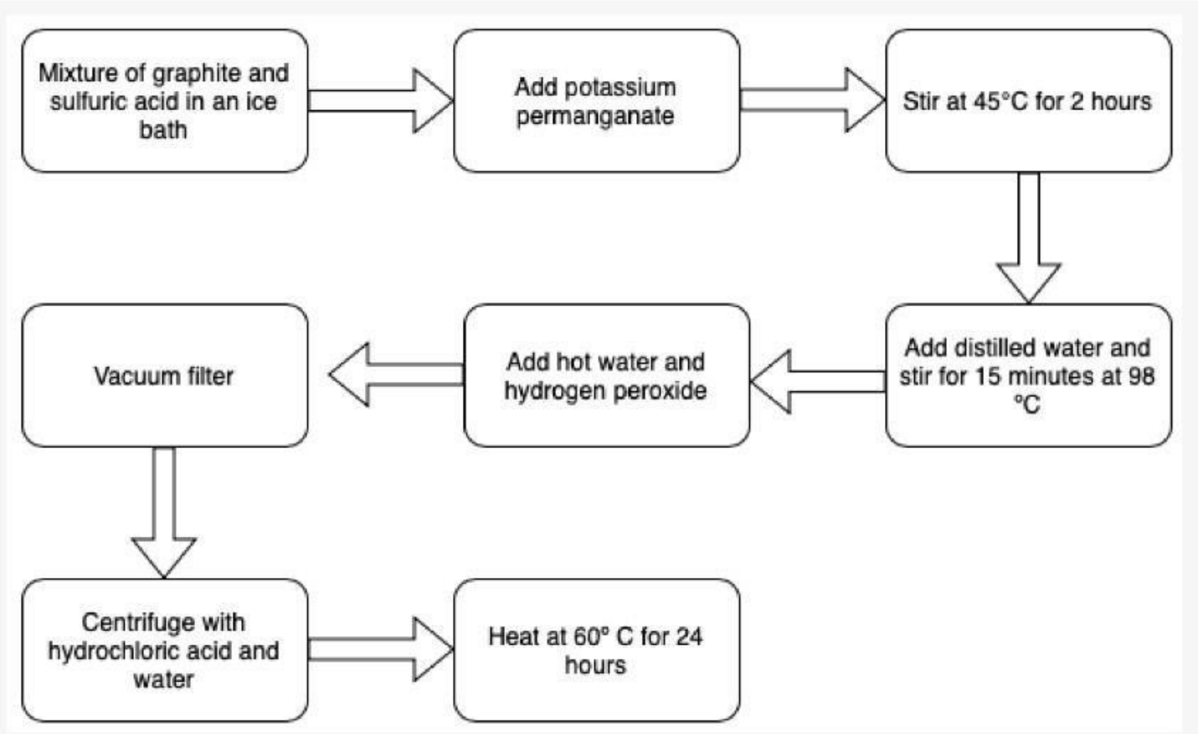


Figure 2.2.4(a) GO synthesis by the Hummers method at 60 °C and 90 °C for 24 h.

2.2.5 Thermal Reduction

Thermal reduction is the reduction of graphene oxide to obtain RGO by heating it at high temperatures after graphene oxide has been obtained using modified hummer method. To make rGO from GO, place the dried GO powder in an empty beaker. The beaker is covered with aluminum foil with punched pores and placed on a hot plate set to 350˚C for 10 minutes in a hood. The resulting black powder of rGO was then removed from the beaker [2].

CHAPTER 3

3.1 METHODOLOGY

This section details the methodology employed for the synthesis of Graphene Oxide (GO) from orange peels. It includes two experimental trials, with the second one addressing limitations identified in the first. In our first trial, we used Citrus Limetta peels instead of orange peels while in our second trial, we used orange peels.

3.1.1 Precautions

Here are some important safety precautions to consider while following the methodology for synthesizing Graphene Oxide (GO) from orange peels:

Chemical Hazards:

- **Strong Acids:** Sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) are highly corrosive and can cause severe burns upon contact with skin or eyes. Always wear appropriate personal protective equipment (PPE) such as chemical resistant gloves, goggles, and a lab coat while handling these acids. Work in a fume hood to avoid inhalation of fumes.
- **Potassium Permanganate ($KMnO_4$):** This oxidizer is a strong irritant and can stain skin. Wear gloves, goggles, and a respirator when handling $KMnO_4$. It is also fire-prone when combined with organic materials. Avoid contact with combustible materials and keep a fire extinguisher nearby.
- **Hydrogen Peroxide (H_2O_2):** Concentrated H_2O_2 can cause irritation and burns. Wear gloves and eye protection while handling it. Avoid contact with flammable materials as it can decompose exothermically.

General Safety:

- **Heating:** The carbonization process involves heating the orange peels in a furnace. Always wear heat-resistant gloves when handling hot crucibles or glassware.
- **Glassware:** Broken glassware can cause cuts. Use caution while handling beakers, flasks, and other glassware.
- **Sharp Objects:** Grinding and milling processes may involve using sharp blades or grinding media. Handle these tools with care to avoid injuries.

- **Vacuum Oven:** Ensure the vacuum oven is functioning properly before use. Be aware of potential pressure hazards associated with vacuum equipment.

3.1.2 Preparation of Carbonized Orange Peel Powder

3.1.3 Collection and Washing

- Oranges were procured, and their peels were carefully separated from the flesh.
- The peels were thoroughly washed with deionized (DI) water to remove any adhering dirt, impurities, or residues.
- Washed peels were air-dried at room temperature for 24 hours.

Fig 3.1.3: Washed Citrus Limetta Peels

3.1.4 Carbonization

- The dried orange peels were placed in a furnace and carbonized at 300°C for 5 hours.
- This process was repeated to optimize the balance between temperature and time for achieving a high carbon yield with minimal ash content.

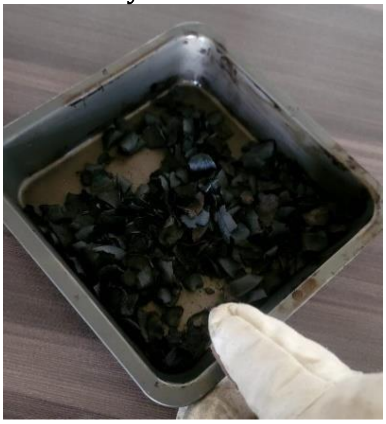


Fig 3.1.4: Burnt Orange Peels

3.1.5 Post-Combustion Processing

- Following carbonization, the charred orange peels were washed to remove residual ashes and then dried in an oven at **110°C** for **3 hours**.
- Following carbonization, the charred peels were ground using a mortar and pestle to obtain a coarse powder.

3.1.6 Grinding and Milling

- The dried powder was further refined using a ball mill at 300 rpm for 24 hours with appropriate grinding media (e.g., Steel Balls). This wet ball milling process helps achieve a finer and more uniform particle size distribution.

Fig 3.1.6 : Ball Milling 300RPM

3.1.7 Characterization:

- A representative sample of the final carbonized orange peel powder was collected for characterization using techniques such as Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR). These techniques provide information about the morphology, crystallinity, and functional groups present in the carbon powder.

3.2 Synthesis of Graphene Oxide (GO)

Trial 1:

This section details the first attempt at synthesizing GO using the modified Hummers method with the prepared carbonized orange peel powder.

3.2.1 Acid Mixture Preparation

- In a fume hood (due to the hazardous nature of the chemicals), 45 ml of concentrated sulfuric acid (H_2SO_4) was mixed with 6 ml of phosphoric acid (H_3PO_4) in a beaker. The mixture was stirred for 10 minutes to ensure homogeneity.

3.2.2 Addition of Carbon Powder

- 3 g of the prepared carbonized orange peel powder was gradually added to the pre-mixed acid solution under constant stirring for 1 hour. This allows for the intercalation of acid molecules between the carbon layers. A thick brown paste forms during this step.

Fig 3.2.2: Thick Brown Paste

3.2.3 Oxidation Process

- While maintaining the reaction temperature using a cold bath, 6 g of potassium permanganate ($KMnO_4$) was slowly added to the mixture with continuous stirring. This initiates the oxidation process, converting the carbon into graphene oxide. Temperature of the reaction was around 35°C even after using a cold bath which gives a low-quality GO. The reaction is exothermic, so controlling the temperature is crucial. The paste becomes denser and darker after this step.

3.2.4 Dilution and Termination

- The reaction mixture was then diluted with a significant amount of DI water, causing a color change to a dark green, as depicted in Fig 3.2.4(a).

Fig 3.2.4(a): Dark Green Paste

- To terminate the oxidation process and prevent over-oxidation, 8 ml of hydrogen peroxide (H_2O_2) was cautiously added. This step leads to further color change and the formation of a foam-like material on the surface Fig 3.2.4(b) .

Fig 3.2.4(b): paste

3.2.5 Washing and pH Neutralization.

- This step proved to be challenging due to substantial powder loss during multiple centrifugation washes at high rpm in an attempt to achieve a neutral pH of 7. The low yield obtained in this trial limited further characterization using techniques like XRD.

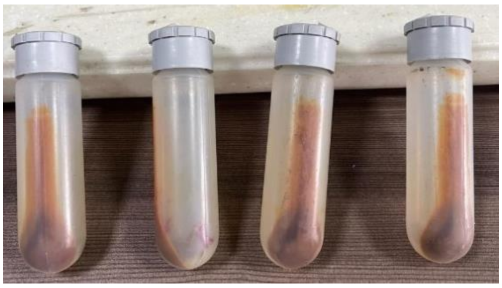


Fig 3.2.5(a): Centrifuging Tubes

Trial 2 (Addressing limitations from Trial 1):

In this trial we used orange peels instead of the Citrus Limetta peels. This trial addresses the limitations encountered in the first attempt, particularly the significant powder loss during the pH neutralization process.

All steps from Trial 1 (3.2.1 to 3.2.5) were repeated with doubled quantities due to the use of 6 g of carbonized orange peel powder as the starting material.

Also, we used a mechanical stirrer in Trial 2 instead of the magnetic stirrer because magnetic stirrer was struggling in stirring the thick pasts causing the localized heating in reaction during $KMnO_4$ addition.

In modified hummers method Ice bath was used maintaining a temperature below 10°C according to literature to achieve the good quality GO sheets.

Fig 3.2.5 (b): Orange Peels

3.2.6 Improved Washing and pH Neutralization:

- Instead of repeated centrifugation, a large volume of DI water was added to the diluted reaction mixture after step 3.2.4.
- The mixture was stirred for 30 minutes to facilitate the dispersion of the GO sheets in the water.
- The suspension was then allowed to settle overnight. During this time, the denser GO sheets would precipitate at the bottom, while impurities and residual salts would remain suspended in the water.

- After settling, the supernatant (upper layer of liquid) containing impurities was carefully removed using a pipette or decantation.
- Fresh DI water was then added to the remaining solid GO pellet.

This process of adding fresh DI water, stirring, settling, and removing the supernatant was repeated several times until a neutral pH of 7 was achieved in the final rinse water.

3.2.7 Exfoliation and Drying:

- Following the successful pH neutralization, the remaining GO suspension was transferred to a petri dish.
- The suspension was gently stirred for 30 minutes to promote exfoliation, allowing individual GO sheets to disperse more effectively in the water.
- The exfoliated GO suspension was then poured into a shallow container suitable for vacuum drying.
- The container was placed in a vacuum oven set at 55°C for 24 hours. The low pressure and moderate temperature facilitate the removal of water molecules while minimizing thermal degradation of the GO sheets.

3.2.8 Final Characterization Methods

In simpler terms, studying materials (characterization) is crucial in Materials Science and Engineering. Over time, characterization techniques have helped us understand how materials behave, their microscopic structure, and their properties based on their chemical makeup and physical look.

To check the composition of our powder, we used a technique called X-ray Diffraction (XRD) to identify the products we made and the phases they formed. For XRD, we crushed any slightly clumpy powder with a mortar and pestle, then dried it in a vacuum oven to remove moisture. We then analyzed the samples using the XRD equipment at SCME, a facility specializing in analyzing powder samples.

Similarly, we prepared samples for Scanning Electron Microscopy (SEM), also available at SCME, to see the powder's shape (morphology). Again, we crushed the slightly clumpy powder with a granite mortar and pestle, then dried it in a vacuum oven. In addition to SEM, we also performed Energy-Dispersive X-ray spectroscopy (EDX) at the same time to identify any impurities present in the powder.

3.2.8.1 X-ray Diffraction

Scientists and engineers rely heavily on a technique called X-ray Diffraction (XRD) to understand materials at the atomic level. Based on Bragg's Equation, XRD shines X-rays on a material. These X-rays have a size similar to the gaps between atoms in crystals. Because of this, the X-rays bounce off the crystal at specific angles depending on the crystal's exact structure. By measuring these scattered X-rays at different angles, a unique fingerprint is created for each material. This fingerprint allows scientists to identify the material and any different forms (phases) it might exist in.

3.2.8.2 Quantitative Analysis

X-ray Diffraction (XRD) is a versatile tool that goes beyond just identifying materials. It can also analyze how crystalline a material is, find defects in its microscopic structure, and, importantly for our project, reveal how many different phases are present in the sample.

Several methods can be used to calculate the amount of each phase from XRD data. The most common and well-established approach is Rietveld Refinement. However, with the development of sophisticated analysis software, we can now get a reasonably quick estimate of phase quantities, albeit with some margin of error. In our case, we used Diffrac EVA software for this semi-quantitative analysis. This software employs algorithms that compare the relative intensity of peaks matching specific phases to provide us with the amounts present in the sample.

3.2.8.3 SEM:

Just like X-ray Diffraction (XRD), another key tool in materials research is Scanning Electron Microscopy (SEM). This technique lets us see the microstructure of materials, and in our case, the exact shapes (morphologies) of our powders. Before SEM, traditional optical microscopes were limited. SEM revolutionized science by allowing us to view objects in much more detail, at significantly smaller sizes.

In our project, we used SEM to examine the morphologies of both our raw materials and final products. Understanding these shapes and how they affect the final properties of the material was critical to our research.

3.2.8.4 EDX:

Spectroscopic techniques are like fingerprints for materials, helping us identify the elements they're made of. These techniques work by shining energy, like electrons, at a sample and analyzing the unique electromagnetic emissions that come back. Similarly, Energy-Dispersive X-ray Spectroscopy (EDX) uses an electron beam, often from the same instrument used for SEM imaging, to excite the atoms in our sample. These excited atoms then emit specific X-rays that reveal their identity. EDX can even tell us how much of each element is present.

In our case, we used EDX to check for any unwanted elements (impurities) in our final product. Any elements detected besides our desired products or those naturally introduced during the process (like carbon from the sample holder) would indicate impurities. We didn't use the quantitative analysis function of EDX in this instance because we were more interested in the phases of Silicon Nitride, not the overall amount of each element.

3.2.8.5 FTIR:

Fourier-Transform Infrared Spectroscopy (FTIR) is another powerful tool in a materials scientist's toolbox. It helps us understand a material's chemical makeup by analyzing how it interacts with infrared light. Different bonds between atoms vibrate at specific frequencies when infrared light hits them. By measuring the infrared light absorbed by a sample, FTIR creates a unique fingerprint that reveals the chemical bonds and functional groups present in the material.

In our research, we weren't concerned with identifying the specific chemical compounds in our sample. However, FTIR could potentially be useful for future studies to confirm the presence of functional groups expected in Silicon Nitride or to identify any unexpected organic compounds.

3.2.9 Comparison of Trials:

- We used a mechanical stirrer instead of magnetic stirrer in Trial 2 for better stirring of thick pastes.

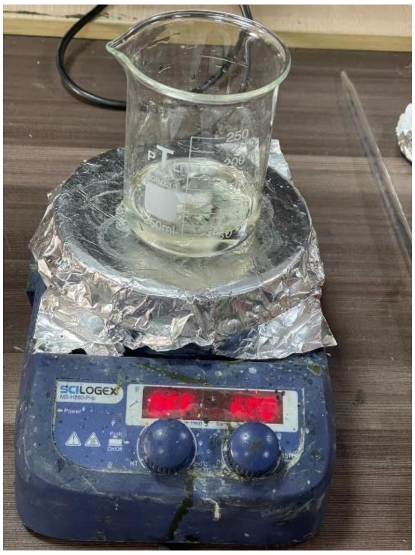


Fig 3.2.9(a): Stirrer in Trial 1 (Magnetic)

Fig 3.2.9(b): Stirrer in Trial 2 (Mechanical)

- We used ice bath in trial 2 maintaining a temperature below 10°C hence an improved quality of GO was achieved. Which was rather resembling with rGO according to the XRD results comparing with literature.

Fig 3.2.9©: Ice Bath in Trial 2

- Trial 2 addressed the powder loss issue encountered in Trial 1 and ultimately yielded a sufficient amount of GO for characterization.

Fig 3.2.9(d): Yield in Trial 1

Fig 3.2.9(e): Yield in Trial 2

CHAPTER 4

4.1 RESULTS AND CHARACTERIZATION

4.1.1 Characterization

Several Characterization and testing techniques were performed for the carbonized biomass samples and graphene oxide samples (synthesized by Orange Peel waste and citrus limetta), including Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction Analysis (XRD).

4.1.2 Scanning Electron Microscopy (SEM)

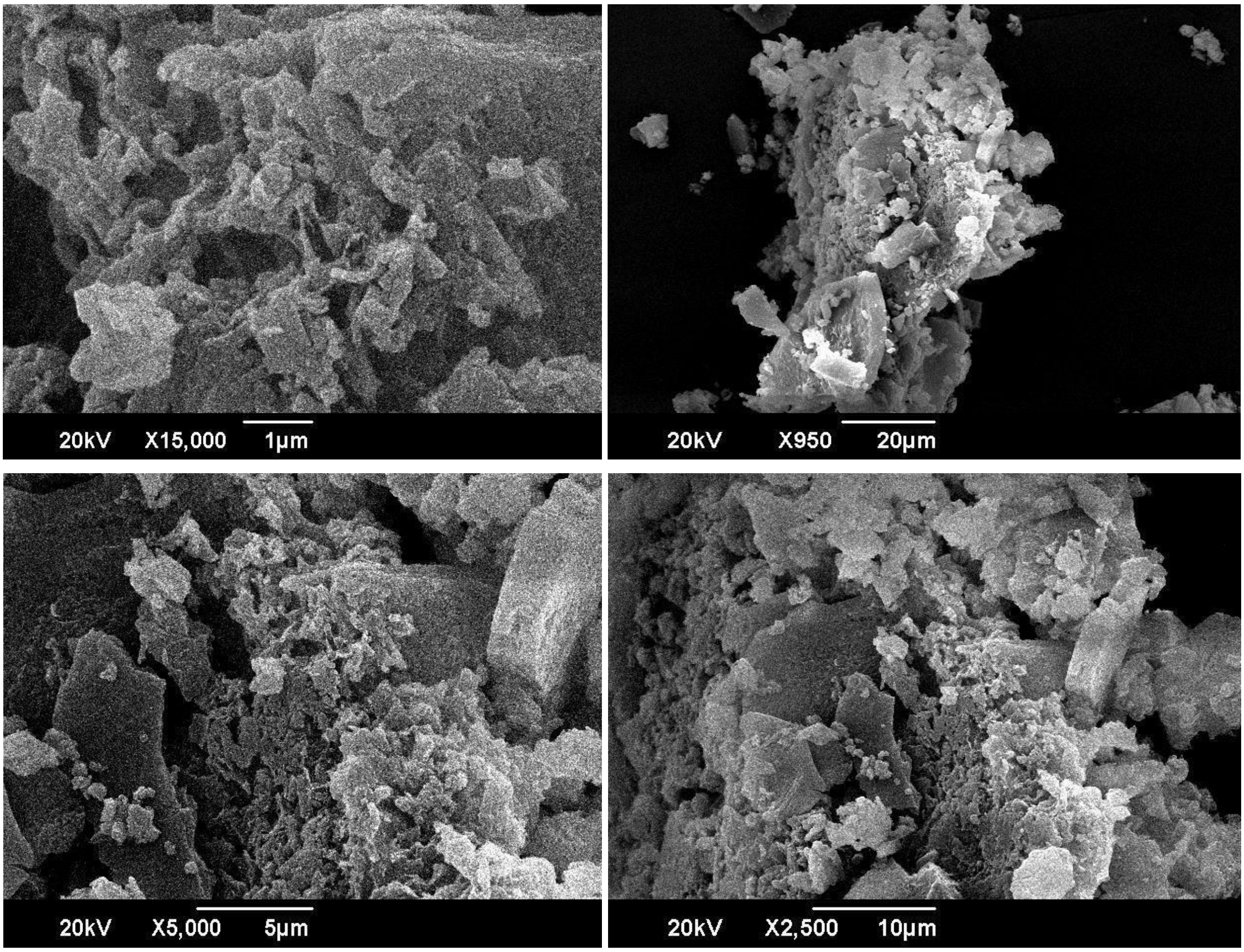


Figure 4.1.2(a): SEM micrograph for Graphene Oxide prepared using Citrus Limetta as a precursor

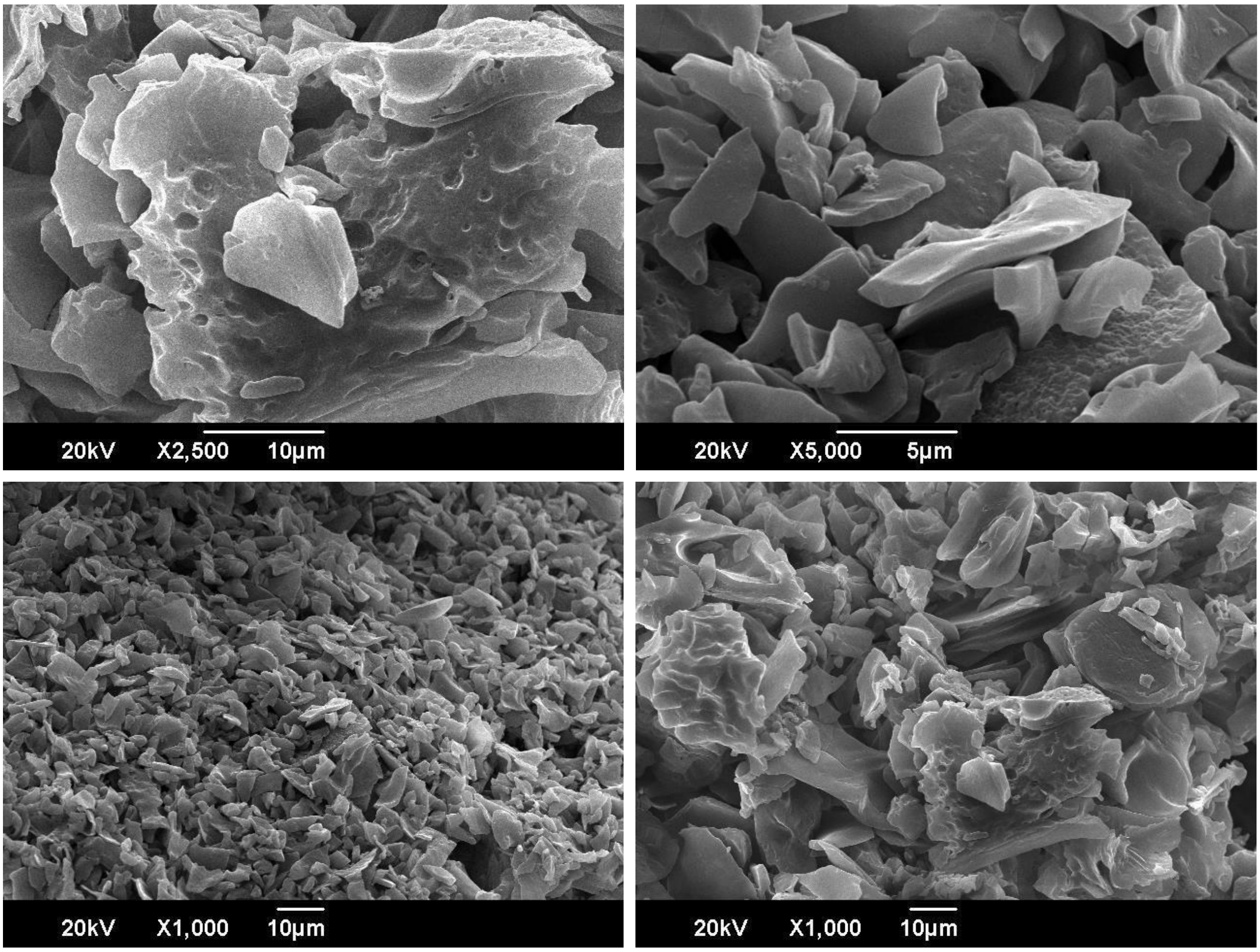
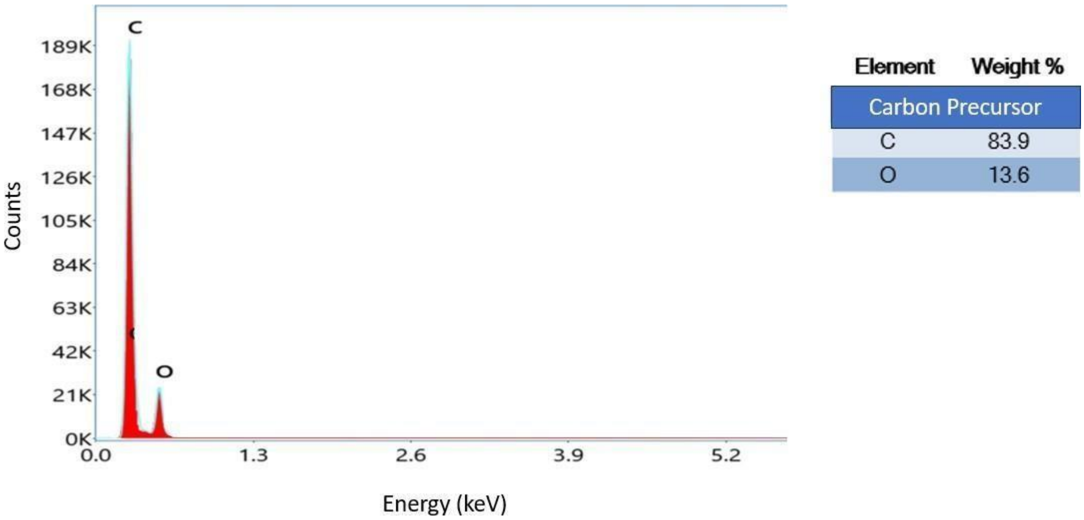


Figure 4.1.2(b): SEM micrograph for Graphene Oxide prepared using Orange Peels as a precursor

Figure 4.1.2(a) shows Graphene Oxide (GO) SEM Micrograph prepared using the Citrus Limetta as a carbon precursor. We can observe agglomerated carbon powder particles at lower magnification of X950 in image. Overall, the micrographs appear to be a network of inter-connected sheets. However, further improved magnification is required to closely analyze the nano sample in detail.

Figure 4.1.2(b) shows SEM Micrograph for Graphene Oxide prepared using orange peels as a carbon precursor. These images show the sheets appearance as wrinkled and folded which is a common feature of graphene nano-sheets and the oxidation process during modified hummers process can cause the sheets to curl up. Overall, we can observe an arrangement of inter-connected and closely spaced sheets, however, further magnification needs to be enhanced to go into detail.

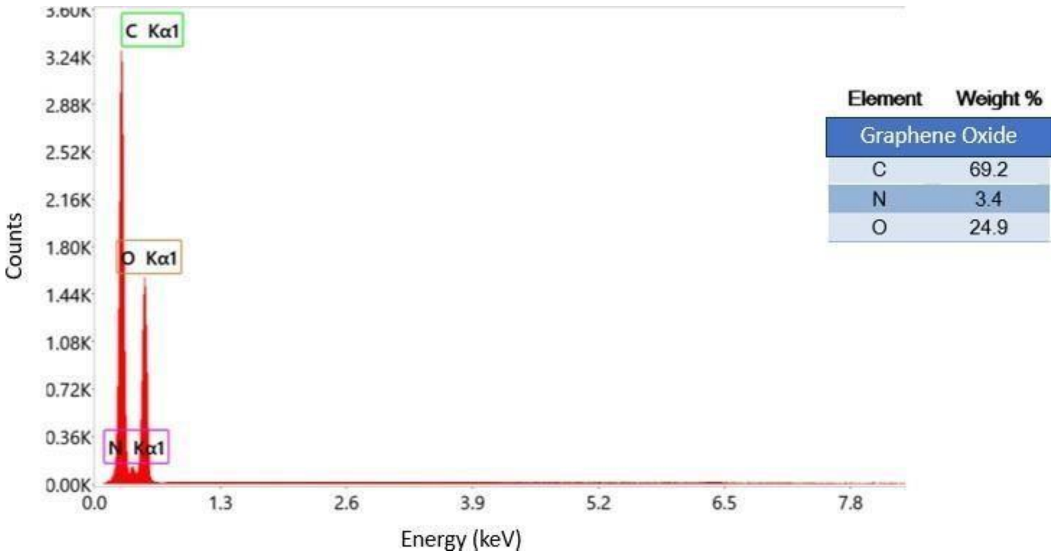
4.1.3 Energy Dispersive Spectroscopy (EDS)



Element	Weight %
Carbon Precursor	
C	83.9
O	13.6

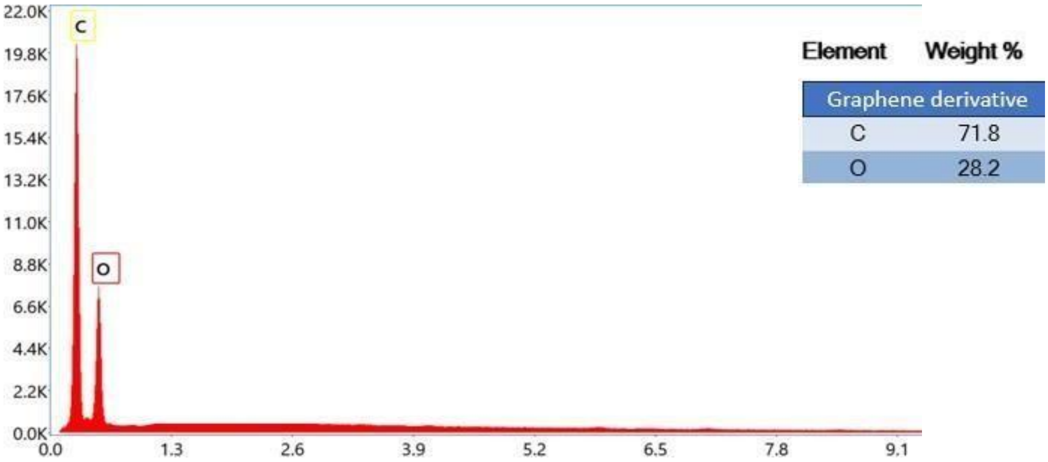
Figure 4.1.3(a): Energy Dispersive Spectra for carbon precursor (gold peak removed)

EDS analysis was conducted on the recycled carbon precursor sample and synthesized Graphene Oxide from biomass for the Elemental composition. EDS provided information about the elemental composition of the powder sample. It helped identify the presence and distribution of various elements within the sample, which is crucial for understanding its chemical properties and potential applications as observed in Figure 4.1.3(a). Since the sample was synthesized using a biomass precursor, we confirmed that no traces of impurities were present in the sample after synthesis. Impurities in the synthesized sample can show up in form of volatile species and ash content which have a negative effect on the properties of the material. However, we observed contents of Nitrogen in the Graphene Oxide sample which might appear from the environment or from the chemicals used during modified hummers process. Overall, the Fig 4.1.3(b) and 4.1.3(c) represents the successful oxidation process by the oxygen content and the compositional amounts of carbon and oxygen present in the sample.



Element	Weight %
Graphene Oxide	
C	69.2
N	3.4
O	24.9

Figure 4.1.3(b): Energy Dispersive Spectra for Graphene Oxide(trial 1 with gold peak removed)



Element	Weight %
Graphene derivative	
C	71.8
O	28.2

Figure 4.1.3©: Energy Dispersive Spectra for Graphene Oxide (trial 2 with gold peak removed)

4.1.4 Fourier Transform Infrared Spectroscopy (FTIR)

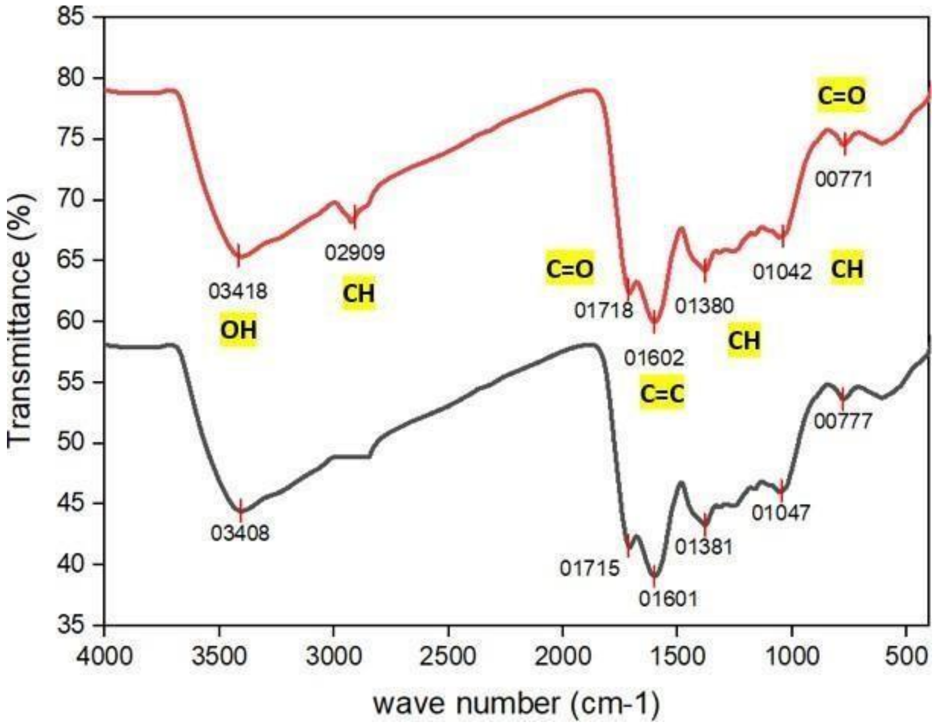


Fig 4.1.4(a): FTIR spectra for carbon precursors (Trial 2=red, Trial 1=black)

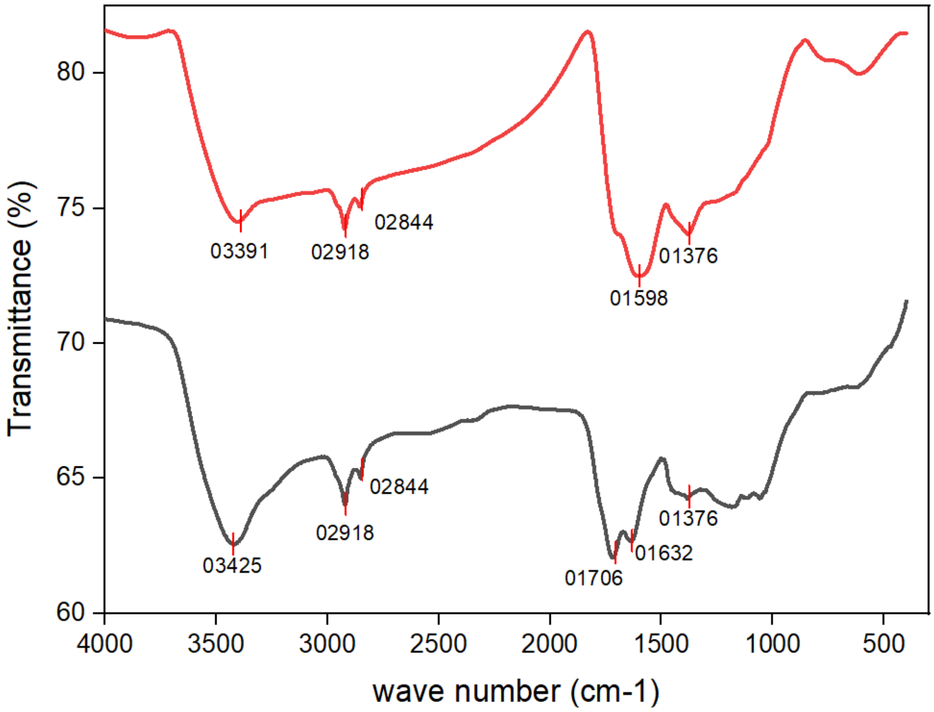


Fig 4.1.4(b): FTIR spectra of graphene oxide (trial 2=red, trial 1=black)

FTIR analysis was conducted for extracted carbon precursor and graphene oxide. Fig 4.1.4(a) shows the presence of functional groups such as C=C, C-H, and C-O at 1600 cm-1, 2923 cm-1 and 1718 cm-1 respectively which indicate that the powder contains the required functional groups of graphite powder and can be used for graphene synthesis.

Similarly, Fig 4.1.4(b) shows the FTIR spectra for graphene oxide, the functional groups at 1706cm-1, 1091 cm-1, 1376 cm-1, and 1706 cm-1 correspond to the presence of C-O(C=O) functional groups which confirm the oxidation of the sample and formation of Graphene Oxide. Other groups such as O-H are due to the moisture present inside the sample.

4.1.5 X-ray Diffraction Analysis

The XRD pattern has a dominant peak around 24-26 (2θ) which is a characteristic of graphene and reduced graphene oxide. The smaller peaks around 42-44 (2θ) and 54-56 (2θ) corresponding to the (100) and (004) planes of graphene, respectively. The peaks show a broad and amorphus like structure which is an indication of reduced graphene oxide. The peaks also show a relatively broader pattern and some extra peaks which are an indication of the presence of imperfections in the crystal structure, defects or variations in the stacking of the graphene layers in the material. Overall, the XRD pattern does not correspond to Graphene Oxide rather it appears that the sample is reduced due to a broad peak around 20-25 (2θ), as observed in the figure 4.1.5(b)(trial 2). Similarly, for trial 1, a relatively crystalline peak order is observed which shows the presence of more oxygen bonds and graphene oxide. Surprisingly, in comparison to the literature Fig 4.1.5(c), it is seen that directly reduced structure of graphene oxide is formed by using a green precursor oforange peel (because orange peel is a natural reducing agent).

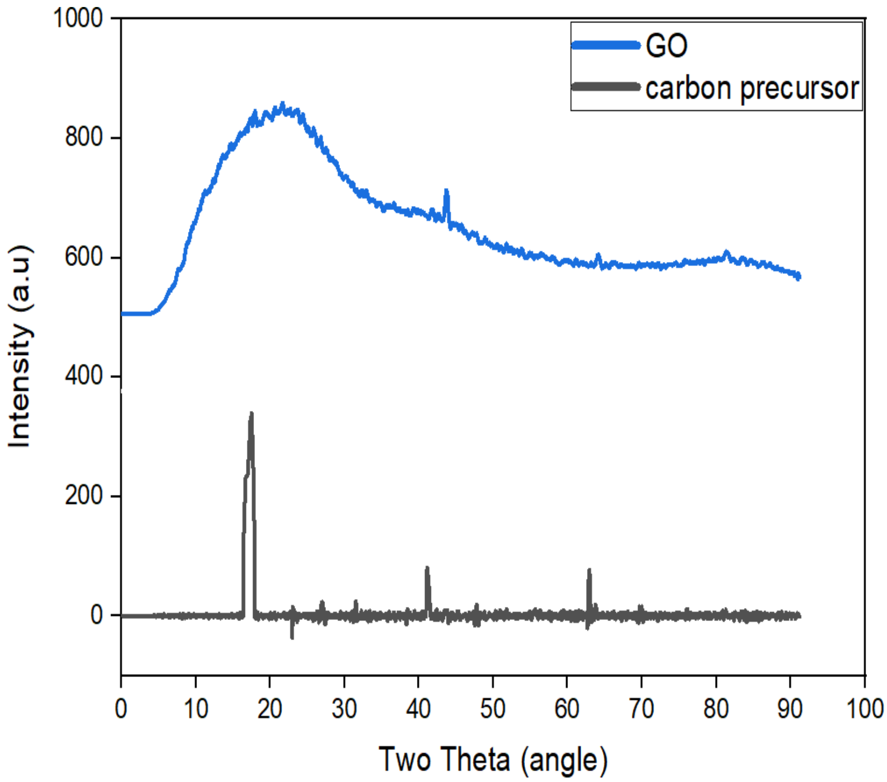


Fig 4.1.5(a): XRD peaks of carbon precursor and rGO

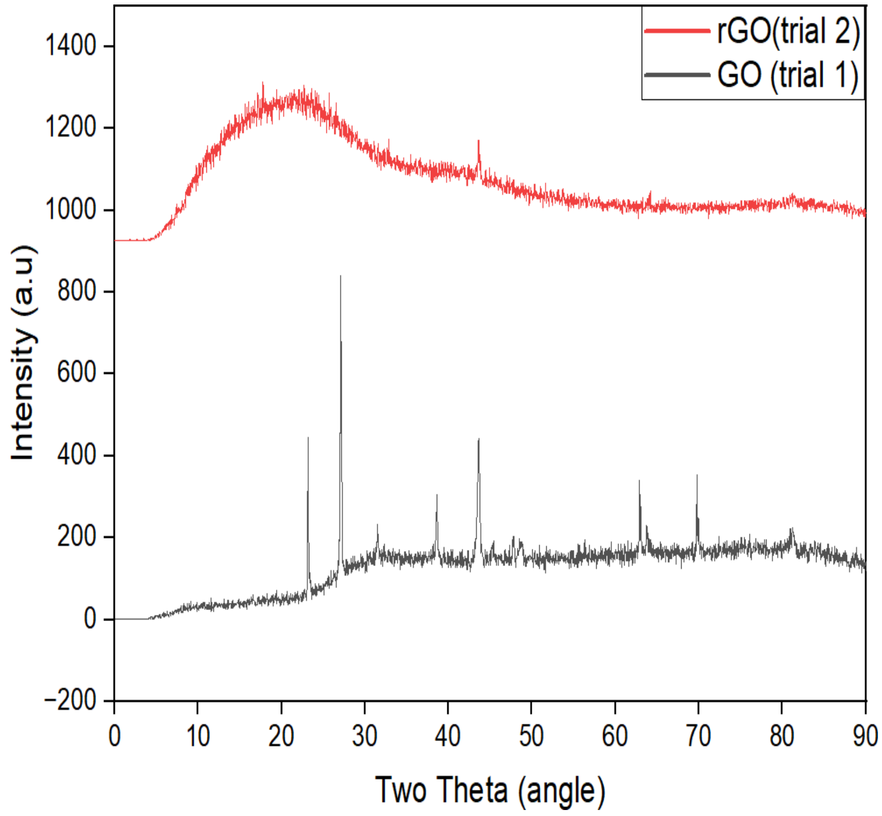


Fig 4.1.5 (b): XRD peaks of graphene oxide (trial 1) and reduced graphene oxide (trial 2)

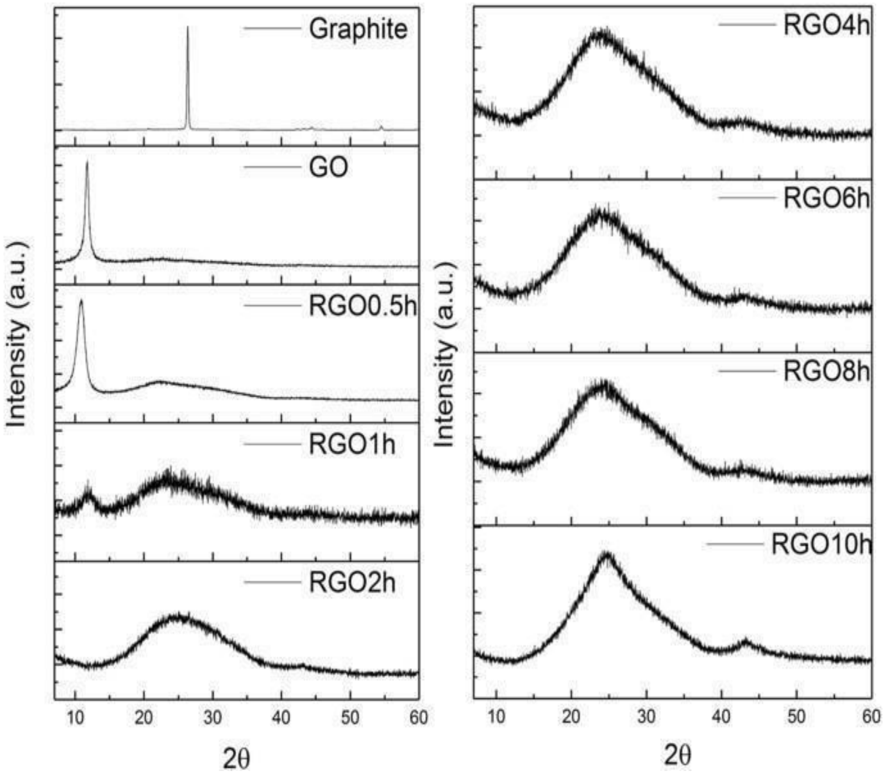


Figure 4.1.5©: Literature XRD peaks of rGO reduction w.r.t time

Hence, according to the Figure 4.1.5©, we can see that the Reduction of graphene as a functionof time. It is concluded that due to the resemblance of our graphene peak with the 6 to 8 hour reduction of literature, the peak observed in Figure 4.1.5(b) is a directly reduced graphene oxide.

CONCLUSIONS

In conclusion, this project represents a significant step forward in addressing the pressing challenges of global green transition demand and environmental sustainability. By focusing on the development of a sustainable carbon-based precursor for graphene nanosheets synthesis, the project offers a promising alternative to conventional unsustainable graphite powders and contributes to reducing reliance on scarce and environmentally harmful resources such as graphite. We were successfully able to conclude our research work in following points:

- Successful synthesis of graphene derivatives was achieved by modified hummers method.
- Through the novel source of biomass waste (i.e., orange peel), direct reduced graphene oxide (rGO) was achieved.
- It was proved that green sources can be recycled to produce graphene and enhance sustainability.

Future Outlook:

- The synthesized rGOs have exceptional water purification properties such as separation of toxic metal ions due to unique hexagonal structure and nano-channels, in the next phase of the project, graphene-based membrane will be synthesized and its potential for separation will be analyzed.
- Membrane testing of sustainable graphene will be used in comparison with conventional polymeric membranes which are un-sustainable, have lower strength and shorter lifetime.

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