

COMPARATIVE STUDY OF VARIOUS CARBONACEOUS MATERIALS FOR ADSORPTION OF INORGANIC AND ORGANIC POLLUTANTS IN WASTEWATER



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COMPARATIVE STUDY OF VARIOUS CARBONACEOUS MATERIALS FOR ADSORPTION OF INORGANIC AND ORGANIC POLLUTANTS IN WASTEWATER

by

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A dissertation submitted in accordance with the requirements of the degree of

Master of Science in Nanoscience

in the

Department of Chemistry

Faculty of Natural and Agricultural Sciences

at the



University of the Free State

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2023

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to the individuals who have played a crucial role in the completion of this thesis. Their support, encouragement, and guidance have been extremely helpful in shaping this work.

First and foremost, I would like to express my deepest appreciation and gratitude to my supervisor Professor Karel von Eschwege, without him, this work would not be as it is today. I profoundly thank him for his patience, constructive feedback and expert guidance throughout the course of this research.

I would also like to extend my appreciation to Dr. Anwar Noreljaleel for generously providing his knowledge and expertise every time it was needed.

Moreover, I could not have undertaken this journey without the support of the National Nanoscience Postgraduate Teaching and Training Platform which enabled me to conduct the research work and access essential resources that aided in realizing the goals of this research.

I am also grateful to Deidre van der Westhuizen for the assistance she provided throughout this work.

I would like to sincerely thank my friends for being there during stressful times and for all the entertainment they provided during the challenging phases of this journey.

Lastly, words cannot express my gratitude to my parents and siblings, their belief in me kept me focused, disciplined and motivated during this process.

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LIST OF ABBREVIATIONS

WHO	World Health Organization
AM	Atrazine mercapturate
DIA	Deisopropylatrazine
DACT	Diaminochlorotriazine
DAE	Desethylatrazine
CVD	Chemical Vapor Deposition
CNTs	Carbon nanotubes
SWCNTs	Single-walled carbon nanotubes
AAS	Atomic absorption spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
EDS	Energy Dispersive X-ray Spectroscopy
LCMS	Liquid Chromatography-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
HPLC	High Pressure Liquid Chromatography
AC	Activated carbon
AC-COOH	Carboxylated activated carbon
AC-NH₂	Aminated activated carbon
G	Graphite
G-COOH	Carboxylated graphite
G-NH₂	Aminated graphite

CHAPTER 1: INTRODUCTION

Over the years, environmental pollution has grown to be a worldwide problem affecting every part of the world where life exists. Water pollution, in particular, is one of the most worrying forms of environmental pollution, as water is vital to all life forms and human activities. Water pollution or contamination is defined as the introduction of foreign substances to water bodies, which consequently renders the water unusable for consumption, cooking, cleaning, and other activities. These foreign substances can be classified as inorganic pollutants, organic pollutants, nutrients and agriculture pollutants, pathogens and suspended solids. These pollutants find their way into water bodies through various pathways originating from municipal, industrial, and/or mine effluents as shown in Figure 1. For example, inorganic and organic pollutants end up in water bodies from the runoff of sewage and industrial effluents. As water bodies become increasingly contaminated with these pollutants, ecosystems and human health continue to be threatened.

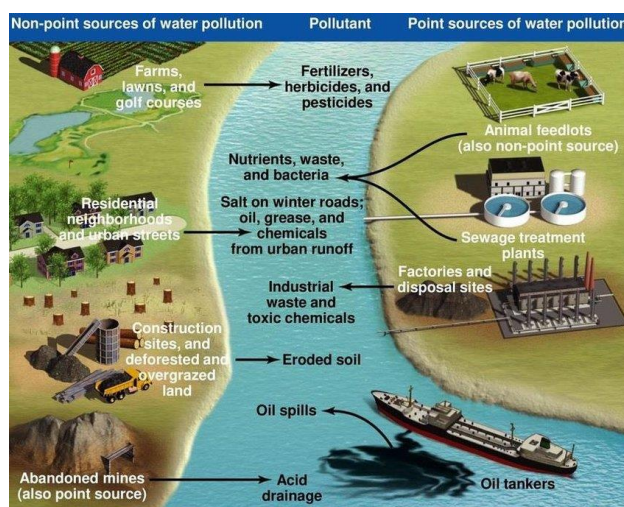


Figure 3. Various pathways of contaminants into water bodies.¹

According to WHO guidelines for drinking quality water, water pollution is responsible for about 14 000 deaths every day.² Heavy metal ions and concentrated organic pollutants in water pose a significant threat to human health because of their non-biodegradable, bioaccumulation properties, toxicity and persistence in nature. Several heavy metal-based

¹ Elmustafa SAA., and Mujtaba. "Internet of things in smart environment: Concept, applications, challenges, and future directions." *World scientific news*, 134.1 (2019) 1-51.

² World Health Organization (Ed.), *Guidelines for Drinking-Water Quality: Incorporating First Addendum Recommendations*, 3rd ed., vol. 1, World Health Organization, Geneva, Switzerland (2006). 375–376.

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compounds are highly soluble in water, which then readily transfer to animals and thus into the human food chain.³ The metals contained in these compounds are transferred to animals and human food chains through assimilation and processes of biomethylation and bioaccumulation. Some of these metal pollutants have the capability to exist in the environment in more than one oxidation state, for example, mercury can exist as Hg(II) and Hg (I) and chromium as Cr (VI) and Cr (III). The toxicity, bioavailability and relative mobility of these metals are determined by their oxidation state. Cadmium, lead, zinc, nickel and copper are the most widely used heavy metals in various industries such as tannery, mining, metallurgy, chemical manufacturing and electroplating.⁴ To avoid indirect or direct consumption of these metals, industries need to decontaminate their wastewater before discharging into ponds or rivers. The maximum acceptable concentrations of some heavy metals in drinking water according to the World Health Organization (WHO) or Environmental Protection Agency (EPA) for copper, lead, nickel, arsenic, cadmium and chromium have been determined as 1.5, 0.05, 0.1, 0.01, 0.005 and 0.1 mg/L, respectively. Several disorders in humans have been reported as a result of ingestion of heavy metals, for instance, hypertension, cell death and impaired renal function have been reported due to lead exposure.⁵ Exposure to chromium over a long period can damage the kidneys, circulatory system, liver and nerve tissues, and cause skin irritation. Other metals, for instance, cadmium and arsenic are carcinogens, therefore exposure to it can cause bladder, liver, lung and skin cancer.⁶ In addition, with exposure to high concentrations of mercury, brain functioning can be affected and a variety of symptoms are seen, including irritability, shyness, tremors, impaired vision and hearing, and memory loss.

Exposure to organic pollutants also has adverse effects on human health. For the past 20 years there has been significant growth in the utilization of synthetic chemicals, most of which are categorized as emerging persistent organic pollutants due to the abovementioned

³ Byber K., et al. "Cadmium or cadmium compounds and chronic kidney disease in workers and the general population: a systematic review." *Critical reviews in toxicology*, 46.3 (2016) 191-240.
<https://doi.org/10.3109/10408444.2015.1076375>.

⁴ Gutwiński P., et al. "Long-term effect of heavy metals Cr (III), Zn (II), Cd (II), Cu (II), Ni (II), Pb (II) on the anammox process performance." *Journal of water process engineering*, 39 (2021) 101668.
<https://doi.org/10.1016/j.jwpe.2020.101668>.

⁵ Jaishankar M., et al. "Toxicity, mechanism and health effects of some heavy metals." *Interdisciplinary toxicology*, 7.2 (2014) 60.

⁶ Mirzabeygi M., et al. "Heavy metal contamination and health risk assessment in drinking water of Sistan and Baluchistan, Southeastern Iran." *Human and ecological risk assessment: An international journal*, 23.8 (2017) 1893-1905. <https://doi.org/10.1080/10807039.2017.1322895>.

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properties.⁷ These persistent organic pollutants include a diverse range of synthetic chemicals such as agrochemicals (e.g. growth regulators and pesticides), pharmaceuticals, surfactants, personal care products, illicit drugs, industrial additives, plasticizers and fire-flame retardants. Some of these pollutants commonly found in Bloemfontein drinking water include atrazine, carbamazepine, terbuthylazine, metolachlor, fluconazole and tebuthiuron.^{8,9} For example, atrazine is a widely used herbicide across the globe, it has been detected in groundwater and drinking water with concentrations exceeding the recommended maximum permissible limit (3.0 ug L⁻¹ by WHO). Atrazine amongst other organic pollutants can undergo degradation and transform into its metabolites such as atrazine mercapturate (AM), deisopropylatrazine (DIA), diaminochlorotriazine (DACT) and desethylatrazine (DAE). However, in most cases, it does not degrade, it retains its structure and remains in water bodies for a long time, until it enters into the food chain and consequently into animal and human systems. High concentrations of atrazine and its metabolites in wastewater and effluents have a variety of adverse effects on humans and animals, including reduced sperm count in males, endocrine disruption, heart, liver, and nerve damage and impaired olfactory function.¹⁰ Fluconazole on the other hand is a pharmaceutical drug used for the prevention and treatment of yeast and fungal infections such as fungal meningitis, esophageal candidiasis, oropharyngeal candidiasis, vaginal candidiasis and other candida infections. A study conducted over three seasons has also detected it in drinking water and wastewater with concentrations up to 9959 ng. L⁻¹.¹¹ According to the human health risk assessment, fluconazole poses a high risk in drinking water and, in addition, the risk estimates showed that the levels found for fluconazole may lead to a moderate or high risk of developing antifungal resistance.

As a result of sustained industrial activity and rapid population growth, contamination of freshwater bodies has increased significantly leading to a shortage of safe and clean water. This disruption to the global water system has become an enormous problem, especially for

⁷ Pintado-Herrera G., et al. "Distribution, mass inventories, and ecological risk assessment of legacy and emerging contaminants in sediments from the Pearl River Estuary in China." *Journal of hazardous materials*, 323 (2017) 128-138. <https://doi.org/10.1016/j.jhazmat.2016.02.046>.

⁸ Odendaal C., et al. "An LC-MS/MS based survey of contaminants of emerging concern in drinking water in South Africa." *South african journal of science*, 111.9-10 (2015) 01-06. <http://dx.doi.org/10.17159/SAJS.2015/20140401>.

⁹ Patterson Hugh-G. Scoping Study and Research Strategy Development on Currently Known and Emerging Contaminants Influencing Drinking Water Quality: Main report. Pretoria: Water Research Commission, 2013.

¹⁰ Nápoles-Armenta J., et al. "The Influence of the Configuration of Two Electrochemical Reactors on the Process of Removing Atrazine from Water." *Sustainability*, 13.9 (2021) 5267. <https://doi.org/10.3390/su13095267>.

¹¹ Assres H.A., et al. "Occurrence and risk assessment of azole antifungal drugs in water and wastewater." *Ecotoxicology and environmental safety*, 187 (2020) 109868. <https://doi.org/10.1016/j.ecoenv.2019.109868>.

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water-scarce countries such as South Africa. As a result of this global problem, researchers have been putting in strenuous efforts to develop viable, cost-effective and efficient solutions to assist in the treatment of wastewater. In a quest to address the problem, researchers have developed various methods aimed at removing the inorganic and organic pollutants introduced into freshwater bodies. These methods include membrane filtration, ion exchange, chemical precipitation, electrochemical treatment and adsorption.^{12,13,14,15} Among these methods, the most widely used is adsorption, which involves the solid material's ability to attract molecules of solutions or gases with which it is in contact to its surface. According to extensive literature data, Ahmaruzzaman points out that liquid-phase adsorption is one popular method for extracting harmful and poisonous pollutants from wastewater.¹⁶

The adsorption method is widely used for water purification because of several advantages it possesses over other methods. It is simple and easy to operate and does not require complex machinery, which consequently reduces maintenance costs. It has the capacity for regeneration of the adsorbents used which reduces operational costs and environmental impact as it does not result in secondary pollution and it is efficient in the removal of a wide variety of pollutants. Although adsorption is characterized by these advantages, the most crucial factor for it to perform effectively is the appropriate adsorbent selection. The adsorbent can be an inorganic, organic or mineral material. Various adsorbents have been employed in an attempt to remove organic and inorganic pollutants in wastewater. Some of these adsorbents include carbon-based nanomaterials, polymer materials, bio-fuels, zeolite, industrial byproducts, activated clay minerals, etc.¹⁷ Each of these materials has different adsorption capacities toward specific contaminants in wastewater.

¹² Wang X., et al. "Removal of Cu (II) ions from contaminated waters using a conducting microfiltration membrane." *Journal of hazardous materials*, 339 (2017) 182-190.

<https://doi.org/10.1016/j.jhazmat.2017.06.038>.

¹³ Dong B., et al. "Sono-electrochemical recovery of metal ions from their aqueous solutions." *Journal of hazardous materials*, 318 (2016) 379-387. <https://doi.org/10.1016/j.jhazmat.2016.07.007>.

¹⁴ Kołodziejńska D., et al. "Uptake of heavy metal ions from aqueous solutions by sorbents obtained from the spent ion exchange resins." *Microporous and mesoporous materials*, 244 (2017) 127-136.

<https://doi.org/10.1016/j.micromeso.2017.02.040>.

¹⁵ Ahmaruzzaman M., and Vinod K.G. "Rice husk and its ash as low-cost adsorbents in water and wastewater treatment." *Industrial & engineering chemistry research*, 50.24 (2011) 13589-13613.

<https://doi.org/10.1021/ie201477c>.

¹⁶ Ahmaruzzaman M. "Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals." *Advances in colloid and interface science*, 166.1-2 (2011) 36-59.

<https://doi.org/10.1016/j.cis.2011.04.005>.

¹⁷ Dubey S.P., Gopal K., and Bersillon J.L. "Utility of adsorbents in the purification of drinking water: a review of characterization, efficiency and safety evaluation of various adsorbents." *Journal of environmental biology*, 30.3 (2009) 327-332.

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Amongst these adsorbents, carbonaceous nanomaterials have been observed to be ideal candidates for effective and efficient removal of pollutants during wastewater treatment due to their unique surface and structural chemistry, low densities, higher porosity, larger surface areas and most importantly, its less expensive source materials.¹⁸ Carbonaceous nanomaterials are a class of materials that are mainly made up of carbon molecules that are primarily arranged in a hexagonal honeycomb lattice structure as shown in Figure 2. The carbonaceous nanomaterials include activated carbon, graphite, graphene and carbon nanotubes. A detailed description of each of the nanomaterials is provided in Chapter 2 along with previous and recent applications in water treatment.

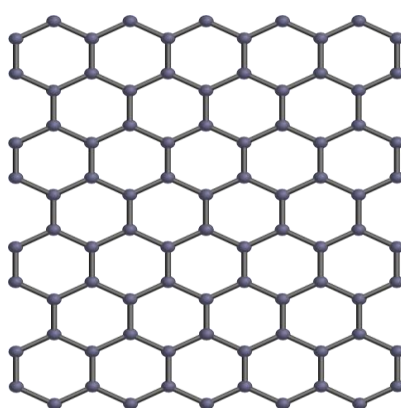


Figure 4. The hexagonal honeycomb lattice structure of carbonaceous materials.

The crisis of the ever-growing water pollution as a result of the industrial revolution and population growth demands continuous innovation or development of cheap effective and environmentally friendly adsorbent materials that have a high affinity range towards various organic and inorganic pollutants. Such adsorbent materials will prevent human exposure to toxic and harmful pollutants that dissolve and persist in water, which consequently could lead to adverse health effects due to continuous consumption of the polluted water. Based on the literature research conducted, carbonaceous nanomaterials are promising adsorbent materials and therefore the study is based on the use of these nanomaterials together with its modified counterparts for adsorption of the commonly found water pollutants in drinking water.

¹⁸ Scaria J., et al. "Carbonaceous materials as effective adsorbents and catalysts for the removal of emerging contaminants from water." *Journal of cleaner production*, 350 (2022) 131319.
<https://doi.org/10.1016/j.jclepro.2022.131319>.

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2. The carbonaceous nanomaterials discussed in this study include activated carbon, graphite, graphene and carbon nanotubes. A detailed description of each nanomaterial is provided below along with its previous and recent applications in water treatment.

2.1 Activated carbon

2.1.1 Properties and application in water purification

Activated carbon also termed, activated charcoal, is a black, highly porous carbon-based powdered material. It consists of a well-defined pore structure with various pore sizes ranging from meso, micro and macropores as illustrated in Figure 3. Activated carbon has numerous functional groups present on its surface that are derived from its precursor material. The aforementioned characteristics, as well as its high surface area (500 to $1500\text{ m}^2\text{ g}^{-1}$), chemical inertness, hydrophobicity and lightness, make it a multifaceted material that can be applied in various fields such as the chemical industry, energy storage, medicine, gold recovery, but primarily in environmental fields.¹⁹ Due to these properties, activated carbon has been reported as an excellent adsorbent material for various types of water contaminants.²⁰

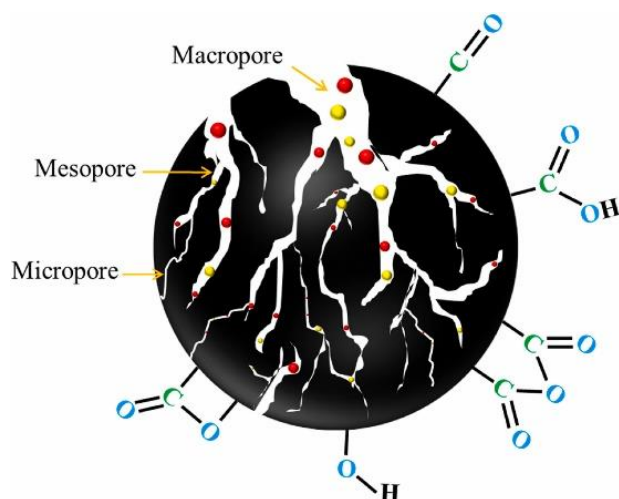


Figure 3. Diagrammatic representation of activated carbon's pores and surface functional groups.

¹⁹ Yin C.Y., Aroua M.K., and Daud W.M.A.W. " Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions." *Separation and purification technology*, 52.3 (2007) 403-415. <https://doi.org/10.1016/j.seppur.2006.06.009>.

²⁰ Yang R.T. *Adsorbents: fundamentals and applications*. John Wiley & Sons, 2003.

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Numerous studies have been conducted using activated carbon as an adsorbent for the removal of heavy metal ions and organic contaminants.^{21,22,23} As an adsorbent with a strong adsorption capacity and porous structure, activated carbon is extensively used in wastewater treatment. It is often used for decolorization and removal of chloramines, chlorine, organic contaminants as well as odor-causing compounds. Several surface functional groups on activated carbon promote the adsorption of pollutants from aqueous solutions, and these include carbonyl, carboxyl, quinones, phenols and lactones. Activated carbon is known to be more efficient in the removal of toxic organic compounds compared to heavy metal inorganic compounds. Despite the fact that activated carbon is well known for its effectiveness as an adsorbent for a wide range of contaminants, there is a growing interest in the modification of activated carbon due to the need to develop more affinity for specific contaminants in order to remove it from various types of industrial wastewater. The different modification strategies are discussed in the section on functionalization of carbonaceous materials.

2.1.2 Methods of Synthesis

Activated carbon is produced through an activation process that is either chemical or physical with both methods involving carbon-rich materials such as sawdust, coal, coconut shells, wood and peat. The physical activation process involves exposing the carbon-rich material to extremely high temperatures (800 – 1200°C) in the presence of a gas, usually steam or carbon dioxide, which results in the formation of a highly porous structure²⁴. Then, the chemical activation process involves the impregnation of the carbon-rich material with chemicals such as potassium hydroxide, phosphoric acid or zinc chloride.²⁵ In the absence of oxygen, the impregnated material is then heated to high temperatures (800 – 1100°C) resulting in a network of pores forming within the material. In terms of porosity, specific surface area,

²¹ Guo J., et al. "Preparation and characterization of nanoporous activated carbon derived from prawn shell and its application for removal of heavy metal ions." *Materials*, 12.2 (2019) 241. <https://doi.org/10.3390/ma12020241>.

²² Medhat A., et al. "Efficiently activated carbons from corn cob for methylene blue adsorption." *Applied surface science advances*, 3 (2021) 100037. <https://doi.org/10.1016/j.apsadv.2020.100037>.

²³ Li X., et al. "Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process: A review." *Separation and purification technology*, 235 (2020) 116213. <https://doi.org/10.1016/j.seppur.2019.116213>.

²⁴ Arslanoğlu H. "Direct and facile synthesis of highly porous low-cost carbon from potassium-rich wine stone and their application for high-performance removal." *Journal of hazardous materials*, 374 (2019) 238-247. <https://doi.org/10.1016/j.jhazmat.2019.04.042>.

²⁵ Gao Yuan., et al. "Insight into activated carbon from different kinds of chemical activating agents: A review." *Science of the total environment*, 746 (2020) 141094. <https://doi.org/10.1016/j.scitotenv.2020.141094>.

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and total pore volume, chemical activation with KOH is more effective than physical activation which only involves heating using a furnace or microwave.²⁶ Therefore, the chemical and physical characteristics of activated carbon are dependent on a variety of factors which include activation methods, precursor materials, as well as processing parameters.

2.2 Graphite

2.2.1 Properties and application in water purification

Graphite, also historically known as plumbago or black lead, is an iron-black to steel-gray native mineral that is made of widely stacked horizontal sheets composed of rings of six carbon atoms. Due to this arrangement, graphite is known to crystallize in the hexagonal system. The distance between the plane and the bond length of the carbon atoms in the hexagonal system is 0.335 nm and 0.142 nm respectively.²⁷ Figure 4 provides an illustration of the bond length and the bond distance between the layers. Weak van der Waals forces are bonds that are responsible for the interactions between the layers of sheets. Graphite is tremendously soft and has a greasy feel because of its ability to break into very delicate flexible flakes that simply slide over one another. Under standard conditions, graphite is the most stable form of carbon.

It is similar to activated carbon in that it has unique properties that make it a multifaceted material. It is the only non-metal element that has good electrical conductivity and this is because of the presence of the unpaired valence electron. Since thermal conductivity is anisotropic in graphite, it has a high thermal conductivity in the direction parallel to the plane of the layers.²⁸ It has a high surface area resulting from the edges and interlayer spaces of the sheets and that provides sufficient sites for the adsorption of ions or molecules. Graphite is also non-reactive toward numerous chemicals and possesses an extremely high melting point of approximately 3550 °C. Graphite has a 2.266 g/cm³ crystal density, however its specific gravity measurements range from 2.20 to 2.30, depending on purity; high values are primarily attributable to impurities, whereas low values are linked to trapped porosity.²⁹

²⁶ Song M., et al. "The comparison of two activation techniques to prepare activated carbon from corn cob." *Biomass and bioenergy*, 48 (2013) 250-256. <https://doi.org/10.1016/j.biombioe.2012.11.007>.

²⁷ Kharissova O.V., and Kharisov B.I. "Variations of interlayer spacing in carbon nanotubes." *Rsc advances*, 4.58 (2014) 30807-30815. <https://doi.org/10.1039/C4RA04201H>.

²⁸ Graphite (2023) Minerals Education Coalition. Available at: <https://mineralseducationcoalition.org/minerals-database/graphite/> (Accessed: 11 October 2023).

²⁹ Keeling J. "Graphite: properties, uses and South Australian resources." *MESA J*, 84.3 (2017) 28-41.

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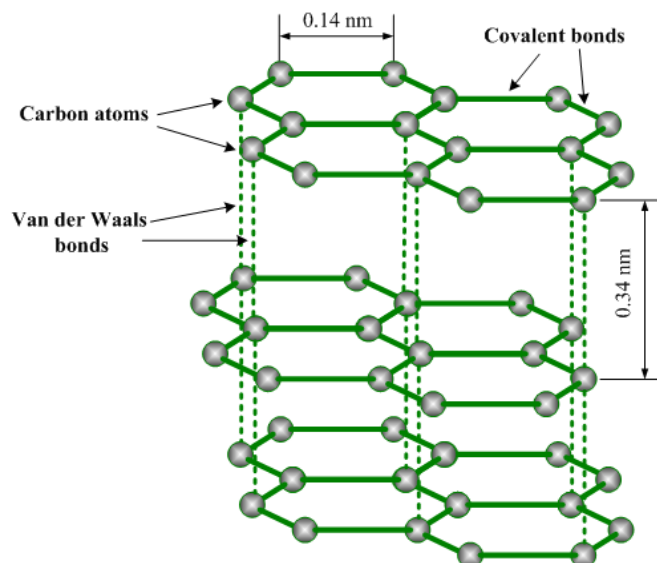


Figure 4. Schematic representation of the graphite structure and its existing bond length and distance between carbon atoms.²⁷

Some of these graphite properties can be exploited to provide alternative ways of water purification. Recent studies that have been conducted about water purification using graphite, mostly modified or incorporated graphite with other materials forming hybrid systems or composites before using it as an adsorbent. For example, Verma A *et al*, incorporated graphite powder with sodium alginate to form a porous sodium alginate/graphite hydrogel for the adsorption of malachite green dye.³⁰ Olanipekun O *et al*, modified graphite powder to graphite oxide and reduced graphite oxide, then deposited poly 1,5-diaminoaphthalene and poly 1,4-diaminoanthraquinone to the reduced graphite oxide for adsorption of lead.³¹ Therefore, there is a gap for research to be conducted using pure graphite as an adsorbent material for various organic and inorganic pollutants to assess its adsorption capacity and affinity for contaminants.

2.2.2 Methods of Synthesis

Graphite is a mineral that occurs naturally in metamorphic and igneous rocks, its formation involves subjecting carbon to high temperatures and pressures that convert it into graphite through compression. For the past few years, graphite has gained significant interest

³⁰ Verma A., et al. "Graphite modified sodium alginate hydrogel composite for efficient removal of malachite green dye." *International journal of biological macromolecules*, 148 (2020) 1130-1139. <https://doi.org/10.1016/j.ijbiomac.2020.01.142>.

³¹ Olanipekun O, et al. "Synthesis and characterization of reduced graphite oxide–polymer composites and their application in adsorption of lead." *Spectrochimica acta part A: Molecular and biomolecular spectroscopy*, 149 (2015) 991-996. <https://doi.org/10.1016/j.saa.2015.04.071>.

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because of the properties already discussed above, this significant increase has raised a supply risk issue for graphite because of its huge demand. Graphite was then created synthetically through the exposure of carbon-rich materials (e.g. coal-tar pitch or petroleum coke) to heating at temperatures between 2500 – 3000 °C. These temperatures are hot enough to decompose any impurities from the carbons, allowing the formation of hexagonal sheets.³²

2.3 Graphene

2.3.1 Properties and application in water purification

Graphene refers to a material with a honeycomb lattice structure made of a single layer of carbon atoms. Graphene is derived from graphite and the suffix as traditionally used in polycyclic aromatic hydrocarbon nomenclature and terminology.³³ It is the main part of all graphitic allotropes and was the first 2-D material to be found. Geim and Novoselov first discovered graphene in 2004 at the University of Manchester and were later awarded a Nobel Prize in Physics in 2010 for the discovery. They managed to mechanically exfoliate and isolate graphene from graphite by using adhesive Scotch tape.³⁴ Before this breakthrough, it was thought impossible to thermodynamically isolate graphene based on the argument that 2-D lattice materials melt because of thermal fluctuations which prevent the long-range crystalline order of the material.^{35,36} Graphene is believed to be the thinnest material to ever be created. Various structural materials can be formed from graphene based on how it can be arranged, it is therefore regarded as the main building block of all graphitic materials. For instance, buckminsterfullerene is a material which is interconnected by single and double bonds of five to seven carbon atoms forming a partially closed or fully closed mesh. Wrapping up graphene therefore results in the formation of these zero-dimensional structures. Stacking up graphene leads to the formation of 3-D graphite and rolling it up forms 1-D carbon nanotubes (Figure 5).

³² "Graphite (2023) Minerals Education Coalition. Available at:

<https://mineralseducationcoalition.org/minerals-database/graphite/> (Accessed: 11 October 2023).

³³ Boehm H.P., Setton R., and Stumpp E. "Nomenclature and terminology of graphite intercalation compounds." *Carbon*, 24.2 (1986) 241-245. <https://doi.org/10.1351/pac199466091893>

³⁴ Novoselov K.S., et al. "Electric field effect in atomically thin carbon films." *Science*, 306.5696 (2004) 666-669. <https://doi.org/10.1126/science.1102896>

³⁵ Peirls R.E. "Bemerkungen uber umwandlungs temperature." *Helv. Phys. Acta*, 7 (1934) 81-83.

³⁶ Mermin, N.D. "Crystalline order in two dimensions." *Physical review*, 176.1 (1968) 250. <https://doi.org/10.1103/PhysRev.176.250>

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Before the discovery or isolation of graphene, it had been previously studied by Semenoff, McClure, and Wallace.^{37,38,39}

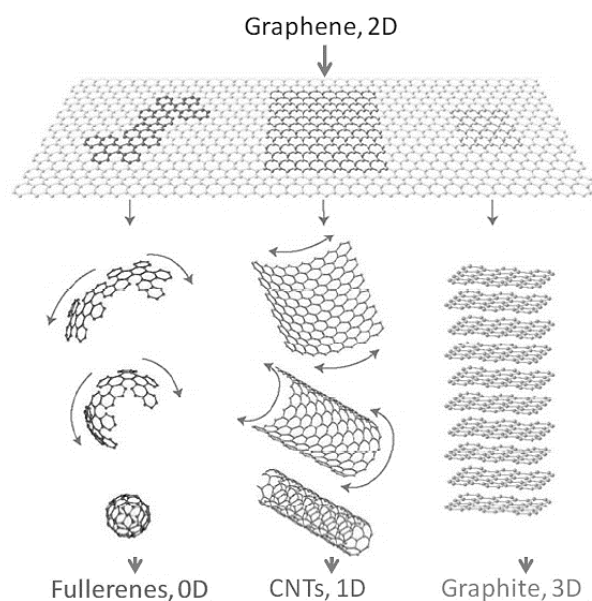


Figure 5. Carbon materials are derived from monolayer graphene (2-D), fullerene (0-D), carbon nanotubes (1-D), and graphite (3-D).⁴⁰

Graphene is also a carbon allotrope that has attracted a lot of researchers' attention because of its extraordinary properties. It is a nanomaterial that is one atom thick and is comprised of sp^2 hybridized carbon atoms arranged in a hexagonal structure. Graphene has a large surface area, high electrical conductivity, high surface functionality, high thermal conductivity, and superior mechanical flexibility. Other properties of graphene have been summarized in Table 1. These properties can be finetuned through alterations of various parameters such as number of layers, porous structure and defect density to meet the desired characteristics for a particular application. Figure 6 shows a graphical representation of various applications in which graphene is used. Numerous studies using graphene as an adsorbent have been conducted and have shown its capability to adsorb various contaminants in different

³⁷ Semenoff G.W. "Condensed-matter simulation of a three-dimensional anomaly." *Physical review letters*, 53.26 (1984) 2449. <https://doi.org/10.1103/PhysRevLett.53.2449>

³⁸ McClure J.W. "Diamagnetism of graphite." *Physical review*, 104.3 (1956) 666. <https://doi.org/10.1103/PhysRev.104.666>

³⁹ Wallace P.R. "The band theory of graphite." *Physical review*, 71.9 (1947) 622. <https://doi.org/10.1103/PhysRev.71.622>

⁴⁰ Geim A.K., and Novoselov K.S. "The rise of graphene." *Nanoscience and technology: a collection of reviews from nature journals*, (2010) 11-19.

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aqueous solutions.^{41,42} Moreover, graphene has shown enhanced adsorption capacities for the treatment of several contaminants all at once.⁴³ Recently, graphene and its composites have been widely used to remove dyes and heavy metal ions from aqueous solutions.^{44,45}

Table 1. Selected properties of graphene.⁴⁶

Parameter	Value
Breaking strength	42 N m ⁻¹
Current density	~10 ⁹ A cm ⁻¹
Elastic limit	~20%
Electronic mobility	2 × 10 ⁵ cm ² V ⁻¹ s ⁻¹
Tensile strength	~1.5 TPa
Thermal conductivity	~5000 W m ⁻¹ K ⁻¹
Transparency	~97.7%
Surface area	~2360 m ² g ⁻¹
Velocity of electron	~10 ⁶ m s ⁻¹

2.3.2 Methods of Synthesis

There are many methods for the synthesis of graphene which include chemical vapor deposition, mechanical exfoliation, electrochemical exfoliation, liquid phase exfoliation and epitaxial growth. These methods are either top-down or bottom-up methods as shown in Figure 6. The top-down method involves breaking down a bulk material (e.g. graphite) into its smallest component parts (graphene) while the bottom-up method is the contrary; it involves

⁴¹ Yusuf M., et al. "Applications of graphene and its derivatives as an adsorbent for heavy metal and dye removal: a systematic and comprehensive overview." *RSC advances*, 5.62 (2015) 50392-50420. <https://doi.org/10.1039/C5RA07223A>.

⁴² Leng Y., et al. "Removal of antimony (III) from aqueous solution by graphene as an adsorbent." *Chemical engineering journal*, 211 (2012) 406-411. <https://doi.org/10.1016/j.cej.2012.09.078>.

⁴³ Zhao G., et al. "Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management." *Environmental science & technology*, 45.24 (2011) 10454-10462. <https://doi.org/10.1021/es203439v>.

⁴⁴ Kumar V., et al. "Potential applications of graphene-based nanomaterials as adsorbent for removal of volatile organic compounds." *Environment international*, 135 (2020) 105356. <https://doi.org/10.1016/j.envint.2019.105356>.

⁴⁵ Attia, Nour F., et al. "Greener approach for fabrication of antibacterial graphene-polypyrrole nanoparticle adsorbent for removal of Mn²⁺ from aqueous solution." *Synthetic metals*, 282 (2021) 116951. <https://doi.org/10.1016/j.synthmet.2021.116951>.

⁴⁶ Dash S., and Amalendu P. "Material selection for TH z antennas." *Microwave and optical technology letters*, 60.5 (2018) 1183-1187. <https://doi.org/10.1002/mop.31127>.

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the formation of bulk material starting from individual small components.^{47,48} The most commonly used bottom-up approaches for synthesizing graphene include thermal pyrolysis, chemical vapor deposition (CVD), and epitaxial growth.^{49,50,51} Each of these techniques have both advantages and disadvantages for the formed graphene, other may produce structural defects within the layer of the synthesized graphene, while others may produce a smaller number of layers of the graphene sheets. CVD is a bottom-up technique that is said to be the best in the synthesis of graphene it involves the deposition of gaseous materials onto a substrate. During CVD, gas molecules are combined (often with carrier gases) in a reaction chamber at ambient temperature, where it is reacted. The reaction takes place when the combined gas reactants contact the substrate, which leads to the formation of a material film on the surface of the substrate.

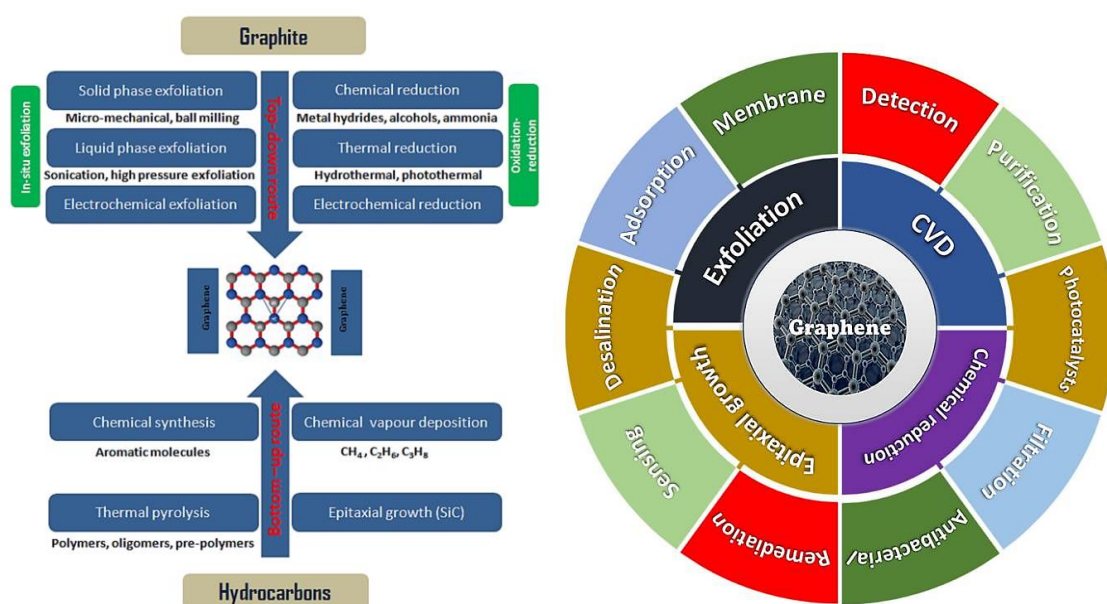


Figure 6. Different synthesis techniques and applications of graphene.⁵²

⁴⁷ Kumar N., et al. "Top-down synthesis of graphene: A comprehensive review." *FlatChem*, 27 (2021) 100224. <https://doi.org/10.1016/j.flatc.2021.100224>.

⁴⁸ Gutiérrez-Cruz A., et al. "A review of top-down and bottom-up synthesis methods for the production of graphene, graphene oxide and reduced graphene oxide." *Journal of materials science*, 57.31 (2022) 14543-14578. <https://doi.org/10.1007/s10853-022-07514-z>.

⁴⁹ Sun L., et al. "Chemical vapour deposition." *Nature reviews methods primers*, 1.1 (2021) 5. <https://doi.org/10.1038/s43586-020-00005-y>.

⁵⁰ Shang W., et al. "Facile one-pot pyrolysis synthesis of carbon quantum dots and graphene oxide nanomaterials: All carbon hybrids as eco-environmental lubricants for low friction and remarkable wear-resistance." *Tribology international*, 118 (2018) 373-380. <https://doi.org/10.1016/j.triboint.2017.09.029>.

⁵¹ Gao Z., et al. "Large-area epitaxial growth of curvature-stabilized ABC trilayer graphene." *Nature communications*, 11.1 (2020) 546. <https://doi.org/10.1038/s41467-019-14022-3>.

⁵² Abbas Q., et al. "Graphene Synthesis Techniques and Environmental Applications." *Materials*, 15.21 (2022) 7804. <https://doi.org/10.3390/ma15217804>.

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2.4 Carbon Nanotubes

2.4.1 Properties and application of water purification

Carbon nanotubes refer to graphene sheet(s) rolled up into hollow cylindrical tubes with diameter sizes of a few nanometers as shown in Figure 7. The name “nanotube” was derived from the size of the diameter of the tubes. Their length can extend up to several millimeters. Carbon nanotubes (CNTs) were first discovered in 1991 by Sumio Iijima, a Japanese physicist, and Toshinari Ichihashi an academic researcher.^{53,54} The first discovered carbon nanotubes were single-wall carbon nanotubes (SWCNTs) with a diameter of 1 nm. These were synthesized by carbon-arc discharge. Researchers from the University of Cincinnati came up with a method to prepare long-aligned CNT arrays. This team of researchers managed to create 18 mm long aligned CNTs that can be turned into nanofibers. CNTs are composed of carbon atoms arranged in a hexagonal lattice structure and fall under the structural family of fullerenes. Quantum chemistry, especially orbital hybridization, describes the bonding nature of carbon nanotubes.

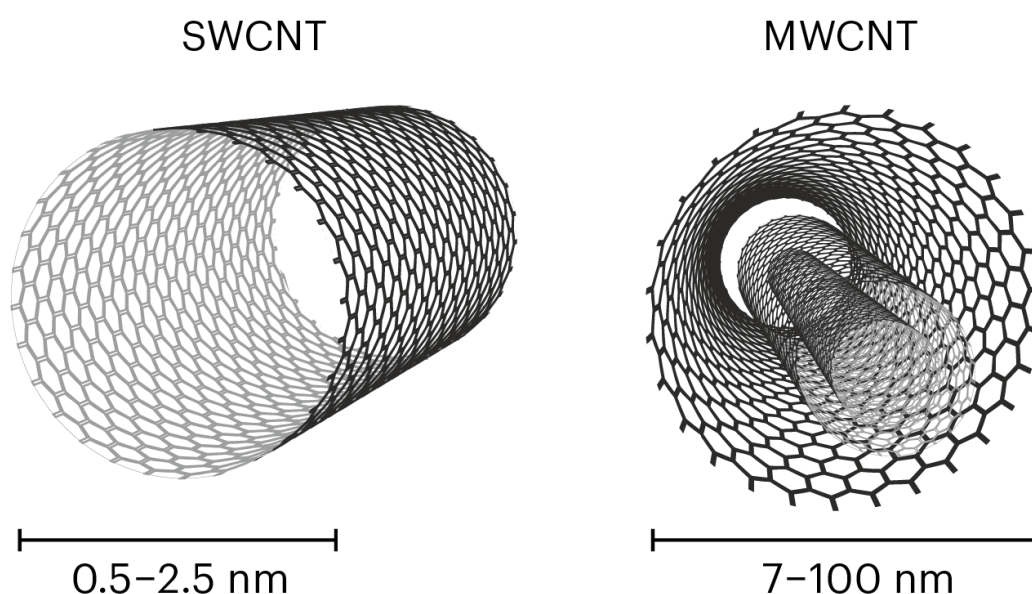


Figure 7. Pictorial representation of single-walled (left) and multi-walled (right) carbon nanotubes.

⁵³ Iijima S. "Helical microtubules of graphitic carbon." *Nature*, 354.6348 (1991) 56-58.

<https://doi.org/10.1038/354056a0>

⁵⁴ Iijima S., and Ichihashi T. "Single-shell carbon nanotubes of 1-nm diameter." *Nature*, 363.6430 (1993) 603-605. <https://doi.org/10.1038/363603a0>

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Chemical bonds existing in CNTs are similar to those existing in graphite. CNTs are entirely composed of sp^2 bonds which are known to be very strong compared to sp^3 bonds existing in diamond. Figures 8 a & b illustrate the sp^2 bonds existing in a carbon atom and sp^2 hybrid bonds existing in graphene due to one carbon interconnecting with three other neighboring carbon atoms in graphene respectively. Carbon nanotubes arrange itself naturally into ropes, with Van-der Waals forces holding the fibers together. When carbon nanotubes are pressed under intense pressure, some sp^2 bonds can convert to sp^3 bonds, enabling strong, long-length wires to be produced.⁵⁵⁻⁵⁶ It is important to note that pressure is the main method of inducing sp^2 to sp^3 bond changes in carbon. The produced metastable phases depend heavily on the hybridization scheme and crystal structure of raw carbon atoms as well as on the non-hydrostatic/hydrostatic applied pressure. For example, when graphite is experimentally compressed it may form hexagonal and cubic diamonds, also a cold compressed graphite phase that is super hard.^{57,58,59}

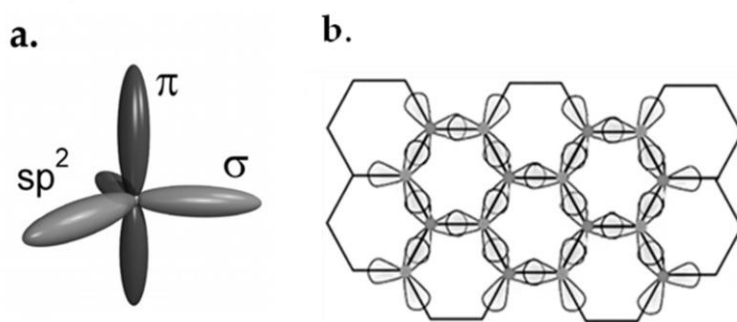


Figure 8. a) sp^2 bonds of carbon and b) sp^2 hybrids of carbon atom connecting with neighboring carbons in graphene.

Carbon nanotubes are one of various forms in which carbon can exist, i.e. being amongst the allotropes of carbon. CNTs can be distinguished into three variants; single, double and multi-walled nanotubes. Table 2 shows classifications of the various CNTs and their structural comparisons. CNTs are referred to as “materials of the 21st century” because of their

⁵⁵ Dai H. "Carbon nanotubes: synthesis, integration, and properties." *Accounts of chemical research*, 35.12 (2002) 1035-1044. <https://doi.org/10.1021/ar0101640>

⁵⁶ Hirlekar R., et al. "Carbon nanotubes and its applications: a review." *Asian journal of pharmaceutical and clinical research*, 2.4 (2009) 17-27.

⁵⁷ Bundy F.P., and Kasper J.S. "Hexagonal diamond—a new form of carbon." *The Journal of chemical physics*, 46.9 (1967) 3437-3446. <https://doi.org/10.1063/1.1841236>

⁵⁸ Yagi T., et al. "High-pressure in situ x-ray-diffraction study of the phase transformation from graphite to hexagonal diamond at room temperature." *Physical review b*, 46.10 (1992) 6031. <https://doi.org/10.1103/PhysRevB.46.6031>

⁵⁹ Zhao Z.S., et al. "High-pressure behaviors of carbon nanotubes." *Journal of superhard materials*, 34.6 (2012) 371-385. <https://doi.org/10.3103/S1063457612060111>

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unique characteristics summarized in Table 3, which are dependent on the length and diameter of the tube, and how the graphene or graphite sheets are rolled.^{60,61} These variants differ in terms of length, thickness, various structures as well as the number of layers. The way graphene sheets are rolled determines the structural pattern, which is represented by two indices (n, m) which denote the number of unit vectors in the lattice structure of the CNTs along two directions.⁶² For instance, zigzag nanotubes are defined as those where $m = 0$ (Figure 9a). In contrast, armchair nanotubes are where $n = m$ (Figure 9b). All others are referred to as chiral nanotubes (Figure 9c). Furthermore, the chirality, or how carbon atoms are arranged, determines whether a carbon nanotube is an insulator, semiconductor or conductor⁶³. The diameter of a nanotube increases with increasing n and/or m values. In nanotubes, the number of unit cells stacked together determines the height and length.⁶⁴

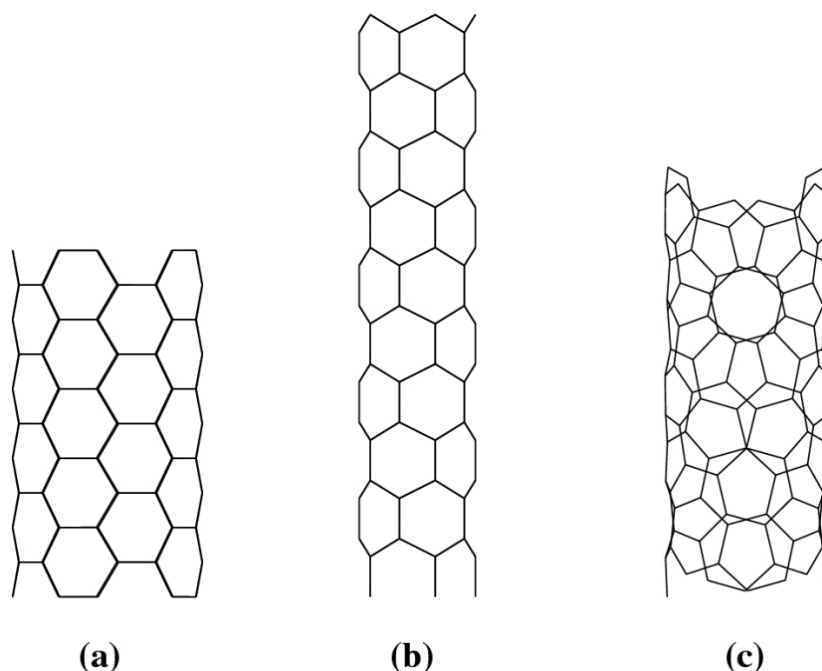


Figure 9. Illustration of a) armchair, b) zigzag, and c) chiral carbon nanotubes.⁵⁴

⁶⁰ Britz D.A., and Andrei N.K. "Noncovalent interactions of molecules with single walled carbon nanotubes." *Chemical society reviews*, 35.7 (2006) 637-659. <https://doi.org/10.1039/B507451G>.

⁶¹ Thostenson E.T., Zhifeng R., and Tsu-Wei C. "Advances in the science and technology of carbon nanotubes and their composites: a review." *Composites science and technology*, 61.13 (2001) 1899-1912. [https://doi.org/10.1016/S0266-3538\(01\)00094-X](https://doi.org/10.1016/S0266-3538(01)00094-X).

⁶² Dresselhaus M.S., Dresselhaus G., and Saito R. "Physics of carbon nanotubes." *Carbon*, 33.7 (1995) 883-891. [https://doi.org/10.1016/0008-6223\(95\)00017-8](https://doi.org/10.1016/0008-6223(95)00017-8)

⁶³ De Volder M.F.L., et al. "Carbon nanotubes: present and future commercial applications." *Science*, 339.6119 (2013) 535-539. <https://doi.org/10.1126/science.1222453>

⁶⁴ Lönnecke K., Eberhardt O., and Wallmersperger T. "Electrostatic charge distribution in armchair and zigzag carbon nanotubes: A numerical comparison of CNT charge models." *Acta mechanica*, (2021) 1-16. <https://doi.org/10.1007/s00707-021-03085-3>

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Table 2. Classifications and structural comparisons of SWCNTs and MWCNTs.

SWCNTs	MWCNTs
Made from single-layer graphene	Made from multiple layers of graphene
Requires catalyst for synthesis	Can be synthesized without a catalyst
Difficult to synthesize in bulk	Easy to synthesize in bulk
More defects during functionalization	Less defects but difficult to improve
Purity is poor	Purity is high
Characterization and evaluation are easy	Characterization and evaluation are difficult
Accumulates less in the body	Accumulates more in the body
Easy to twist	Difficult to twist

Like most of the previously discussed carbon nanomaterials, CNTs have several qualities and properties that make them appealing for use in various fields and applications. CNTs are widely used in energy storage devices, electrode materials, field emission displays, semiconductor materials, catalyst carriers, composite reinforcement, etc. The scale of all these applications mainly depends on the quality, output, and cost of CNTs. CNTs have large specific surface areas, chemical inertness, high porosity, light mass density and its structure is uniform and well-defined at an atomic scale. It possesses both high tensile strength and high Young's modulus, making CNTs one of the strongest materials ever discovered. Some of these mentioned properties offer possible strong interactions between CNTs and other compounds, either organic or inorganic.⁶⁵

CNTs as a new type of adsorbent have attracted the attention of most researchers because of its exceptional properties and ability to remove various organic and inorganic pollutants as well as radionuclides in wastewater. Owing to its excellent water transport, chemical inertness, high mechanical strength, and high specific surface properties, it has received significant interest in the development of new composite membranes for water treatment applications.^{66,67,68} Additionally, CNTs have alluring catalytic, electrochemical, and adsorption properties that are applicable for integration with membrane separation processes

⁶⁵ Chen C., et al. "Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni (II) and Sr (II)." *Journal of hazardous materials*, 164.2-3 (2009) 923-928.

<https://doi.org/10.1016/j.jhazmat.2008.08.089>.

⁶⁶ De Volder M.F.L., et al. "Carbon nanotubes: present and future commercial applications." *Science*, 339.6119 (2013) 535-539. <https://doi.org/10.1126/science.1222453>

⁶⁷ Das R., et al. "Carbon nanotube membranes for water purification: A bright future in water desalination." *Desalination*, 336 (2014) 97-109. <https://doi.org/10.1016/j.desal.2013.12.026>

⁶⁸ Goh, P. S., A. F. Ismail, and B. C. Ng. "Carbon nanotubes for desalination: Performance evaluation and current hurdles." *Desalination*, 308 (2013) 2-14. <https://doi.org/10.1016/j.desal.2012.07.040>

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and augmenting the efficiency of CNTs-based composite membranes for water treatment. CNTs have the ability to adsorb and remove different biological, inorganic and organic pollutants. Molecular simulations, experimental measurements, and theoretical calculations have been conducted extensively to study the removal of toxic contaminants from large volumes of aqueous solutions and gas streams.^{69,70,71,72} CNTs have various sites in which the adsorption of different contaminants may occur, as shown in Figure 10. Firstly, there is the internal site, which is the hollow interior of each tube when it is open. Secondly, the exterior surface of the nanotube, thirdly, in the interstitial channels that are between the nanotubes, and lastly on the external groove site.

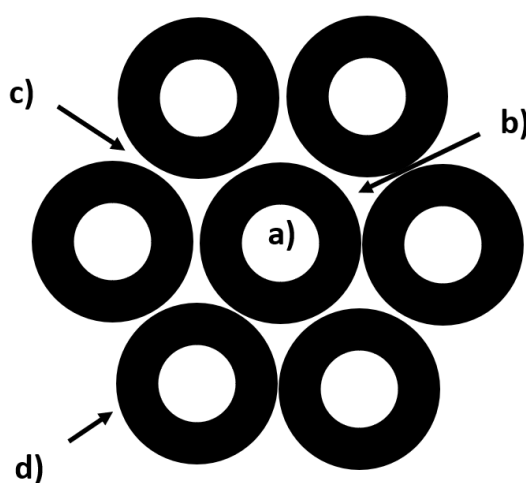


Figure 10. Various adsorption sites for organic and inorganic pollutants on CNTs, a) interior site, b) interstitial channel, c) exterior groove site and d) exterior surface.⁷³

⁶⁹ Long, R.Q., and Ralph T.Y. "Carbon nanotubes as a superior sorbent for nitrogen oxides." *Industrial & engineering chemistry research*, 40.20 (2001) 4288-4291. <https://doi.org/10.1021/ie000976k>.

⁷⁰ Long, R.Q., and Ralph T.Y. "Carbon nanotubes as superior sorbent for dioxin removal." *Journal of the american chemical society*, 123.9 (2001) 2058-2059. <https://doi.org/10.1021/ja003830l>.

⁷¹ Di Z., et al. "Adsorption of chromium (VI) ions from water by carbon nanotubes." *Adsorption science & technology*, 22.6 (2004) 467-474. <https://doi.org/10.1260/0263617042879537>.

⁷² Tan X., et al. "Counterion effects of nickel and sodium dodecylbenzene sulfonate adsorption to multiwalled carbon nanotubes in aqueous solution." *Carbon*, 46.13 (2008) 1741-1750. <https://doi.org/10.1016/j.carbon.2008.07.023>.

⁷³ Agnihotri S., et al. "Theoretical and experimental investigation of morphology and temperature effects on adsorption of organic vapors in single-walled carbon nanotubes." *The journal of physical chemistry B*, 110.15 (2006) 7640-7647. <https://doi.org/10.1021/jp060040a>.

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Table 3. Summarized properties of CNTs.⁷⁴

Electrical transport	
Maximum current density	10^{13} A/m
Conductance quantization	$n \times (12.9 \text{ k}\Omega)^{-1}$
Resistivity	$10^{-4} \text{ }\Omega\text{cm}$
Optical gap	
For (n, m); n-m is divisible by 3 [Metallic]	0eV
For (n, m); n-m is not divisible by 3 [Semi-Conducting]	~0.5eV
Thermal transport	
Thermal conductivity (298K)	~2000W/mK
Phonon mean free path	~100 nm
Relaxation time	10 ps
Elastic behavior	
Young's modulus (SWNT)	~1 TPa
Young's modulus (MWNT)	1.28 TPa
Maximum tensile strength	30 GPa

2.4.2 Methods of Synthesis

There are several synthesis methods for CNTs, as illustrated in Figure 11. The most common methods are chemical vapor deposition, laser ablation, and arc discharge. Then, the other method that has recently been used is the microwave irradiation method. Generally, all these methods have varying or specified reaction parameters, such as the atmosphere of reactions, temperature, time, and heat source. Each method has its advantages and disadvantages regarding production, as well as the quality of the CNTs formed. Laser ablation refers to a technique in which a material is broken down into its microfeatures using a laser beam. During the interaction of the laser beam with precursor material, the surface of the material is heated and it vaporizes as the temperature of the laser exceeds the material's boiling point and at times it exceeds the critical temperature. The laser beam continues to heat up the evaporated particles for a while until a plasma plume forms that gradually expands. During the expansion, the plasma cools down and then the catalyst and carbon atoms condense and form CNTs.

In the synthesis of CNTs by CVD, a catalyst is deposited on a substrate and then nucleation of the catalyst is performed via chemical etching (as ammonia) or thermal annealing. The pre-prepared supported material is then placed in a tubular reactor for the growth process.

⁷⁴ See C.H., and Harris A.T. "A review of carbon nanotube synthesis via fluidized-bed chemical vapor deposition." *Industrial & engineering chemistry research*, 46.4 (2007) 997-1012.
<https://doi.org/10.1021/ie060955b>

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After the reactor/furnace is heated to a sufficient reaction temperature (600–1200 °C), a mixture of hydrocarbon gas (methane, ethylene, acetylene, etc.) and a process gas (hydrogen, nitrogen, argon) is reacted in a reaction chamber over the surface of metal catalysts for a given time period (usually 15–60 min). When decomposition of the carbon precursor takes place, CNTs grow on the catalyst particle in the reactor which is collected from the reactor walls and support surfaces after cooling the system to room temperature. Catalyst particles may stay at the bottom or top of the growing carbon nanotube. Formation of single-walled carbon nanotubes requires the use of a catalyst and usually metal catalyst nanoparticles (e.g. iron-molybdenum alloys, nickel, cobalt, iron, etc.) are used. Ferrocene is a compound that has a dual function, it can act as a carbon source and catalyst because of its chemical structure. When vaporized at temperatures above 400 °C, it decomposes into hydrocarbon (i.e. C₅H₆ and CH₄) and Fe catalyst.

The microwave heating process differs from conventional heating techniques in that it does not depend on high-temperature furnaces, high-energy laser beams or external high-voltage. On the contrary, it is dependent on the inherent microwave absorption characteristics of the catalysts and substrate materials to realize a specific and targeted heating mechanism during the growth of CNTs. Differentiation of the microwave absorption characteristics or penetration depths between the catalyst and substrate can aid in realizing selective heating for the CNTs growth process. Additionally, advantages possessed by the microwave irradiation method over conventional methods include rapid reaction times, environmental and economical friendliness, volumetric heating and ease of manipulation.⁷⁵

The principle behind the growth mechanism of CNTs when using CVD applies to microwave irradiation synthesis. However, the difference in microwave irradiation synthesis is that materials are heated to a high temperature in a short time using high-frequency waves. Dipolar polarization and ionic conduction are the two basic mechanisms that may be used to explain the heating mechanism of microwave irradiation. When microwave radiation is applied to the dipolar molecules or ion molecules of the samples, it becomes sensitive to the electric field and causes the dipolar molecules or ions to rotate in alignment with the electric field. Oscillation and molecular friction that occur during this process impact the dipolar or ion molecules, which heat the samples when it is exposed to microwave radiation.

⁷⁵ Bajpai R., and Wagner HD. "Fast growth of carbon nanotubes using a microwave oven." *Carbon*, 82 (2015) 327-336. <https://doi.org/10.1016/j.carbon.2014.10.077>.

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The growth mechanisms of CNTs have been a subject of debate, however, to date only two mechanisms have been widely accepted and can be summed up as follows. Initial contact of a hydrocarbon vapor with heated metal nanoparticles results in decomposition of the vapor into carbon and hydrogen. The carbon produced is then dissolved into the metal catalyst while the hydrogen gas produced departs with the reducing or carrier gas. Decomposition of hydrocarbons is exothermic and therefore results in a temperature increase. As the temperature reaches the metal's carbon solubility limit, the formation of CNTs occurs as a result of precipitation and crystallization of decomposed carbon particles. Crystallization of carbon particles is an endothermic process and therefore the process of formation of CNTs is continued due to this thermal gradient. Existence of two growth mechanisms of CNTs stems from the difference in the interaction between the substrate and the catalyst. The catalyst can either interact weakly or strongly with the substrate. In cases where the catalyst interacts weakly with the substrate, carbon derived from the decomposed hydrocarbon disseminates from the top of the metal catalyst to the bottom and then precipitates between the metal catalyst and the substrate thus fostering the growth of the whole metal catalyst nanoparticles. Growth ceases as soon as the metal nanoparticles are completely engulfed by the excess carbon. This growth mechanism is regarded as tip-growth. Conversely, in cases where the catalyst strongly interacts with the substrate, carbon derived from decomposed hydrocarbon precipitates without pushing up the metal particles. This forces the carbon particles to precipitate from the top of the metal. This growth mechanism is referred to as the root growth or the basic growth model.

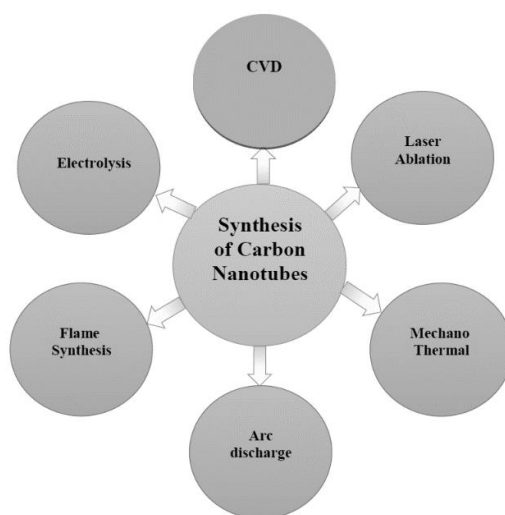


Figure 11. Common synthesis techniques for CNTs.⁷⁶

⁷⁶ Mirabootalebi S.O., and Akbari G. "Methods for synthesis of carbon nanotubes—review." *International journal of bio-Inorganic Hybrid nanomaterial*, 6.2 (2017) 49-57.

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2.5 Functionalization of carbonaceous materials

The industrial revolution and population growth have brought about the accumulation of pollutants in water and air. This has left researchers with the objective of developing efficient adsorbents with improved adsorption capacities for a wide range of pollutants in order to reduce rising pollution. Nowadays, enormous efforts have been carried out to innovate or modify currently used carbonaceous materials in water treatment systems. Various modification strategies have been implemented for activated carbon as it is one of the most widely used adsorbents in wastewater treatment. These modification strategies (Figure 12) involve biological, chemical and physical treatment of activated carbon to enhance its adsorption capacity and affinity for certain contaminants. These methods continue to be extensively investigated to determine which is more efficient in modifying activated carbon.⁷⁷ To date, chemical modification has been reported as the best strategy for the modification of activated carbon for the adsorption of heavy metals and organic compounds such as dyes.⁷⁸

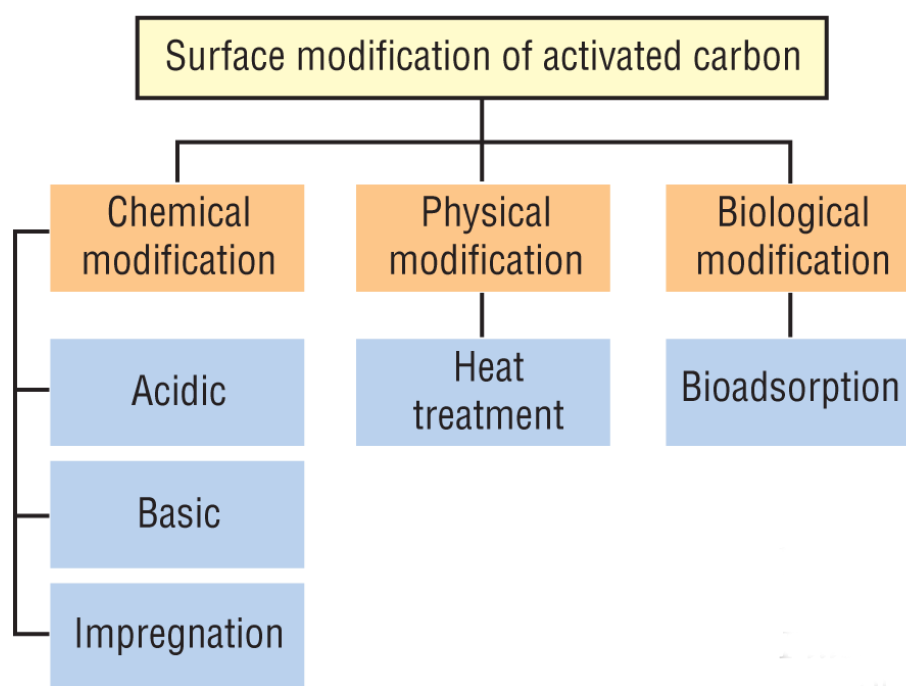


Figure 12. Surface modification strategies for activated carbon.

⁷⁷ Rivera-Utrilla J., et al. "Activated carbon modifications to enhance its water treatment applications. An overview." *Journal of hazardous materials*, 187.1-3 (2011) 1-23.
<https://doi.org/10.1016/j.jhazmat.2011.01.033>.

⁷⁸ Sultana M., et al. "A review on experimental chemically modified activated carbon to enhance dye and heavy metals adsorption." *Cleaner engineering and technology*, 6 (2022) 100382.
<https://doi.org/10.1016/j.clet.2021.100382>.

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Physical modification is performed through thermal heating of the adsorbent material. One of the major drawbacks of the physical modification strategy is the use of extremely high temperatures which results in the loss of functional groups that are thermally unstable. This reduces the chelation of metal species and thus only a few metal ions can be adsorbed on the modified activated carbon. Biological modification involves the immobilization of microorganisms to activated carbon. When biologically modified activated carbon is applied to wastewater treatment, the microorganism converts the organic contaminants to carbon dioxide and waste products. The disadvantage of this strategy is that the thick biofilm that forms could cause strenuousness in the diffusion of the adsorbate to the sites of adsorption, therefore lowering the adsorption rate. Chemical modifications include the treatment of activated carbon either through impregnation or acid-base treatment. Acid treatment augments the acidic functional groups on activated carbon and thus enhances its ability to chelate with heavy metals, while on the contrary, alkali treatment improves the adsorption of organic compounds onto activated carbon.^{79,80} Chemical impregnation refers to filling or loading of activated carbon with suitable chemicals that will boost its adsorption capacity.⁸¹

For modification of graphite, graphene and carbon nanotubes, the methods commonly used are categorized into mixed or filled carbon nanomaterials, electron-donating grafted carbon nanomaterials and magnetic carbon nanomaterials.⁸² The mixed or filled method involves the addition of different adsorbents, each with different strengths and weaknesses, together in a proper way to form a new adsorbent with enhanced superior performance than the individual adsorbents. Additionally, the dispersion of active fillers (e.g. biomass, polymers and metal oxides) to the matrix of the adsorbents is a helpful strategy to improve chemical stability and mechanical strength. For example, polyethylenimine-modified magnetic graphene oxide nanocomposites were used by Sui *et al* for the removal of copper ions in an aqueous solution.⁸³ Then, the grafting of electron-donating groups (like chlorine, sulfur, oxygen and nitrogen-containing groups) to the carbon nanomaterials is also another method

⁷⁹ Jia Y.F., and Thomas K.M. "Adsorption of cadmium ions on oxygen surface sites in activated carbon." *Langmuir*, 16.3 (2000) 1114-1122. <https://doi.org/10.1021/la990436w>.

⁸⁰ Przepiórski J. "Enhanced adsorption of phenol from water by ammonia-treated activated carbon." *Journal of hazardous materials*, 135.1-3 (2006) 453-456. <https://doi.org/10.1016/j.jhazmat.2005.12.004>.

⁸¹ Adhoum N., and Lotfi M. "Removal of phthalate on modified activated carbon: application to the treatment of industrial wastewater." *Separation and purification technology*, 38.3 (2004) 233-239. <https://doi.org/10.1016/j.seppur.2003.11.011>.

⁸² Yu G., et al. "Carbon nanotubes, graphene, and their derivatives for heavy metal removal." *Advanced composites and hybrid materials*, 1 (2018) 56-78. <https://doi.org/10.1007/s42114-017-0004-3>.

⁸³ Sui N., et al. "Polyethylenimine modified magnetic graphene oxide nanocomposites for Cu 2+ removal." *RSC advances*, 5.1 (2015) 746-752. <https://doi.org/10.1039/C4RA11669K>.

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effective for enhancement of heavy metal ions adsorption ability. Because the grafted atoms are more hydrophilic than carbon atoms, this method also optimizes carbon dispersions in water. According to Tan *et al* lone pair electrons in amine groups are attracted to heavy metal ions, so they aminated graphene oxide using L-tryptophan to examine its removal of Pb(II) and Cu(II).⁸⁴ The adsorption capacity of the material was greatly enhanced. The other method mentioned above for modifying graphite, graphene and carbon nanotubes, is the incorporation of magnetic materials. The magnetic materials commonly used include Fe₃O₄, MFe₂O₄ (M = Mn, Ni, Cu, Co, Mg, Zn, etc.) and γ -Fe₂O₃.^{85,86} Cobalt ferrite/MWCNT magnetic hybrids were synthesized by Tan *et al*, using a hydrothermal method; pore volume, surface area and adsorption capacity were larger than those of CoFe₂O₄.⁸⁷

These magnetic materials usually not only improve adsorption ability but also facilitate adsorbent recovery. Adsorption, desorption, and recovery are the main steps in the removal of metal ions and organic compounds from wastewater. In practical applications, an adsorbent must be capable of regeneration. During regeneration, the adsorbent is prepared for the next adsorption cycle by desorbing the adsorbed adsorbate/analyte from the surface. Regeneration of adsorbents can be accomplished using a variety of techniques, such as acid-base treatment, hot gas purging, conductive heating, solvent extraction and hybrid methods.^{88,89} However, among these techniques, some have numerous disadvantages, for instance, some are time-consuming, while operations require the use of tremendous amounts of energy, whereas others cause irreversible modifications to the physical, chemical and structural attributes of adsorbents. In this regard, regeneration conditions such as pressure, time, humidity, temperature, etc. play a crucial role, especially for analytes that show enhanced affinity toward

⁸⁴ Tan M., et al. "Enhancing sorption capacities for copper (II) and lead (II) under weakly acidic conditions by L-tryptophan-functionalized graphene oxide." *Journal of chemical & engineering data*, 60.5 (2015) 1469-1475. <https://doi.org/10.1021/acs.jced.5b00015>.

⁸⁵ Xiong Y., et al. "Synthesis of magnetic porous γ -Fe₂O₃/C@ HKUST-1 composites for efficient removal of dyes and heavy metal ions from aqueous solution." *RSC advances*, 5.7 (2015) 5164-5172. <https://doi.org/10.1039/C4RA12468E>.

⁸⁶ Santhosh C., et al. "CoFe₂O₄ and NiFe₂O₄@ graphene adsorbents for heavy metal ions—kinetic and thermodynamic analysis." *Rsc advances*, 5.37 (2015) 28965-28972. <https://doi.org/10.1039/C5RA02905H>.

⁸⁷ Tan L., et al. "Removal of uranium (VI) ions from aqueous solution by magnetic cobalt ferrite/multiwalled carbon nanotubes composites." *Chemical engineering journal*, 273 (2015) 307-315. <https://doi.org/10.1016/j.cej.2015.01.110>.

⁸⁸ Fayaz M., et al. "Using microwave heating to improve the desorption efficiency of high molecular weight VOC from beaded activated carbon." *Environmental science & technology*, 49.7 (2015) 4536-4542. <https://doi.org/10.1021/es505953c>.

⁸⁹ Faccini, Johanna, Shelir Ebrahimi, and Deborah J.R. "Regeneration of a perchlorate-exhausted highly selective ion exchange resin: Kinetics study of adsorption and desorption processes." *Separation and purification technology*, 158 (2016) 266-274. <https://doi.org/10.1016/j.seppur.2015.12.019>.

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the adsorbent. Tan *et al* reported that it was easy to separate $\text{CoFe}_2\text{O}_4/\text{MWCNTs}$ from the solution that was loaded with U(VI) by using a magnet.

This study aimed to modify some carbonaceous nanomaterials and to examine its adsorption capacity and percentage removal efficiency for various inorganic and organic compounds, using Bloemfontein tap water as point of reference. Based on the wide range of organic compounds and heavy metals found in tap water, for the organic compounds, the study focused on removal of atrazine and fluconazole, while for heavy metals, the focus was on removal of Pb(II) , Ni(II) and Hg(II) . Various characterization methods were used to determine the morphological characteristics of the modified carbonaceous nanomaterials.

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3.1. Chemicals

Activated carbon (99.997%), adipic acid (99%), graphite, methanol, sulfuric acid (H_2SO_4 , 98%), fuming nitric acid (98%), 55% nitric acid (HNO_3), hydrochloric acid (HCl , 32%), hydrogen peroxide (H_2O_2 , 99.9%), dimethylformamide (DMF), ferrocene (98%), dichloromethane (DCM), potassium chlorate (KClO_4 , 99%), ammonium formate (99.995%), lead nitrate ($\text{Pb}(\text{NO}_3)_2$, 99.5%), nickel sulfate hexahydrate ($\text{NiSO}_4(\text{H}_2\text{O})_6$, 99.999%) and mercury acetate ($\text{Hg}(\text{OAc})_2$, 98.0%) – all chemicals used in this study were used without further purification.

3.2 Preparation of carbon nanotubes through microwave irradiation, using the method by Algadri N.A *et al*⁹⁰

Different graphite/ferrocene powder mixture ratios (70:30, 50:50, 40:60 and 80:20) were prepared by firstly dissolving ferrocene in dichloromethane (5 mL) followed by addition of graphite powder to the solution. The mixture was stirred for 2 mins to ensure complete and homogeneous mixing of graphite and ferrocene and then left to stand, allowing evaporation of dichloromethane to obtain a dry uniform mixture of powders. Uniform mixing of the graphite/ferrocene mixture enabled microwave heat to be distributed homogeneously at each point of the mixture. The step-by-step procedure of the synthesis is illustrated in Figure 13. The microwave irradiation procedure was performed using a 700 W domestic microwave oven operating at 2.45 GHz. The mixture was placed in the microwave oven and the timer set at 30 s. The microwave heating procedure was stopped when a pop-up flame was observed. The various microwave irradiation times are listed in Table 4.

⁹⁰ Algadri N.A., et al. "Cost-effective single-step carbon nanotube synthesis using microwave oven." *Materials research express*, 4.8 (2017) 085602. <https://doi.org/10.1088/2053-1591/aa817b>.

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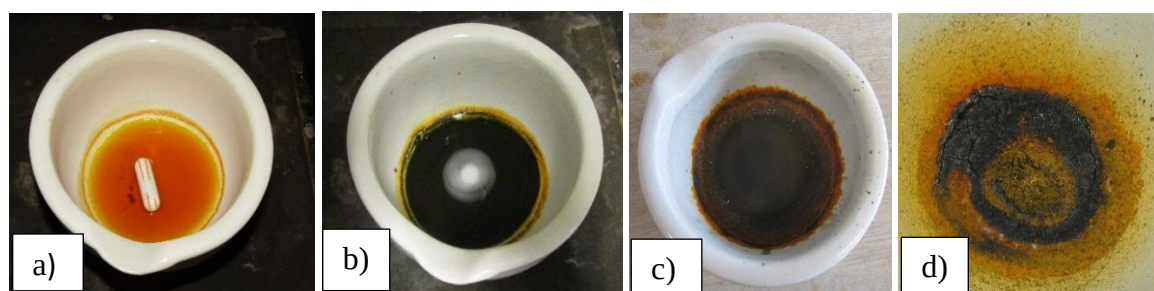


Figure 13. a) Ferrocene solution in DCM, b) stirring mixture of graphite and ferrocene in DCM, c) mixture after evaporation of DCM and d) reaction product after irradiation.

Table 4. Graphite/ferrocene mixture masses and microwave irradiation times.

Mixture	Graphite (mg)	Ferrocene (mg)	Time (s)
1	700	300	15
2	600	400	10
3	800	200	15
4	500	500	20
5	400	600	20

3.3 Preparation of graphene from fine graphite powder using various methods

3.3.1. Preparation of graphene using the method by Al-Hazmi *et al*⁹¹

A solution of adipic acid was prepared by dissolving adipic acid powder (4.0 g) in water (50 mL). The solution was stirred and heated for 2 mins to ensure complete dissociation of adipic acid. The solution was cooled down after which graphite powder (5.0 g) was immersed into the acid (30 mL) and left in the fridge overnight. The graphite powder was filtered and then left to stand for an hour. The pretreated graphite powder was heated at 700 °C for 1 min to expand the interlayer spacing between the graphite layers. The expanded graphite powder (499.7 mg) was dispersed in methanol (50 mL) and sonicated for 10 min to ensure complete dispersion of pretreated graphite in the methanol solution. The graphite solution was then introduced into a Teflon autoclave and put into a microwave oven set at 200 °C and the solution was heated for 40 mins. After that, the reaction was terminated by cooling down the Teflon autoclave. The resulting solution was centrifuged for 10 mins and the supernatant was

⁹¹ Al-Hazmi F.S., et al. "One pot synthesis of graphene based on microwave-assisted solvothermal technique." *Synthetic metals*, 200 (2015) 54-57. <https://doi.org/10.1016/j.synthmet.2014.12.028>

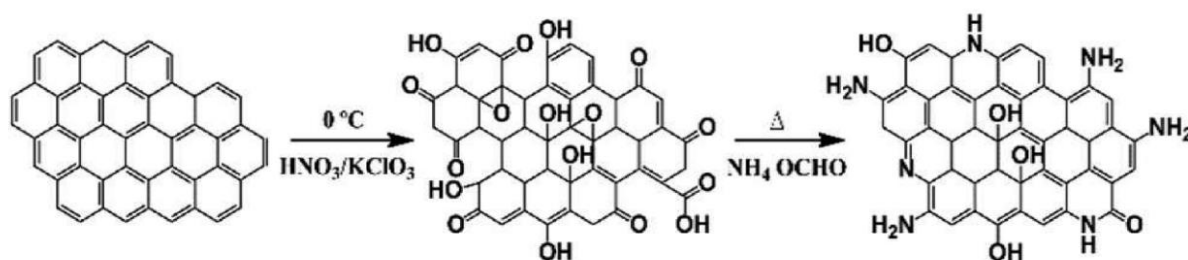
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collected and washed several times with deionized water and HCl (10%). The reaction product was dried in an oven at 70°C. The mass of the black product was 486 mg.

3.3.2 Preparation of graphene using the method by Xin G *et al*⁹²

Graphite powder (1.00 g) was mixed with a 20:1 volume ratio mixture of sulfuric acid (98 %) and hydrogen peroxide (30 %). The mixture was stirred for 1 h and then quenched with 250 mL H₂O. The mixture was filtered and washed with 750 mL H₂O to neutralize the mixture. The filtered graphite powder was heated at 100 °C for 24 h and then microwave irradiated for 10 s. The microwave-irradiated powder was dispersed in DMF (100 mL) and sonicated at 100 W for 5 h and the solution was centrifuged at 5000 rpm for 20 mins, yielding a black powdered product with a mass of 1.2 g.

3.4 Preparation of carboxylated and aminated activated carbon



Scheme 14. Proposed reaction scheme of the carboxylation and amination of activated carbon.⁹³

3.4.1. Carboxylation of activated carbon

Firstly, activated carbon (45 g) was added to fuming nitric acid (100 mL) and placed in a reactor at 0 °C. Then, potassium chlorate (220 g) was slowly added to the mixture and then the mixture was left to react for 22 h. The mixture was poured into cold deionized water (1000 mL), centrifuged at 4000 rpm for 20 min and washed with excess deionized water until a pH of 4.50 was reached. The product was then filtered and dried at 70 °C for 12 h. Finally, the dried product was ground to a thin powder and the mass of the powder was recorded to be 55 g. The product was denoted as AC-COOH.

⁹² Xin G, et al. "A graphene sheet exfoliated with microwave irradiation and interlinked by carbon nanotubes for high-performance transparent flexible electrodes." *Nanotechnology*, 21.40 (2010) 405201.
<http://doi.org/10.1088/0957-4484/21/40/405201>

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3.4.2. Reductive amination of AC-COOH using the Leuckart reaction

The prepared AC-COOH (30 g) was mixed with ammonium formate (150 g) and ground to a fine homogeneous mixture. This mixture was left to react under reflux at 135 °C for 4 h. Afterwards, the reaction mixture was recovered using distilled water. The suspension was centrifuged and washed with abundant deionized water till a pH of 7 was reached. The washed product was then filtered and dried at 70 °C for 12 h. Finally, the dried product was ground to a thin powder and the mass of the powder was recorded to be 14 g. The product was denoted as AC-NH₂.

3.5 Preparation of carboxylated and aminated graphite⁹³

3.5.1. Carboxylation of graphite

Graphite (45 g) was added to fuming nitric acid (100 mL) and placed in a reactor at 0 °C. Then, potassium chlorate (360 g) was slowly added and the mixture was left to react for 22 h. The mixture was then poured into cold deionized water (1000 mL), centrifuged at 4000 rpm for 20 mins and washed with deionized water until a pH of 4.50 was reached. The product was then filtered and dried at 70 °C for 12 h. Finally, the dried product was ground to a thin powder and the mass of the powder was recorded to be 57 g. The product was denoted as G-COOH.

3.5.2. Reductive Amination of G-COOH by Leuckart reaction

The prepared graphite oxide (50 g) was mixed with ammonium formate (225 g) and ground to a fine homogeneous mixture. The mixture was left to react under reflux at a temperature of 135 °C for 4 h. Afterwards, the reaction mixture was recovered using distilled water. The suspension was centrifuged and washed with abundant deionized water till a pH of 7 was reached. The washed product was then filtered and dried at 70 °C for 12 h. Finally, the dried product was ground to a thin powder and the mass of the powder was recorded to be 39 g. The product was denoted as G-NH₂.

3.6 Characterization

The shapes and structures of all the materials prepared were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The carbon

⁹³ Aguilar-Bolados H., et al. "Facile and scalable one-step method for amination of graphene using leuckart reaction." *Chemistry of materials*, 29.16 (2017) 6698-6705. <https://doi.org/10.1021/acs.chemmater.7b01438>

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material for scanning electron microscopic examination was mounted on aluminium pin stubs using double sided carbon tape and coated with Iridium (Ir, ± 5 nm) using a Leica EM ACE600 coater (for conductivity). Specimens were imaged using a JEOL JSM-7800F Extreme-resolution Analytical Field Emission SEM. Sample preparation for the TEM was done by dissolving a small amount of the carbon material into ethanol (1 mL) and the solution was ultrasonicated to disperse the material. A drop of the solution was put on a 200 Mesh Thin bar Copper Grid (3.05 mm) and air-dried before analysis. The TEM instrument used was the Philips CM100 Transmission electron microscope (FEI, Netherlands). Determination of carbon and nitrogen content in the adsorbent materials were performed using Leco TruSpec CN elemental analyzer. Energy Dispersive X-ray Spectroscopy (EDS) coupled to SEM was also used for determination of the elements present in the adsorbent materials and at what weight percentages (%wt) of the overall adsorbent.

Organic samples were analysed using an ABSCIEX 4000 QTRAP hybrid triple quadrupole ion trap mass spectrometer with a Shimadzu HPLC stack as a front end. All data acquisition and processing was performed using Analyst 1.5 (AB SCIEX) software. Twenty microliter of each extracted sample was separated on a C18 (150mm x 4.6mm, Gemini NX, Phenomenex) column at a flow rate of 300 μ L/min using a 3 min gradient from, in positive ionisation mode, 5% solvent A ($\text{H}_2\text{O}/0.1\%$ formic acid) to 95% solvent B ($\text{MeOH}/0.1\%$ formic acid). Eluting analytes were ionised by electrospray in the TurboV ion source with 500°C heater temperature to evaporate excess solvent, 30 psi nebuliser gas, 30 psi heater gas and 20 psi curtain gas. The ion spray voltage was set at 5500 V. The targeted analyses of atrazine and fluconazole was performed using 3 MRM (multiple reaction monitoring) transitions shown in Table 5. The peak area on the chromatogram generated from the first and most sensitive transition was used as the quantifier while the second and third transitions are used as a qualifier. The qualifiers serves as an additional level of confirmation for the presence of the analyte, the retention time for these two transitions needs to be the same. The peak areas of the unknown samples were related back to a quantified value using the calibration curve for each analyte, normalised to the peak area of the internal standard.

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Table 5. MRM transitions for atrazine and fluconazole: positive ionization mode.

Q1 mass	Q3 mass	Analyte
216.1	174	Atrazine 1
216.1	68.1	Atrazine 2
216.1	104.1	Atrazine 3
307.1	220	Fluconazole 1
307.1	238.1	Fluconazole 2
307.1	169	Fluconazole 2

Then, analysis of heavy metals was done using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption Spectrophotometer (AAS). The ICP-OES instrument used was the 730 ICP-OES from Agilent technologies. The AAS instrument used was the AA-6300 Shimadzu Double Beam Atomic Absorption Spectrophotometer.

3.7 Water sample collection

A water sample from tap water in the northern suburbs (Waverley) of Bloemfontein was collected. This area's potable water is supplied by the Maselspoort water works, where feed-in water includes both rain water from the Eastern Freestate agricultural area, and illegal wastewater effluents from several towns in the vicinity. The water sample was screened for various organic and inorganic contaminants commonly found in water of the area. The water was also passed through a standard household 6-stadia commercial water filter system (from Water-Pure) and analyzed. Heavy metals were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and organic contaminants by Liquid Chromatography-Mass Spectrometry (LCMS), both before and after filtration through the commercial system.

3.8 Adsorption studies of the heavy metals

Adsorbents: Activated carbon, AC-COOH, AC-NH₂, graphite, G-COOH, G-NH₂

Initial concentrations of 2 ppm for Pb(II), Ni(II) and Hg(II) were prepared individually using Pb(NO₃)₂, NiSO₄·6H₂O and Hg(OAc)₂ respectively. Each metal solution was prepared using three different diluents as summarized in Table 6. The adsorption studies were then carried out by adding 10 mg of each adsorbent to 20 mL of each metal solution. Then, each mixture was stirred at 800 rpm for 30 mins at a constant temperature of 25 °C. Afterwards, the suspensions were separated from the solutions by filtration and the filtrates were collected and

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analyzed by Atomic Absorption Spectrophotometer. The adsorption removal efficiency of each adsorbent was calculated from the expression below;

$$\% \text{ Removal efficiency} = \frac{\text{Initial concentration} - \text{final concentration}}{\text{Initial concentration}} \times 100\%$$

Table 6. Summary of metal solutions prepared using different diluents.

<i>Diluent</i>	<i>Pb(II) (ppm)</i>	<i>Ni(II) (ppm)</i>	<i>Hg(II) (ppm)</i>
5% <i>HNO</i> ₃	2	2	2
<i>H</i> ₂ <i>O</i>	2	2	2
0.1 M <i>NH</i> ₃		2	2

Pb²⁺ ions do not dissolve in 0.1 M NH₃ because NH₃ forms complex ions with Pb²⁺ forming insoluble Pb(OH)₂.

3.9 Regeneration of the spent carbonaceous materials⁹⁴

The method used was adapted from Da'na and Awatif. The regeneration method was done by stirring 5 mg of the spent carbonaceous material with 20 mL HCl (1 M) solution at 25 °C for 1 h. The material was then filtered and thoroughly rinsed with abundant deionized water. Additionally, the material was neutralized with 20 mL NaOH (0.1 M) for 1 h and subsequently rinsed with abundant deionized water. The carbon material was then filtered and dried at 70 °C for 6 h. The adsorption process was then repeated using the dried material.

3.10 Adsorption studies of the organic pollutants

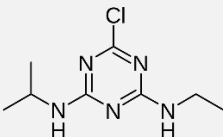
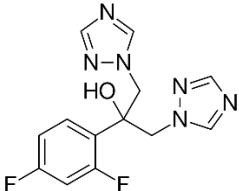
Adsorbents: Activated carbon, AC-COOH, AC-NH₂, graphite, G-COOH, G-NH₂

Stock solutions of 1000 ppm atrazine and fluconazole were prepared. The stock solutions were diluted using deionized water to prepare concentrations of 0.1, 0.2, 0.4, 1 and 10 ppm of each organic pollutant. 20 mL of each organic solution was added to 10 mg of each adsorbent separately and the mixtures were stirred for 30 mins at 800 rpm at room temperature. The adsorbents were then separated by filtration and the filtrates were collected, labeled and analyzed by using LCMS.

⁹⁴ Da'na E., and Awatif A. "Regeneration of spent activated carbon obtained from home filtration system and applying it for heavy metals adsorption." *Journal of environmental chemical engineering*, 5.4 (2017) 3091-3099. <https://doi.org/10.1016/j.jece.2017.06.022>.

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Table 7. Chemical structures and concentrations of stock solutions of organic pollutants.

Organic pollutant	Chemical structure	Stock concentration (ppm)
Atrazine		1000
Fluconazole		1000

3.11 Regeneration of the spent carbonaceous material^{95,96}

The method was adapted from Sirajudheen *et al* and Ghosh *et al*. The regeneration of the adsorbents was carried out in two steps. Firstly, 5 mg of the used adsorbents were each mixed with a solution of 20 mL NaOH (0.1 M) and then stirred for 30 mins. The suspensions were filtered and washed abundantly with deionized water. The adsorbents were then separated and filtered from the solution of deionized water. Secondly, methanol (20 mL) was added to each filtered adsorbent and the mixtures were stirred at 800 rpm for 2 h at 25°C. Following that, the adsorbents were filtered and dried in an oven at 100 °C for 12 h. The adsorption process was repeated using the dried adsorbent.

⁹⁵ Sirajudheen P., et al. "Magnetic carbon-biomass from the seeds of *Moringa oleifera*@ MnFe₂O₄ composite as an effective and recyclable adsorbent for the removal of organic pollutants from water." *Journal of molecular liquids*, 327 (2021) 114829. <https://doi.org/10.1016/j.molliq.2020.114829>.

⁹⁶ Ghosh K.P., Ligy P., and Bandyopadhyay M. "Management of Atrazine bearing wastewater using an upflow anaerobic sludge blanket reactor–adsorption system." *Practice periodical of hazardous, toxic, and radioactive waste management*, 9.2 (2005) 112-121.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The purpose of this study was to compare relative efficiencies of various carbonaceous nanomaterials to remove both inorganic and organic contaminants from water that is otherwise intended for human use. Selected actual organic contaminants were atrazine and fluconazole, and inorganic heavy metals were Pb(II), Ni(II) and Hg(II) salts. The carbonaceous nanomaterials that were selected were carbon nanotubes and graphene, which were synthesized as part of this project, using graphite as precursor. The method of synthesis for preparation of both carbon nanotubes and graphene was microwave irradiation chosen because of advantages it possesses over conventional methods as mentioned in Chapter 2. However, added synthesis costs of these compounds resulted in rather selecting off-the-shelf activated carbon and graphite – as is – for the present study. The final aim for this ongoing investigation is to allow accessibility to the general public and poorer communities. In addition then, graphite and activated carbon were further functionalized to investigate the effect of modification on its removal efficiency for various organic and inorganic contaminants.

4.2 SEM/TEM characterization of carbon nanotubes

During preparation of CNTs the irradiated mixture of graphite and ferrocene had a visual occurrence of an electric spark on the surface of the mixture due to generation of a plasma environment with temperatures exceeding 1000 °C. During the irradiation process, ferrocene is decomposed into iron nanoparticles resulting in rapid temperature increase of the mixture in seconds, causing a very fast reaction that leads to the formation of CNTs. The formed iron nanoparticles serve as catalytic centers for the growth of CNTs. Additionally, during the microwave irradiation process, ferrocene also decomposes into hydrocarbons which serve as primary carbon source. Formation or growth of CNTs can occur *via* two pathways; depending on the type of microwave absorber used, either a medium growth or direct growth pathway may ensue. For this study, graphite powder was used as microwave absorber, due to its ability to adequately absorb microwaves and produce enough heat to achieve high surface temperatures, thereby triggering growth of CNTs. The formation of CNTs in this case therefore follows the direct growth pathway.

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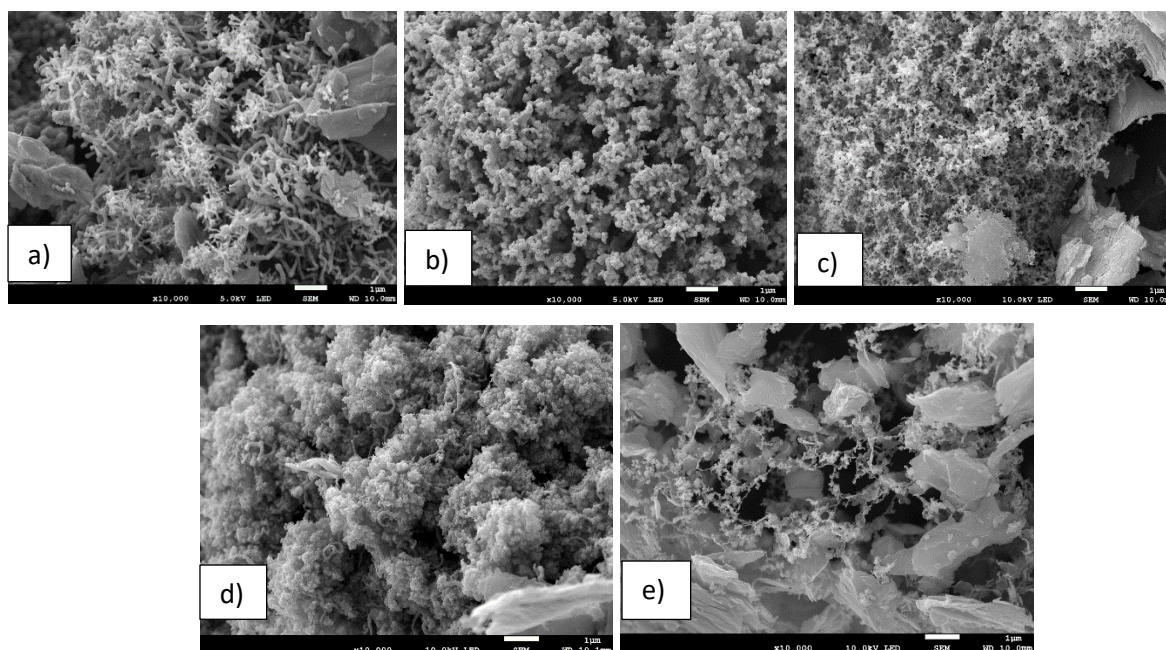


Figure 15. SEM images of CNTs prepared through microwave irradiation of various graphite: ferrocene mixture ratios, a) 7:3 (1 μm), b) 1:1 (1 μm), c) 8:2 (1 μm), d) 6:4 (1 μm) and e) 4:6 (1 μm).

Figure 15 shows SEM images of the prepared CNTs using various mixture ratios of graphite and ferrocene. Confirmation of successful preparation of CNTs is observed in the appearance of highly agglomerated stacked hollow bundles, eg. the fine white structures in the images. However, the degree of formation of CNTs differs per mix ratio. By close inspection of the images in Figure 15 (a-e), the mix ratios producing highest yields of well defined CNTs, are 7:3 and 1:1, of which the products are seen in Figure 15a & c. The observation for 7:3 is consistent with that reported by Algadri *et al.*⁹⁰ The CNTs prepared from the 7:3 product of graphite : ferrocene was further examined by TEM as to analyze its internal structure, see Figure 16. From the observation of the image, it is seen that the growth of the CNTs indeed occurs from the iron nanoparticles generated during the decomposition of ferrocene. The iron nanoparticles are represented by the dark spheres contained or embedded within the CNTs. The formed CNTs are multi-walled (MWCNT) as confirmed by the thickness of the walls.

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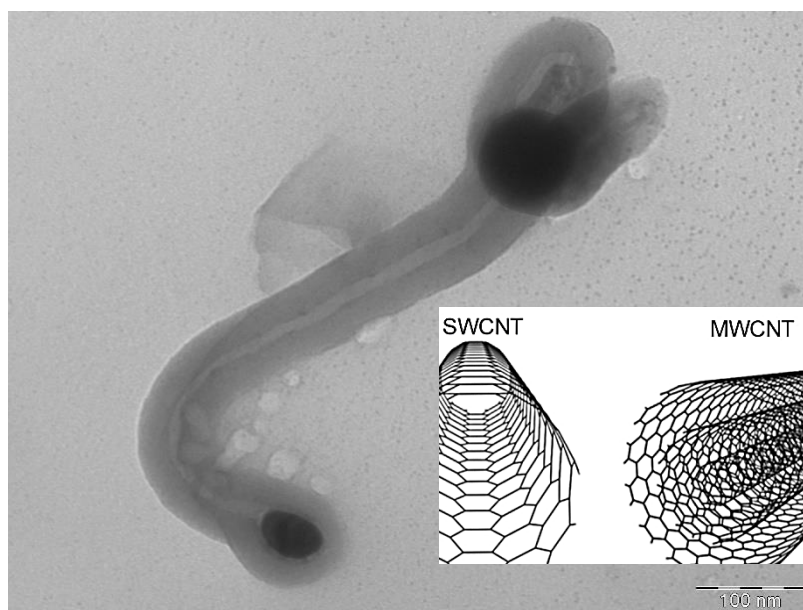


Figure 16. TEM image of the CNTs prepared from graphite:ferrocene 7:3 mixture ratio (100 nm). *Insert:* Left: single walled carbon nanotubes. Right: multiwalled carbon nanotubes.

4.3 TEM characterization of graphene

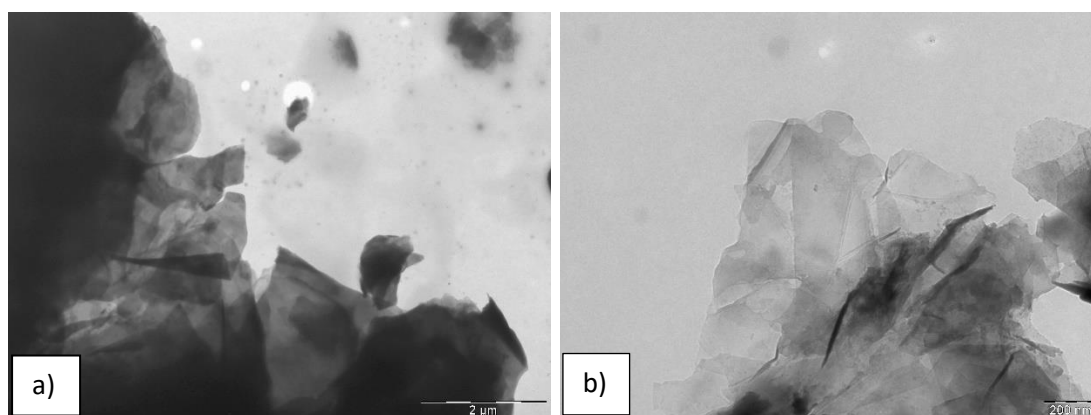


Figure 17. SEM images of the graphene prepared sheets from methods by a) Al-Hazmi F.S *et al* (2 μm) and b) Xin G *et al* (200 nm).

The morphology and structure of the graphene sheets produced from the method by Xin *et al* and Al-Hazmi were characterized using TEM. Figure 17 shows the TEM images of the obtained graphene sheets. Observation of the obtained graphene using the method by Al-Hazmi *et al*, illustrated by Figure 17a, shows multiple layers of graphene sheets stacked on top of each other. The dark color is due to very low transmittance of light through the sheets, suggesting that the graphite layers were not successfully expanded and exfoliated to form loose graphene sheets. However, observation of the obtained graphene sheets using the method by Xin G *et al* as shown in Figure 17b, shows successful formation of the multilayered graphene

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sheets randomly orientated. The ability of light to transmit through the obtained sheets confirms the success of the exfoliation of graphite to graphene. The successful formation of the graphene sheets through the method by Xin G *et al* could be attributed to the pretreatment of the graphite powder with sulfuric acid and hydrogen peroxide that led to the formation of graphite oxide which subsequently was subjected to microwave irradiation. Microwave irradiation achieves extremely high temperatures over a short period of time, which subjects the graphite oxide to thermal shock. The effect is that gas is released, which push the graphite layers away from each other, leading to the formation of graphene sheets.

Despite successful formation of the graphene sheets, the method by Xin G *et al* has a disadvantage in that the separation of the graphite layers is random and thus the higher possibility of forming graphene sheets with defects. The method by Al-Hazmi *et al* on the contrary offered the use of a less harsh oxidant for separation of the graphite layers by using glutaric acid, which is a dicarboxylic acid. In comparison to the commonly used acids, dicarboxylic acids are considered more efficient in intercalating between the graphite layers due to the occurrence of the two hydroxyl groups on either side of their structure. According to Al-Hazmi *et al*, glutaric acid separates the graphite layer nearly at equal distances. Results obtained in the present study are slightly less successful than those reported by Al-Hazmi *et al*. This is ascribed to the use of adipic acid as a dicarboxylic acid instead of glutaric acid, which appears to be less effective in intercalating the graphite layers.

4.4 SEM and EDX examination of activated carbon and derivatives

Based on the results obtained for CNTs and graphene, as well as consideration of costs of production and purification, the precursor material, graphite, was instead considered for modification through the introduction of oxygen and nitrogen functional groups to its surface structure. Activated carbon was also considered for modification as it is already universally used for water purification. As reported in Chapter 2, both graphite (G) and activated carbon (AC) were initially subjected to carboxylation to introduce oxygen functional groups that may readily coordinate metals. The former was followed by reductive amination, namely to introduce amine groups to the surface of the material. The morphologies and structures of the pristine G and AC materials, together with their functionalized counterparts, were then examined by using SEM.

Figure 19 shows the microstructural features of AC and its functionalized counterparts at various magnifications. Figure 19a illustrates the amorphous structure of AC with highly porous microstructures. On the other hand, the carboxylated AC as illustrated in Figure 19b,

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shows the absence of the highly porous microstructures, possibly indicating that the oxygen groups are situated within the pores of the AC structures. The overall structure of AC changed from an amorphous to uneven, rough and round-like structures. Furthermore, the particle sizes of the AC increased following the introduction of oxygen groups and this can be seen by comparison of the overall structures (500x magnifications) of both the pristine and carboxylated ACs. Oxygen-containing functional groups commonly associated with the oxidation of AC include carbonyls, ether, quinones, anhydrides, phenols, lactones and carboxylic acids as illustrated in Figure 18 below.⁹⁷ The presence of these oxygen-containing groups on the surface of the AC as an adsorbent provides more active sites for adsorption and is thus expected to create an adsorbent with high uptake capacity.⁹⁸

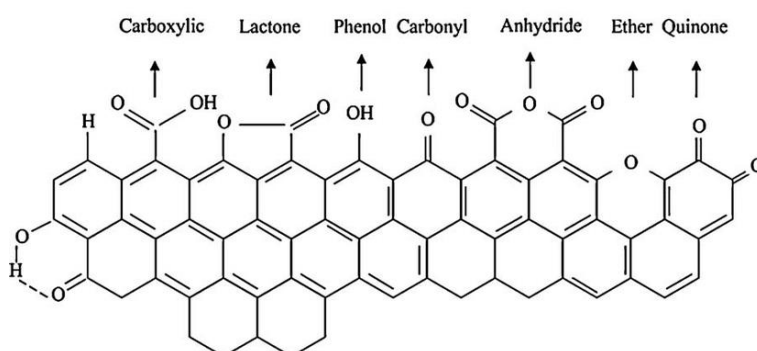


Figure 18. Functional groups commonly associated with oxidation of activated carbon.⁹⁹

Figure 19c illustrates the morphology of the aminated AC, the product of the second synthesis step. By comparing the morphology of the aminated AC with that of the carboxylated AC, it appears that the addition of amines onto the surface of the carboxylated AC further increases AC particle sizes. The overall structure of the aminated AC exhibits relatively larger particles that are uneven, rough and rock-shaped. Leuckart reductive amination involves introduction of amines to carbonyl carbons of aldehydes or ketones by converting the oxygen of the carbonyl group to an amine. Therefore, due to the presence of other oxygen-containing functional groups present on carboxylated AC, the reductive amination is thus expected to only convert ketones to amines. The introduction of amines on the surface of the carboxylated

⁹⁷ Salame I.I., and Teresa J.B. "Surface chemistry of activated carbons: combining the results of temperature-programmed desorption, Boehm, and potentiometric titrations." *Journal of colloid and interface science*, 240.1 (2001) 252-258. <https://doi.org/10.1006/jcis.2001.7596>.

⁹⁸ Mahmoudi E., et al. "Distinguishing characteristics and usability of graphene oxide based on different sources of graphite feedstock." *Journal of colloid and interface science*, 542 (2019) 429-440. <https://doi.org/10.1016/j.jcis.2019.02.023>.

⁹⁹ Shafeeyan, Mohammad Saleh, et al. "A review on surface modification of activated carbon for carbon dioxide adsorption." *Journal of analytical and applied pyrolysis*, 89.2 (2010) 143-151. <https://doi.org/10.1016/j.jaap.2010.07.006>.

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carbon slightly opened up pores filled by oxygen groups, see the middle image (2000x magnification) of Figure 19c.

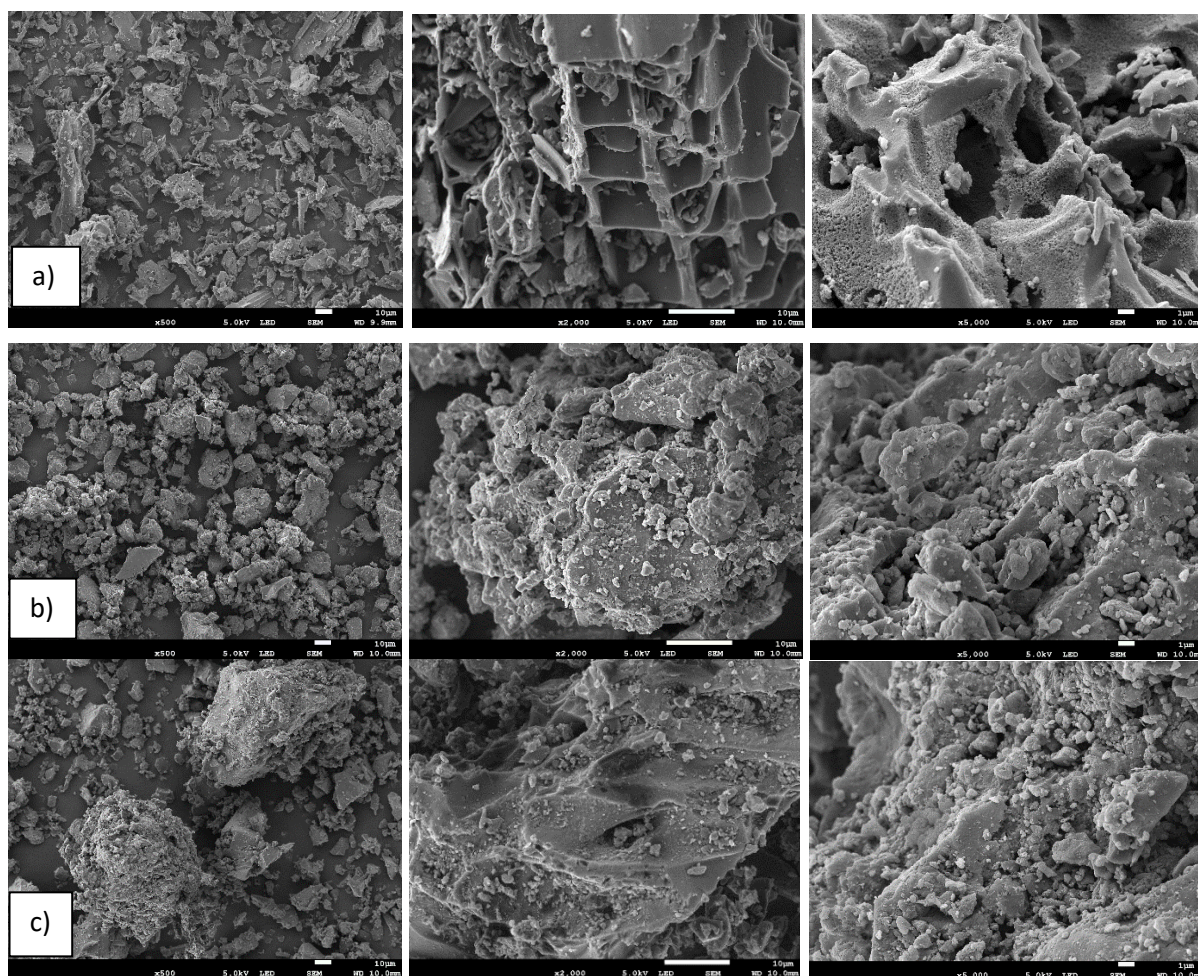


Figure 19. SEM images of a) activated carbon, b) carboxylated activated carbon, and c) aminated activated carbon each at various magnifications [x500 (*left*), x2000 (*middle*) and x500 (*right*)].

EDS elemental mappings together with the EDS spectra of pristine AC, and the carboxylated and aminated ACs are shown in Figures 20 – 22. Analysis of the EDS mapping of pristine AC (Figure 20) shows uniform carbon distribution, as resembled by the red color observed on the surface. The mapping also shows minor spots of oxygen over the carbon surface which is resembled by the green color. Elemental composition of pristine AC before functionalization shows a wt% of carbon at 89.4% and oxygen at 10.6%, which are indicated by data shown at the right top of the EDS spectrum (Figure 20). Post-carboxylation of AC, the wt% of oxygen increased to 27.7% and that of carbon decreased to 68.9%. This suggests successful addition of oxygen functional groups onto the matrix of the AC. EDS elemental

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mapping of the carboxylated AC shows random distribution of oxygen onto the surface of the carbon matrix which, as resembled by the green color (Figure 21).

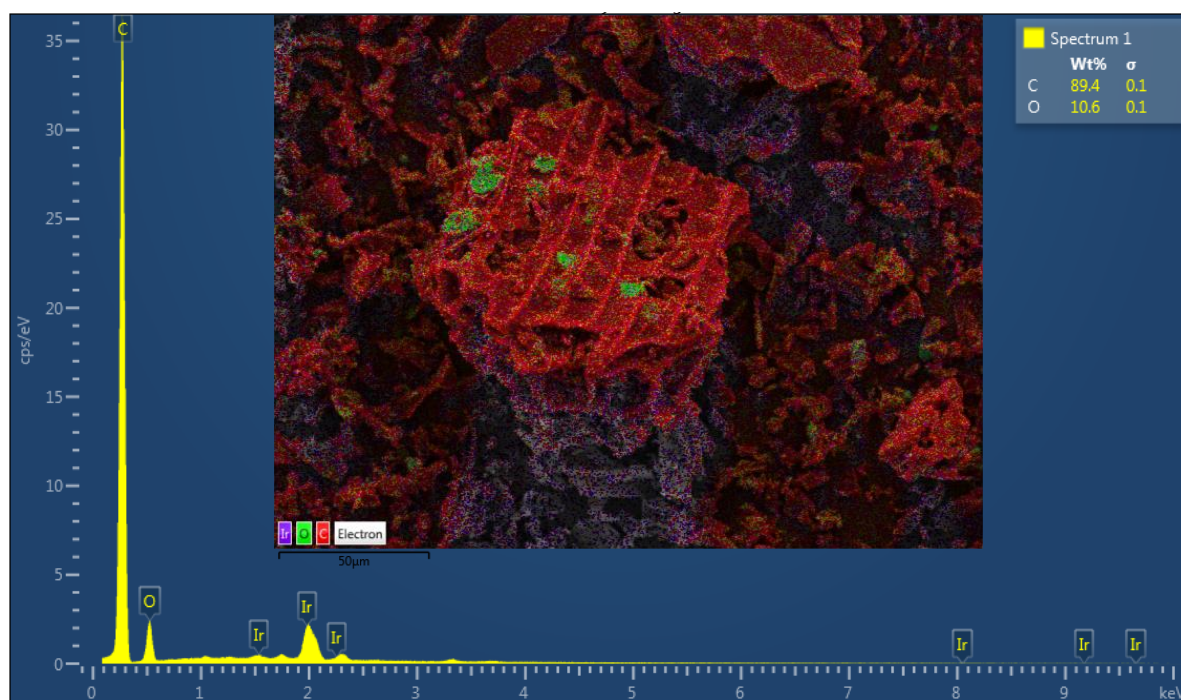


Figure 20. EDS analysis of activated carbon before functionalization.

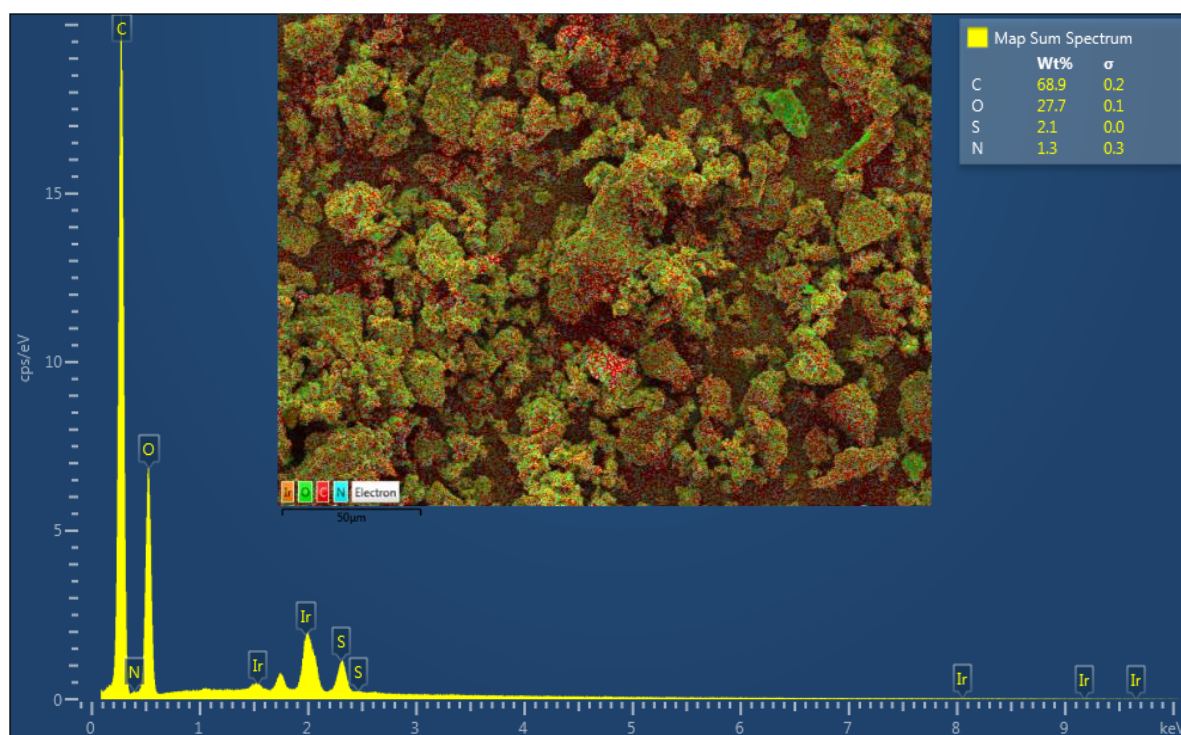


Figure 21. EDS analysis of carboxylated activated carbon.

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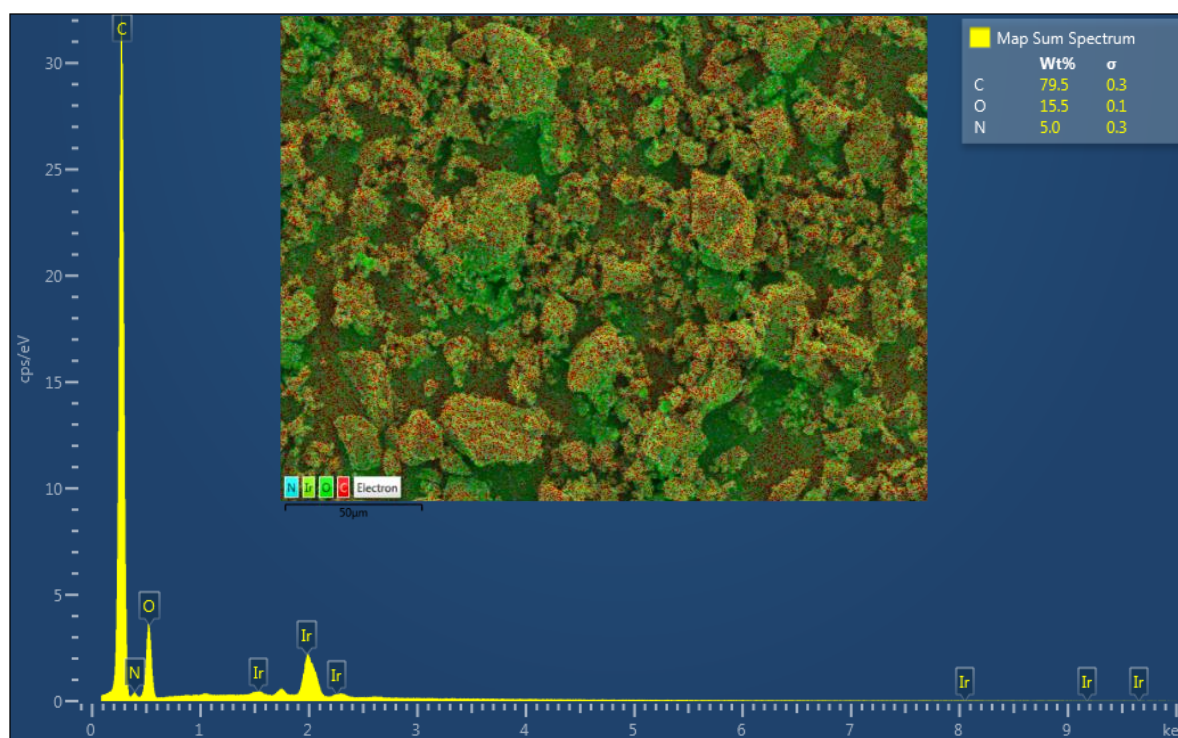


Figure 22. EDS analysis of aminated activated carbon.

Additionally, nitrogen and carbon content in aminated AC were quantitatively determined using the LECO elemental analyzer and the results obtained are shown in Table 8. The carbon and nitrogen content were found to be 75.3 % and 6.0 % respectively. Comparison of the %w of nitrogen and carbon obtained with EDS and the LECO analyzer shows slight differences, being because EDS does not account for the presence of other elements such as hydrogen. Also, the detection limit of the EDS instrument for nitrogen is lower compared to that of the LECO analyzer. In addition, EDS only detects elements that are on the surface of the material while LECO also detects elements embedded within the material. According to Wolfgang, determination of nitrogen content using EDS can produce unreliable data due to most common detector designs for nitrogen producing very weak signal responses, thus causing its detection to be ambiguous for almost all materials, hence the use of the LECO analyzer for this study¹⁰⁰. The degree of amination based on results obtained from the LECO analyzer suggests a successful degree of amination of approximately 6.0 % (w/w) of the total sample mass.

¹⁰⁰ Wolfgang W.J. "Chemical analysis techniques for failure analysis: Part 1, common instrumental methods." *Handbook of Materials Failure Analysis with Case Studies from the Aerospace and Automotive Industries*. Butterworth-Heinemann, (2016) 279-307. <https://doi.org/10.1016/B978-0-12-800950-5.00014-4>.

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Table 8. Weight percentage of nitrogen and carbon content on the aminated activated carbon according to the LECO elemental analyzer.

Sample ID	% N	% C
AC-NH ₂ -rep1	6.0	79.1
AC-NH ₂ -rep2	5.9	79.3
AC-NH ₂ -rep3	6.0	79.4
AVERAGE	6.0	75.3

4.5 SEM and EDX examination of graphite and derivatives

The morphologies of the functionalized graphites, G-COOH and G-NH₂ are shown in the SEM images in Figure 23. Figure 23a shows pristine G at various magnifications and from the images it is apparent that the overall structure of G is discontinuous, however, further magnification of the structure reveals the graphitic nature of G with minor mechanical disruptions due to the inconsistency of the sheets. Figure 23b shows the morphology of G-COOH. The overall surface structure of G-COOH is better developed compared to the overall structure of pristine G. Further magnification into the G-COOH structure shows randomly exfoliated single layers of graphene sheets, suggesting successful exfoliation and separation of the G sheets. Oxidation of G causes the oxidants to intercalate between the G sheets. Subjection of the oxidant-intercalated G to microwave irradiation causes the sheets to separate and form graphene oxide sheets. Common oxygen-containing functional groups associated with oxidation of G to form G-COOH (graphene oxide) include hydroxyl, epoxies, ketones, carbonyls, phenols, lactones, ether and pyrone which are more similar to the groups observed post oxidation of AC.¹⁰¹ These functional groups are depicted in Figure 24. Figure 23c shows the structure of aminated G. The aminated G is seen to have an overall random discontinuous structure more similar to that of pristine G. With increased magnification, the aminated G is seen to have stacked up graphene oxide sheets forming a multilayer structure with random rocky-like structures on the surface of the multilayer structure. This suggests that addition of amine groups to G-COOH leads to reformation of a multilayer structure similar to that of pristine G with minor random structures on the surface.

¹⁰¹ Trusovas R., et al. "Recent advances in laser utilization in the chemical modification of graphene oxide and its applications." *Advanced optical materials*, 4.1 (2016) 37-65.

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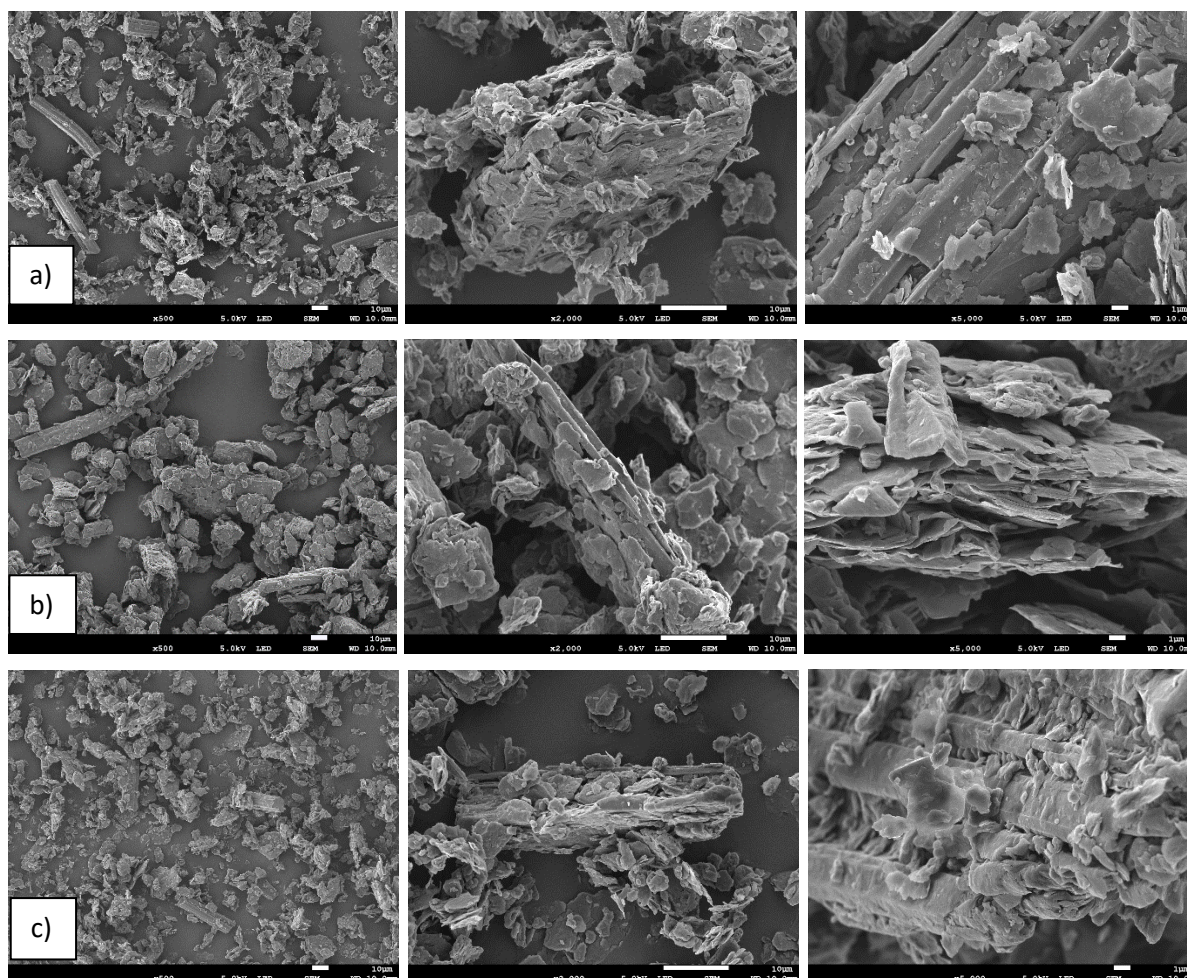


Figure 23. SEM images are a) graphite, b) carboxylated graphite and c) aminated graphite each at various magnifications [x500 (*left*), x2000 (*middle*) and x5000 (*right*)].

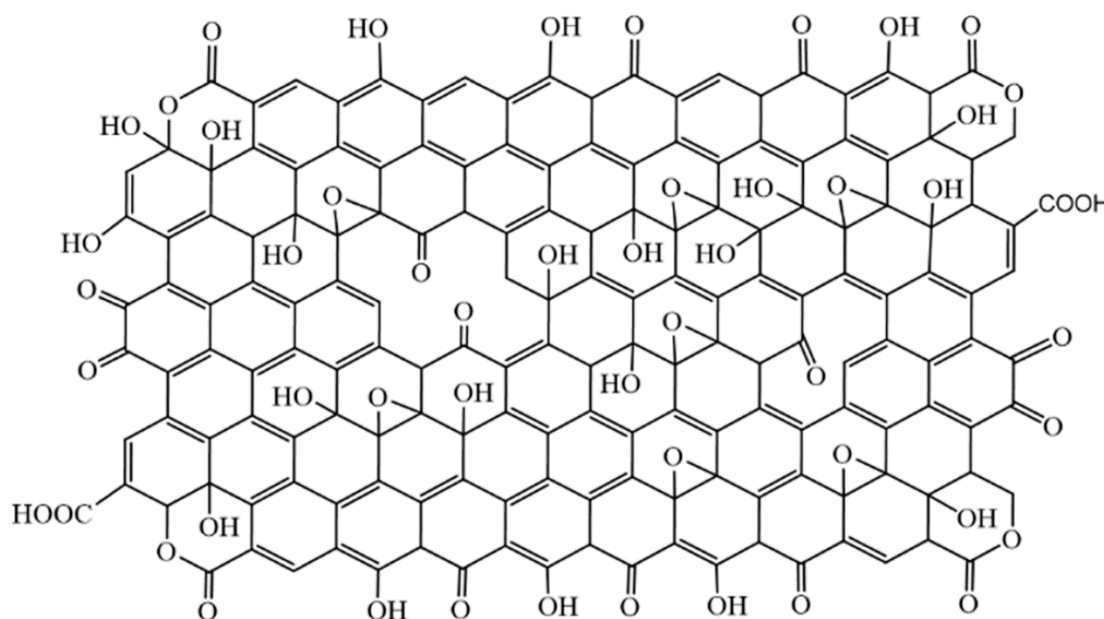


Figure 24. Functional groups associated with oxidation of G.¹⁰¹

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EDS elemental mapping and spectra of pristine G, G-COOH and G-NH₂ are shown in Figures 25 – 27. Analysis of the EDS spectrum of pristine G as illustrated by Figure 25 shows G to be composed of 95.7% and 4.3% carbon and oxygen respectively. Observation of the EDS mapping of pristine G shows a homogeneous distribution of carbon resembled by the red color throughout the surface with an uneven distribution of oxygen onto the carbon surface as resembled by the green color. Then, the EDS spectrum of G-COOH (Figure 26) shows the wt% of carbon at 94.3, oxygen at 4.4, nitrogen at 0.1% and sulfur at 1.2 %. A comparison of the peak heights representing wt% of carbon and oxygen in pristine G to that in G-COOH shows a slight wt% decrease of both carbon and oxygen suggesting a very low degree of oxidation. All the elements composing the G-COOH are unevenly distributed throughout the surface as can be seen from the distribution of the colors on the mapping.

Figure 27 shows the EDS mapping and spectra of G-NH₂. The wt% of carbon, oxygen and nitrogen according to the EDS spectrum is 87 %, 9.5 % and 3.5 % respectively. However, according to results obtained from the LECO analyzer instrument, the wt% of nitrogen and carbon for G-NH₂ are determined as 4.6 and 83.7 respectively (Table 9). Therefore, the degree of amination based on the LECO analyzer is 4.6 % for the aminated G, which is slightly higher than the degree of amination obtained by Aguilar-Bolados *et al.*⁹³

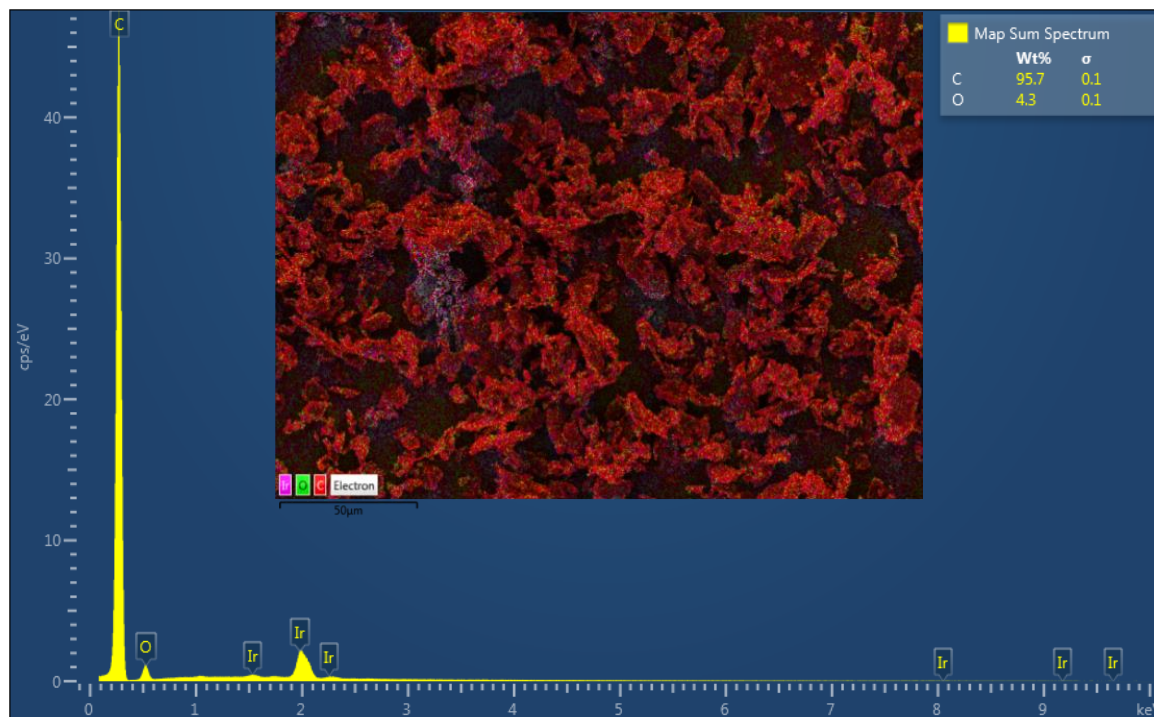


Figure 25. EDS analysis of graphite (G) before functionalization.

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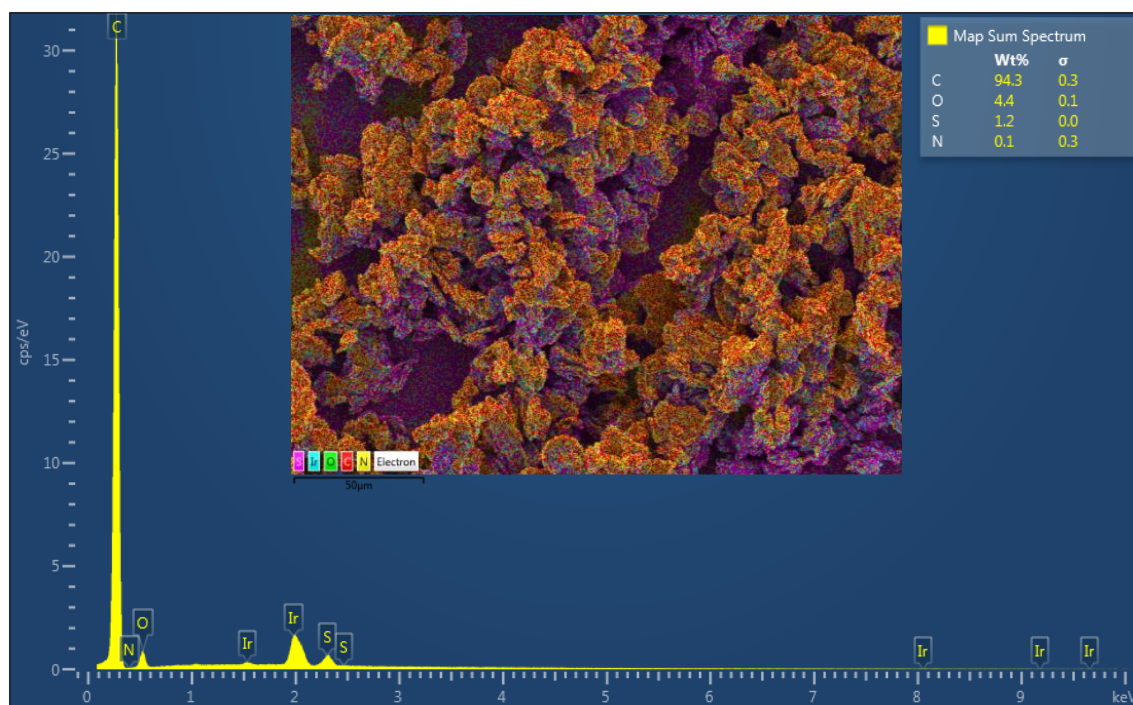


Figure 26. EDS analysis of carboxylated graphite (G-COOH).

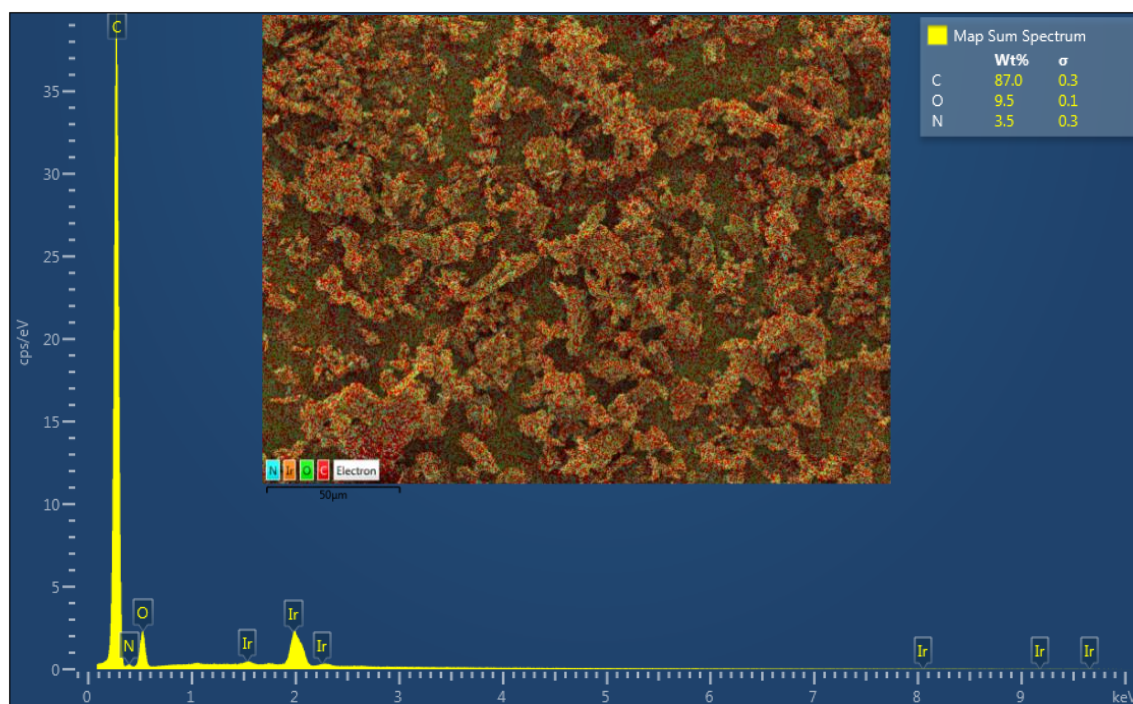


Figure 27. EDS analysis of aminated graphite (G-NH₂).

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Table 9. Percentage weight of nitrogen and carbon content of the aminated graphite according to LECO elemental analyzer.

Sample ID	% N	% C
G-NH ₂ -rep1	4.6	77.7
G-NH ₂ -rep2	4.6	86.2
G-NH ₂ -rep3	4.6	87.1
AVERAGE	4.6	83.7

4.6 Analysis of the collected water sample

The collected water sample was screened for 5 organic contaminants commonly found in the water of the area. The 5 organic pollutants include fluconazole (antifungal drug), metolachlor (herbicide), carbamazepine (anti-epileptic drug), terbuthylazine (herbicide) and atrazine (herbicide). Drugs often typically pass through human bodies, and *via* municipal wastewater end up in groundwater and rivulets. The above herbicides are extensively used by farmers in the area mostly planting maize and sunflower, then being rain- or irrigation-washed into groundwater and rivers that in turn feed water purification plants.

Figure 28 illustrates chromatograms of each contaminant in the water sample before filtration through the standard household 6-stadia commercial water filter system (from Water-Pure). The different colors observed for each contaminant are transitions included to identify or confirm the presence of the contaminant in the sample due to the colors having the same retention time. A transition is a precursor (MS) mass to a fragment mass (MSMS) of the analyte. Therefore, based on the chromatograms, each of the screened contaminants was present in the collected water sample however, at different levels. The y-axes of the chromatograms provide the levels at which the contaminants were present in the water sample. Based on the comparison of the chromatograms, the atrazine level was the highest in the water sample, followed by metolachlor, terbuthylazine, fluconazole and carbamazepine. Figure 29 shows the chromatograms of the contaminants post-filtration. Of all the contaminants, only metolachlor still had detectable levels in the filtered water, however extremely low. The rest of the contaminants were either removed or below the limit of detection of the instrument, suggesting that the commercial filtration system is fully effective in removal of fluconazole, carbamazepine, terbuthylazine and atrazine. The metolachlor concentration was decreased from 43 ppm to 2.9 ppm, thus still a good 93 % decrease.

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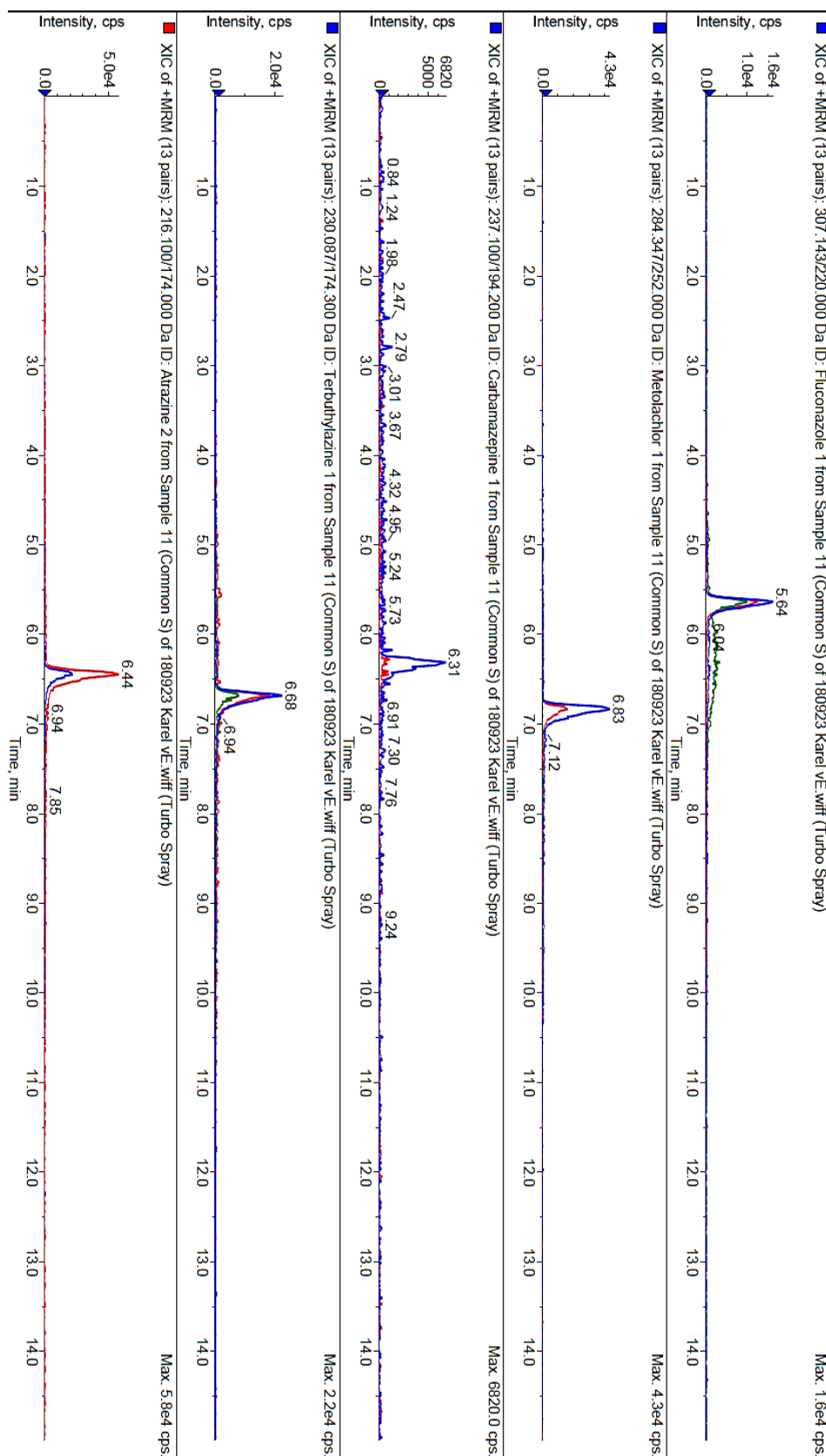


Figure 28. Chromatograms of various contaminants found in tap water collected from Bloemfontein pre-filtration using 6-stadia commercial water filter system. From left to right: atrazine, terbutylazine, carbamazepine, metolachlor and fluconazole.

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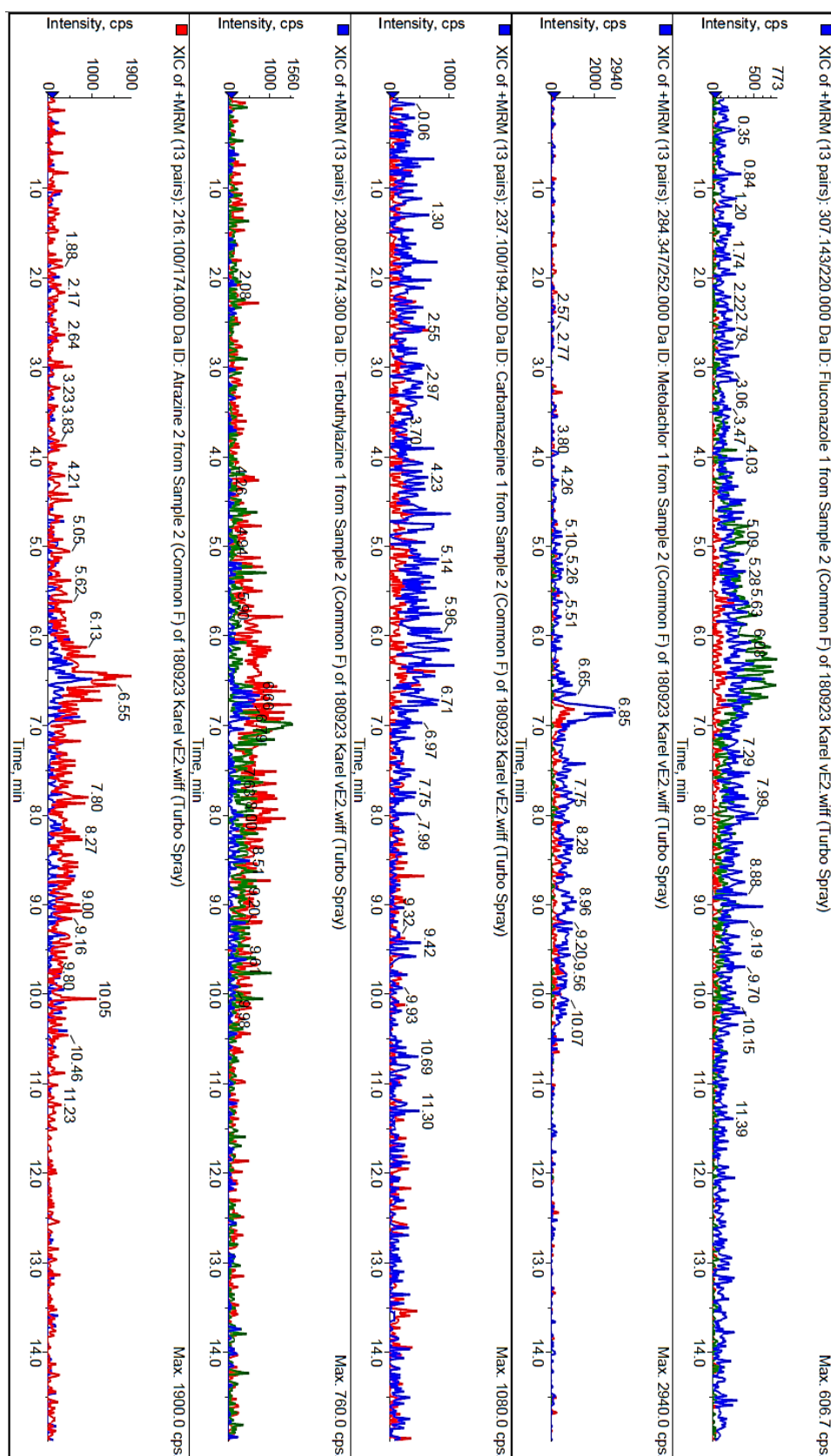


Figure 29. Chromatograms of various contaminants found in tap water collected from Bloemfontein post-filtration using 6-stadia commercial water filter system. From left to right: atrazine, terbuthylazine, carbamazepine, metolachlor and fluconazole.

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Bloemfontein northern suburb tap water originating from the Mangaung municipal waterworks at Maselspoort, was also screened for numerous inorganic contaminants. The chemical report for pre- and post-filtration analyses of the water sample is shown in Table 10. Several heavy metals and anions such as copper, iron, nickel, lead, aluminium, sulphates, nitrates, chloride, fluorides and many others were detected in the water sample at various concentrations before filtration through the commercial water filter system. Post-filtration, concentrations of most of the contaminants were reduced by more than 80 %, while removal of a few others were accomplished at lower percentages only, see Table 10. Based on the obtained results with regard to the removal of both inorganic and organic contaminants, it can be deduced that the commercial water filter system works efficiently.

Despite the efficiency of the stadia filter system, the present study aims to eventually develop filtration systems that may employ less stadia, i.e. for simultaneous removal of both organic and inorganic contaminants. Hence the modification of AC and G materials to determine and compare relative efficiencies of these substrates to remove selected organic and inorganic water contaminants.

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Table 10. Screening chemical report of the water sample for inorganic contaminants pre and post-filtration with the 6-stadia commercial water filter systems (from Water-Pure).

Determinand	Units	Pre-filtration	Post-filtration	Maximum permissible limit by WHO/EPA
pH	pH units	7.34	6.53	
Electrical conductivity	mS/m	54.27	<14.70	
Calcium as Ca	mg/L	38.88	1.23	
Magnesium as Mg	mg/L	20.49	0.35	
Sodium as Na	mg/L	44.11	1.37	
Potassium as K	mg/L	3.23	<1.12	
Alkalinity	mg/L	218.62	11.71	
Fluoride as F	mg/L	0.32	<0.10	
Chloride as Cl	mg/L	54.17	<2.38	
Nitrate as N	mg/L	0.26	0.17	
Sulphate as SO ₄	mg/L	29.17	0.20	
Calcium Hardness	mg/L	97.09	3.06	
Magnesium Hardness	mg/L	84.39	1.44	
Total Hardness as CaCO ₃	mg/L	181.47	4.51	
Total Dissolved Solids	mg/L	410.14	15.63	
Dissolved micro determinants				
Aluminium as Al	ug/L	46	<10	200
Antimony as Sb #	ug/L	<0.065	<0.065	6
Arsenic as As	ug/L	1.246	<0.022	10
Barium as Ba	ug/L	26	<5	2000
Boron as B	ug/L	47	<40	2400
Cadmium as Cd #	ug/L	0.331	0.289	5
Chromium as Cr	ug/L	4.613	2.832	50
Copper as Cu	ug/L	12	<10	1300
Iron as Fe	ug/L	<10	<10	3000
Manganese as Mn	ug/L	23.041	3.083	50
Nickel as Ni	ug/L	2.439	0.322	100
Lead as Pb	ug/L	1.697	1.037	50
Selenium as Se	ug/L	<0.017	<0.017	40
Silicon as Si	ug/L	311	16	Not listed
Uranium as U	ug/L	2.621	0.479	15
Zinc as Zn	ug/L	36	10	50

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4.7 Adsorption and desorption of organic pollutants

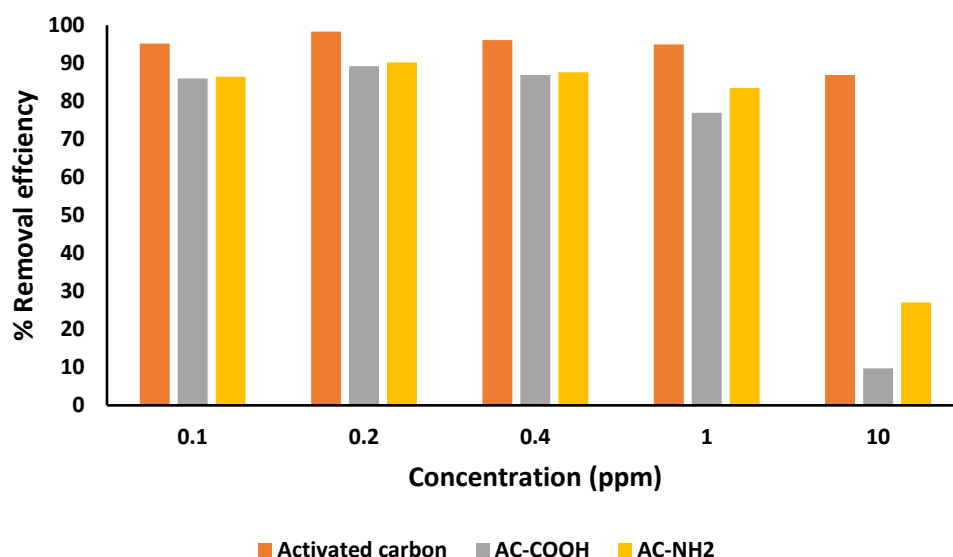


Figure 30. Percentage removal efficiency of pristine activated carbon and its modified counterparts for various concentrations of **atrazine**.

Atrazine and fluconazole are organic contaminants that were selected for investigation of the adsorption or removal efficiency of the carbonaceous materials and its functionalized derivatives. One of the important factors affecting adsorption efficiency is the initial concentration of the contaminant. For the experiment, various concentrations (0.1, 0.2, 0.4, 1 and 10 ppm) of each contaminant were used as initial concentrations to determine the percentage adsorption efficiency of 10 mg of each carbonaceous adsorbent and also to determine its maximum saturation point. Figure 30 illustrates the experimental results obtained for removal of atrazine using AC and its derivatives. As illustrated in Figure 30, utilising AC, the percentage removal efficiency of between 90 and 100% was observed, which is higher than that of its modified counterparts, even when using higher initial concentrations of atrazine. The carboxylated activated carbon (AC-COOH) percentage removal efficiency roughly decreased with increase in initial atrazine concentration, reaching saturation point when the atrazine concentration was 10 ppm. The aminated counterpart of AC (AC-NH₂) showed similar percentage removal efficiencies of atrazine, however when the initial concentration of atrazine reached 1 ppm its removal efficiency became significantly higher than that of the AC-COOH. AC-NH₂ also reached its saturation point when the concentration of atrazine was 10 ppm, adsorbing/removing only 27 % of the contaminant from solution. The performance of pristine AC in comparison to its counterparts could be attributed to its porous nature which provides

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more surface area for adsorption. As seen in Figure 19b and c, the modification of AC resulted in the filling of the pores of AC which thus provide fewer available sites for the adsorption of contaminants that may also get adsorbed deep inside pores.

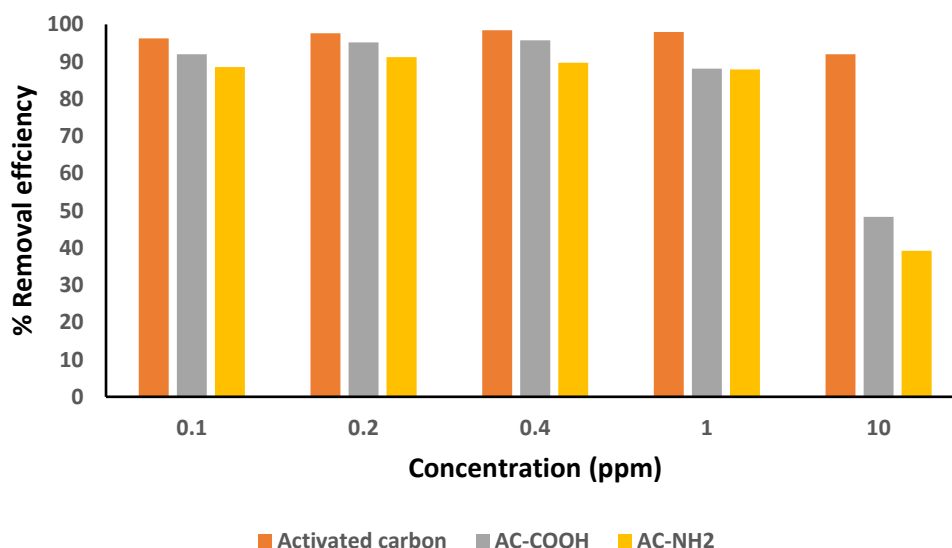


Figure 31. Percentage removal efficiency of pristine activated carbon and its modified counterparts for various concentrations of **fluconazole**.

Figure 31 illustrates the removal efficiencies of the unmodified and modified AC. As shown in Figure 31, the percentage removal efficiency of AC remained above 95% throughout the increase in fluconazole concentration except when the initial concentration was 10 ppm and the removal efficiency slightly decreased to 92%. Initially, AC-COOH and AC-NH₂ removal efficiencies slightly decreased with an increase in the initial concentration of fluconazole. The removal efficiencies of AC-COOH were only slightly higher than those of AC-NH₂ throughout the change in the initial concentration of fluconazole. Both AC-COOH and AC-NH₂ reached saturation points at 10 ppm with AC-COOH and AC-NH₂ able to adsorb only 49 % and 40 % of the 10 ppm respectively. However, comparison of the removal efficiencies of the unmodified AC to its modified counterparts suggests that AC to still be the best adsorbent for the removal of fluconazole as well as atrazine.

Afterwards, the adsorbed atrazine and fluconazole on AC were desorbed as described in Chapter 3, and the AC was regenerated to be used for a second adsorption process. Tables 11 and 12 show removal efficiencies of 5 mg of the regenerated AC for 10 ppm solutions of atrazine and fluconazole. As shown in Table 11, the regenerated AC lost efficiency and was able to adsorb only 50 % of the 10 ppm atrazine solution (compared to the initial 87 %), which

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is 37 % less than the quantity adsorbed prior to the regeneration process. This suggests that 37 % of atrazine molecules were not desorbed from the AC, which may be ascribed to deep penetration of the molecules into the micropores leading to reduced removal efficiency. The same argument holds for the removal efficiency of AC for fluconazole as shown in Table 12 where the percentage removal efficiency post-regeneration dropped to 60 %. Before regeneration it was 92%, suggesting that 32 % of the fluconazole molecules stayed trapped within the microporous structures of AC.

Table 11. *Atrazine* relative concentrations before & after filtration through regenerated AC.

	Analyte Peak Area (counts)	% Removal efficiency
Before filtration:	98600000	
After filtration:	49100000	50

Table 12. *Fluconazole* relative concentrations before & after filtration through regenerated AC.

	Analyte Peak Area (counts)	% Removal efficiency
Before filtration:	82400000	
After filtration:	32600000	60

Tables 13 and 14 show percentage removal efficiencies of pristine G and its modified counterparts for atrazine and fluconazole respectively. In view of G being a less efficient adsorbent than AC, it was not investigated at a variety of contaminant concentrations as was done for AC. G is observed to have the highest removal efficiency for atrazine in comparison to its modified counterparts as shown in Table 13. The percentage removal efficiencies decreased with modification of G, with G, G-COOH and G-NH₂ having percentage removal efficiencies of 69, 56 and 36 % respectively. As shown in Table 14, the same trend is observed for the removal of fluconazole, suggesting that modification of G reduces the ability of G to adsorb atrazine and fluconazole effectively. The possible adsorption sites on G that both atrazine and fluconazole may likely adsorb based on its chemical properties include the basal plane, edge plane or in between the layers. Therefore, it is assumed that further modification of the G structure will potentially reduce the ability of atrazine and fluconazole molecules from being adsorbed, as added oxygen and nitrogen functional groups will occupy these sites, hence the observed decline in percentage removal efficiency in G-COOH and G-NH₂. Interestingly, the fluconazole removal efficiency (Table 14) by the G series is significantly reduced, an observation which may not as yet readily be explained.

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Table 13. *Atrazine* (100 ppb) relative concentrations before & after filtration through G, G-COOH & G-NH₂.

	Analyte Peak Area (counts)	% Removal efficiency
Before filtration:	11000000	
After: G	3450000	69
After: G-COOH	4830000	56
After: G-NH₂	7070000	36

Table 14. *Fluconazole* (100 ppb) relative concentrations before & after filtration through G, G-COOH & G-NH₂.

	Analyte Peak Area (counts)	% Removal efficiency
Before filtration:	6980000	
After: G	5630000	19
After: G-COOH	6140000	12
After: G-NH₂	6270000	10

Table 15. *Atrazine* (100 ppb) relative concentrations before & after filtration through regenerated G.

	Analyte Peak Area (counts)	% Removal efficiency
Before filtration:	11000000	
After: G	10350000	6

Table 16. *Fluconazole* (100 ppb) relative concentrations before & after filtration through regenerated G.

Sample Name	Analyte Peak Area (counts)	% Removal efficiency
Before filtration:	6980000	
After: G	6690000	4.15

Single-used G was subjected to a regeneration process to desorb both atrazine and fluconazole as to perhaps re-use the G for another adsorption process. Tables 15 and 16 illustrate the percentage removal efficiencies of regenerated G following a second cycle of adsorption of both atrazine and fluconazole respectively. The percentage removal efficiency of G towards both atrazine and fluconazole significantly dropped to only adsorbing ~ 6% and ~ 4% of the initial concentration of the atrazine and fluconazole solutions respectively. This is

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in agreement with other published studies where regenerated adsorbents were reported to exhibit significantly reduced adsorption capacity as compared to fresh adsorbents.¹⁰²

4.8 Adsorption and desorption of heavy metals

Being representative of typical heavy metal environmental effluent contaminants, NiSO_4 , PbNO_3 and $\text{Hg}(\text{CH}_3\text{COO})_2$ were selected for adsorption studies. Three different metal solution media; 5 % HNO_3 , neutral (H_2O) and 0.1 M NH_3 , were employed. Atomic Absorption Spectroscopy (AAS) was used to determine the initial and final concentrations of each metal solution before and after the adsorption process. (AAS calibration curves are included in the Appendix.) Tables 17, 18 and 19 show the initial and final concentrations of Ni(II) prepared in 5 % HNO_3 , H_2O (neutral) and 0.1 M NH_3 respectively, before and after adsorption. For the adsorption/removal of Ni(II) under acidic conditions, it is clear that G is the best performing sorbent material compared to the rest, see Table 17. Similarly, even under neutral (Table 18) and alkaline conditions (Table 19) G remains the best sorbent for Ni(II). Overall best results were obtained at neutral pH, with a removal efficiency of 79 %. The adsorption of Ni(II) is clearly influenced by solution pH. Under acidic conditions, the coordination of Ni(II) to all the substrates is low, considering that the solution contains excess H^+ with which the Ni(II) ions are in competition for the same adsorption sites on the carbon substrates. However, when the pH was increased to neutral and alkaline, hardly any or no H^+ bonding is expected, leaving carbon surface sites vacant for coordination with Ni(II) ions, and thus the improved removal efficiencies observed in Tables 18 and 19. Under alkaline conditions, the removal efficiency of Ni(II) decreased to 51 % from the 79 % observed under neutral conditions, this is attributable to the complexation of Ni(II) with ammonium ions forming nickel-ammonium complex.

Table 17. Absorbance and concentrations of *Ni(II)* in 5 % *HNO*₃ before and after adsorption using each substrate.

	Absorbance	Output concentration (ppm)	% Removal efficiency
Initial Ni(II) conc.	0.018	2.3	
AC	0.017	2.1	7
AC-COOH	0.018	2.3	0
AC-NH₂	0.014	1.8	20
G	0.013	1.6	28
G-COOH	0.017	2.1	8
G-NH₂	0.015	1.9	14

¹⁰² Reddy D.H.K., et al. "Valorisation of post-sorption materials: Opportunities, strategies, and challenges." *Advances in colloid and interface science*, 242 (2017) 35-58. <https://doi.org/10.1016/j.cis.2016.12.002>.

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Table 18. Absorbance and concentrations of *Ni(II)* in *H₂O* before and after adsorption using each substrate.

	Absorbance	Output concentration (ppm)	%Removal efficiency
Initial Ni(II) conc.	0.013	2.0	
AC	0.012	1.7	15
AC-COOH	0.012	1.9	3
AC-NH₂	0.009	1.0	52
G	0.007	0.4	79
G-COOH	0.010	1.1	47
G-NH₂	0.007	0.5	77

Table 19. Absorbance and concentrations of *Ni(II)* in *0.1 M NH₃* before and after adsorption using each substrate as well as the removal efficiency of each substrate.

	Absorbance	Output concentration (ppm)	%Removal efficiency
Initial Ni (II) conc.		2.1	
AC	0.0024	1.5	28
AC-COOH	0.0033	1.4	34
AC-NH₂	0.0026	1.4	34
G	0.0036	1.0	51
G-COOH	0.0044	1.8	15
G-NH₂	0.0049	2.0	5

As for the adsorption of Pb(II) ions under acidic media (Table 20), G still showed best adsorption removal efficiency of 43 % compared to the other substrates. However, when the pH of the solutions was increased to neutral (Table 21), the carboxylated G (G-COOH) showed a higher removal efficiency of 63 %, followed by AC-NH₂, with a removal efficiency of 48%. Modification of G through addition of oxygen-containing functional groups showed improved adsorption efficiency, as seen in G-COOH having a lower adsorption efficiency for Pb(II) under acidic media. However, when the pH was increased to neutral, the adsorption efficiency increased from 24 % to 63 %. Furthermore, as the pH was increased, the negative charge on the surface of G-COOH increased due to deprotonation of the oxygen-containing functional groups like carboxylic acids, which then favors the uptake of Pb(II) ions, i.o.w., the electrostatic interaction between G-COOH and Pb(II) ions improved, thereby increasing metal adsorption. As with the other metals, Ni(II) and Hg(II), it was not possible to investigate Pb(II) in basic solution, as the metal salt is insoluble in a solution of 0.1 M NH₃.

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Table 20. Absorbance and concentrations of *Pb(II)* in 5 % *HNO*₃ before and after adsorption using each substrate.

	Absorbance	Output concentration (ppm)	% Removal efficiency
Initial Pb(II) conc.	-0.005	2.9	
AC	-0.004	2.1	21
AC-COOH	-0.004	2	26
AC-NH₂	-0.004	1.8	33
G	-0.003	1.5	43
G-COOH	-0.004	2.0	24
G-NH₂	-0.004	2.2	19

Table 21. Absorbance and concentrations of *Pb(II)* in *H*₂*O* before and after adsorption using each substrate.

	Absorbance	Output concentration (ppm)	% Removal efficiency
Initial Pb(II) conc.	0.003	2.1	
AC	0.003	1.6	23
AC-COOH	0.003	1.7	19
AC-NH₂	0.002	1.1	48
G	0.003	1.9	8
G-COOH	0.002	0.8	63
G-NH₂	0.003	1.5	27

Tables 22, 23 and 24 show the concentrations of Hg(II) before and after adsorption in acidic, neutral and alkaline media respectively, using the various substrates. From Table 22 it can be seen that under acidic media pristine AC has a removal efficiency of 63 % for Hg(II), which is higher than those observed for its modified counterparts. Furthermore, G and its modified counterparts showed significantly lower removal efficiencies for Hg(II) in comparison to AC and its counterparts. Based on these results, it is deduced that there are other mechanisms at play in the adsorption of Hg(II) ions to pristine AC. It would have been expected that under acidic media the adsorption efficiency of Hg(II) ions would be lower, since the adsorption mechanism of Hg(II) is either through ion exchange or electrostatic interaction as has been reported in the literature.¹⁰³ The higher adsorption efficiency by AC of Hg(II) in acidic media observed in this study is ascribed to physical adsorption of mercury species into the microporous structures of AC. By physical adsorption, it means that mercury species fill

¹⁰³ Kadirvelu, K., et al. "Mercury (II) adsorption by activated carbon made from sago waste." *Carbon*, 42.4 (2004) 745-752. <https://doi.org/10.1016/j.carbon.2003.12.089>.

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into the pores of AC, as also reported by Asasian *et al.*¹⁰⁴ It is therefore understandable that the modified counterparts of AC and G have lower adsorption efficiencies; it lacks microporous structures which otherwise would have provided more adsorption sites for the Hg(II) cations. The former is true for G as it is less porous than AC.

Table 22. Absorbance and concentrations of *Hg(II)* in 5 % *HNO*₃ before and after adsorption using each substrate.

	Absorbance	Output concentration (ppm)	% Removal efficiency
Initial Hg(II) conc.	-0.0054	1.6	
AC	-0.004	0.6	63
AC-COOH	-0.004	1.1	30
AC-NH₂	-0.004	1.1	33
G	-0.003	1.4	16
G-COOH	-0.004	1.2	25
G-NH₂	-0.004	1.6	2

Table 23. Absorbance and concentrations of *Hg(II)* in *H*₂*O* before and after adsorption using each substrate.

	Absorbance	Output concentration (ppm)	%Removal efficiency
Initial Hg(II) conc.	0.007	2.2	
AC	0.005	1.2	44
AC-COOH	0.005	1.1	49
AC-NH₂	0.004	0.5	75
G	0.006	1.5	33
G-COOH	0.005	1.3	42
G-NH₂	0.007	2.1	4

Table 24. Absorbance and concentrations of *Hg(II)* in 0.1 M *NH*₃ before and after adsorption using each substrate.

	Absorbance	Output concentration (ppm)	%Removal efficiency
Initial Hg(II) conc.	-0.009	2.6	
AC	-0.004	1.2	56
AC-COOH	-0.008	2.4	9
AC-NH₂	-0.006	1.6	37
G	-0.005	1.3	50
G-COOH	-0.008	2.3	12
G-NH₂	-0.008	2.3	13

¹⁰⁴ Asasian, Neda, Tahereh Kaghazchi, and Mansooreh Soleimani. "Elimination of mercury by adsorption onto activated carbon prepared from the biomass material." *Journal of Industrial and Engineering Chemistry*, 18.1 (2012) 283-289. <https://doi.org/10.1016/j.jiec.2011.11.040>.

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When the adsorption of mercury species was done under neutral conditions (Table 23), AC-NH₂ showed a removal efficiency of 75% for Hg(II), which is the highest in comparison to the other substrates, including pristine AC. AC-NH₂ under acidic conditions, as shown in Table 22, had a removal efficiency of 33%, which improved at higher pH. The presence of the amino functional groups offered enhanced removal efficiency of Hg(II) under neutral conditions suggesting that it possesses a strong affinity for mercury offering better coordination, which led to the formation of a stable metal complex.¹⁰⁵ However, when the pH was alkaline (Table 24), the removal efficiency of AC-NH₂ decreased significantly, which could be due to the formation of mercury hydroxides.

Most of the adsorbent substrates performed better under neutral conditions with higher removal efficiencies than under acidic or alkaline conditions. Therefore, the best adsorbents under neutral pH conditions were chosen to proceed to for the regeneration process, i.e. to determine its reusability. As discussed above, G-COOH, G and AC-NH₂ performed best towards the removal of Pb(II), Ni(II) and Hg(II) respectively. These substrates were then subjected to the adsorption process post regeneration and the results obtained are shown in Tables 25, 26 and 27. Section 3.9 described the method that was used for regeneration.

Table 25. Absorbances and concentration of **Pb(II)** in **H₂O** before and after adsorption using the regenerated substrate.

Substrate	Absorbance	Output concentration (ppm)	% Removal efficiency
Before filtration:	-0.005	2.4	
After: G-COOH	-0.005	2.4	2.12

Table 26. Absorbances and concentration of **Ni(II)** in **H₂O** before and after adsorption using the regenerated substrate.

Substrate	Absorbance	Output concentration (ppm)	% Removal efficiency
Before filtration:	0.017	1.8	
After: G	0.016	1.8	6.78

¹⁰⁵ Zhu X., and Spiro D.A. "Polystyrene-supported amines: affinity for mercury (II) as a function of the pendant groups and the Hg (II) counterion." *Industrial & engineering chemistry research*, 44.23 (2005) 8605-8610. <https://doi.org/10.1021/ie048736i>.

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Table 27. Absorbances and concentration of *Hg(II)* in *H₂O* before and after adsorption using the regenerated substrate.

Substrate	Absorbance	Output concentration (ppm)	%Removal efficiency
Before filtration:	-0.003	2.9	
After: AC-NH ₂	-0.002	2.3	16.94

Table 24 shows the removal efficiency of the regenerated G-COOH and it can be seen that G-COOH following regeneration exhibits a very low removal efficiency which could be attributed to the partial desorption of Pb(II) from the surface of the G-COOH. The same applies to the adsorption of Ni(II) post-regeneration of G, as seen in the low removal efficiency shown in Table 25. Furthermore, the regeneration of AC-NH₂ for adsorption of Hg(II) also showed a low removal efficiency as shown in Table 26, which could also be due to the partial desorption of Hg(II). Therefore, based on the low removal efficiencies observed, it is indicative that the substrates are either not effective in removal of the metals post regeneration, or the method used for regeneration is not effective in desorption of the adsorbed metals and thus hindering the substrates from reuse.

CHAPTER 5: CONCLUSION AND FUTURE PERSPECTIVES

The main objective of this study was to modify and compare the filtration efficiencies of various carbonaceous materials with regard to the removal of both the selected organic and inorganic contaminants. Carbonaceous nanomaterials such as AC, G, carbon nanotubes, graphene and the acid (-COOH) and base (-NH₂) functionalized derivatives of AC and G were selected. Carbon nanotubes and graphene were successfully synthesized using the microwave irradiation method, however, with the aim of low-cost commercial filters and the higher cost of production of these two materials, filtration studies on these materials were discontinued. AC and G were instead used as adsorbents and were modified to investigate whether chemical modification would enhance adsorption efficiency of selected contaminants. Modification of G and AC involved the addition of oxygen-containing functional groups and subsequently addition of amino groups to the former oxidized G and AC. Elemental analyses and EDS characterization confirmed successful addition of the functional groups. Furthermore, SEM and TEM examination revealed the morphological structures of the as-prepared materials.

Organic contaminants investigated in this study were atrazine and fluconazole, while the inorganic contaminants were Ni(II), Pb(II) and Hg(II). For the adsorption of atrazine and fluconazole, various concentrations ranging from 0.1 – 10 ppm were used and determination of the removal efficiencies of AC, AC-COOH, AC-NH₂, G, G-COOH and G-NH₂ were carried out. AC presented the highest removal efficiency for both atrazine and fluconazole compared to AC-COOH and AC-NH₂, and it did not reach its maximum adsorption capacity because even at higher concentrations its removal efficiency was above 85 %. The microporous structures of AC played a vital role in adsorption of atrazine and fluconazole hence, the high observed removal efficiencies. In adsorption studies conducted for removal of atrazine and fluconazole using G and its modified counterparts (G-COOH and G-NH₂), G exhibited the highest removal efficiencies, however at higher concentrations its removal efficiency for both the contaminants decreased. Based on the obtained results it is concluded that unmodified AC and G are better filter materials compared to its functionalized derivatives.

The use of both AC and G and their modified counterparts for the removal of Ni(II), Pb(II) and Hg(II) was different to what was seen with atrazine and fluconazole. The modified counterparts of both G and AC mostly showed improved adsorption efficiencies compared to

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the unmodified materials. pH was one of the factors that played an important role in the adsorption efficiencies of metals. Most of the adsorbents showed better removal efficiencies when the pH of the metal solutions were neutral. For the removal of Ni(II), G showed a removal efficiency of 79 %, suggesting that G had better affinity for Ni(II) compared to the other adsorbents. AC-NH₂ showed better affinity for Hg(II), with removal efficiency of 63 %. G-COOH showed a removal efficiency of 75 % for Hg(II) exhibiting better affinity compared to the other adsorbent materials.

Regeneration of the adsorbents post-adsorption resulted in low removal efficiencies of the contaminants and therefore urges development of effective methods of regeneration of spent adsorbents. The purpose for regeneration of adsorbents is to ensure a circular economy and also prevent generation of unwanted waste.

Various methods for retrieval and regeneration of used adsorbents require closer attention. Currently, methods used for recycling adsorbents include oxidation processes, thermal and chemical desorption and filtration. These methods are dependent on the type of adsorbent and contaminant. Therefore, further exploration into these methods and other alternatives are required in order to develop effective and efficient adsorbent recovery techniques.

Additionally, further exploration into the modification of AC and G is needed to determine its affinity towards other contaminants not investigated in this study. AC and G were chosen for the study due to low cost and with that said, innovation or development of more low-cost materials to be used for extraction of organic and inorganic contaminants is needed for better accessibility to the general public and poorer communities, especially in remote areas or in developing countries that lack water treatments systems. For instance, exploration into the use of non-toxic woods for production of charcoal or AC could allow communities to be able to produce their own filters, and thus gain access to cleaner water.

To date, there have been only a few studies focusing on the use of wood-based materials for the purification of drinking water.¹⁰⁶ Therefore continuation of such investigations and development of single stage filters involving low-cost materials should be further explored. It would be helpful to pursue these research areas to further advance the adsorption-based removal of contaminants in wastewater streams considering the current focus on a circular

¹⁰⁶ Jiao M., et al. "Highly efficient water treatment via a wood-based and reusable filter." *ACS materials letters*, 2.4 (2020) 430-437. <https://doi.org/10.1021/acsmaterialslett.9b00488>.

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economy, improved resource efficiency and zero waste generation in the context of environmental sustainability.

APPENDIX

Table 1. Data for the calibration curve of Ni(II) in %5 HNO₃.

Sample	Input concentration (ppm)	Absorbance	Output Concentration (ppm)
Blank		-0.013	
1	0.4	0.002	0.3
2	0.8	0.007	0.9
3	1.2	0.010	1.3
4	1.6	0.013	1.6
5	2.0	0.018	2.3

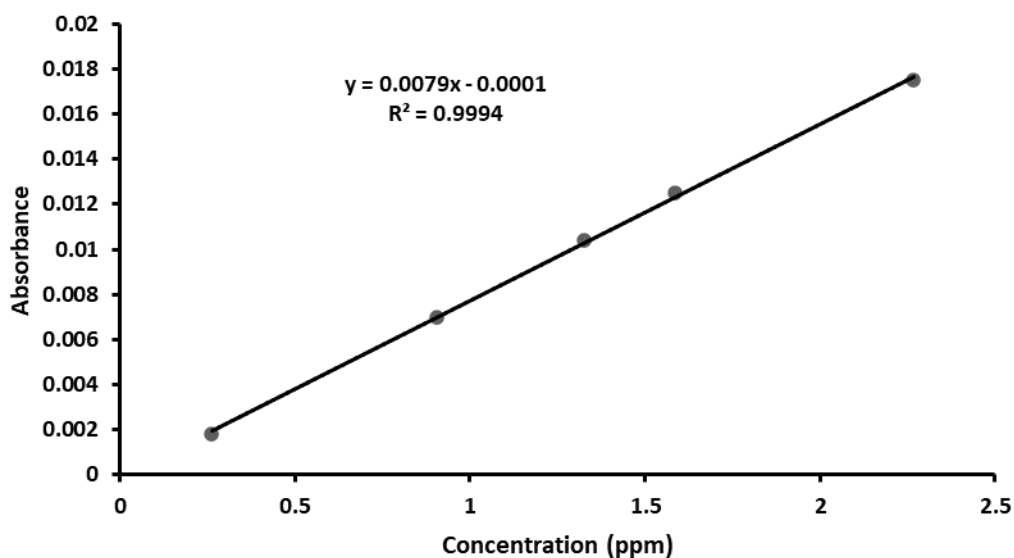


Figure 1. Calibration curve of Ni(II) in %5 HNO₃.

Table 2. Data for the calibration curve of Ni(II) in H₂O.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank	0	-0.018	
1	0.5	0.006	0.3
2	1.0	0.010	1.2
3	1.5	0.011	1.5
4	2.0	0.013	2.0
5	2.5	0.016	2.8
6	3.0	0.016	2.8

APPENDIX

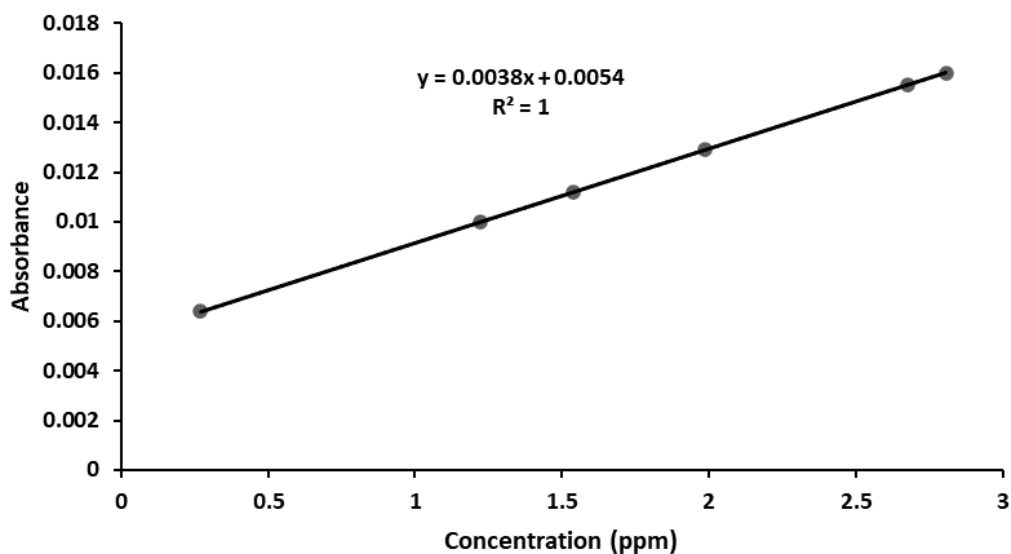


Figure 2. Calibration curve of Ni(II) in H₂O.

Table 3. Data for the calibration curve of Ni(II) in 0.1 M NH₃.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank	0	-0.013	
1	0.4	0.0003	0.4
2	0.8	0.0007	0.5
3	1.2	0.0022	1.1
4	1.6	0.0024	1.2
5	2.0	0.0031	1.5
6	2.4	0.0041	1.8

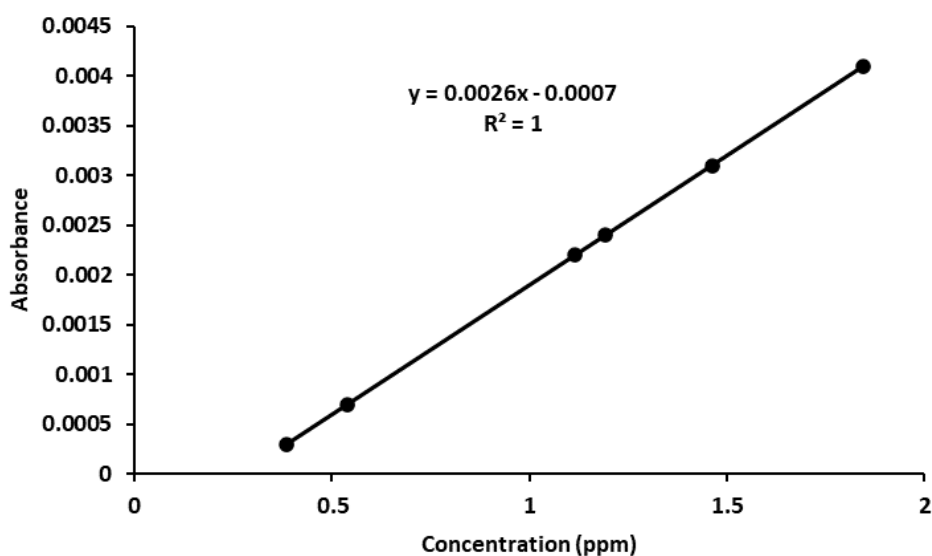


Figure 3. Calibration curve of Ni(II) in 0.1 M NH₃.

APPENDIX

Table 4. Data for the calibration curve of Pb(II) in %5 HNO₃.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank		-0.020	
1	0.5	-0.0006	0.4
2	1.0	-0.003	1.0
3	1.5	-0.003	1.5
4	2.0	-0.005	2.3
5	2.5	-0.005	2.5
6	3	-0.006	2.9

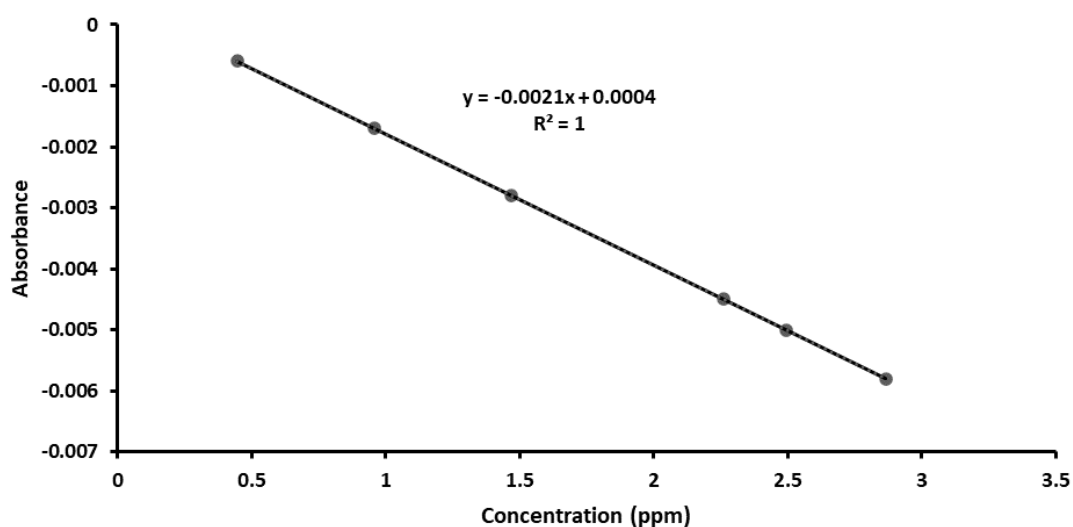


Figure 4. Calibration curve of Pb(II) in %5 HNO₃.

Table 5. Data for the calibration curve of Pb(II) in H₂O.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank		0.0009	
1	0.5	0.0006	0.6
2	1.0	0.002	0.7
3	1.5	0.002	1.5
4	2.0	0.003	2.0
5	2.5	0.003	2.5
6	3.0	0.004	3.2

APPENDIX

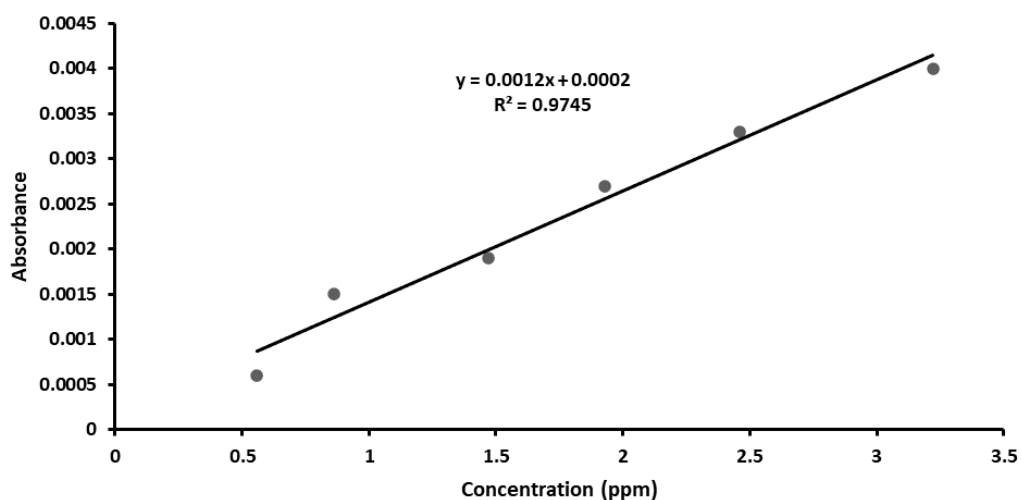


Figure 5. Calibration curve of Pb(II) in H₂O.

Table 6. Data for the calibration curve of Hg(II) in %5 HNO₃.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank		-0.0062	
1	0.3	-0.0004	-0.001
2	0.7	0.0027	1.1
3	1.3	0.0032	1.2
4	1.7	0.0054	2.0
5	2.0	0.0046	1.7

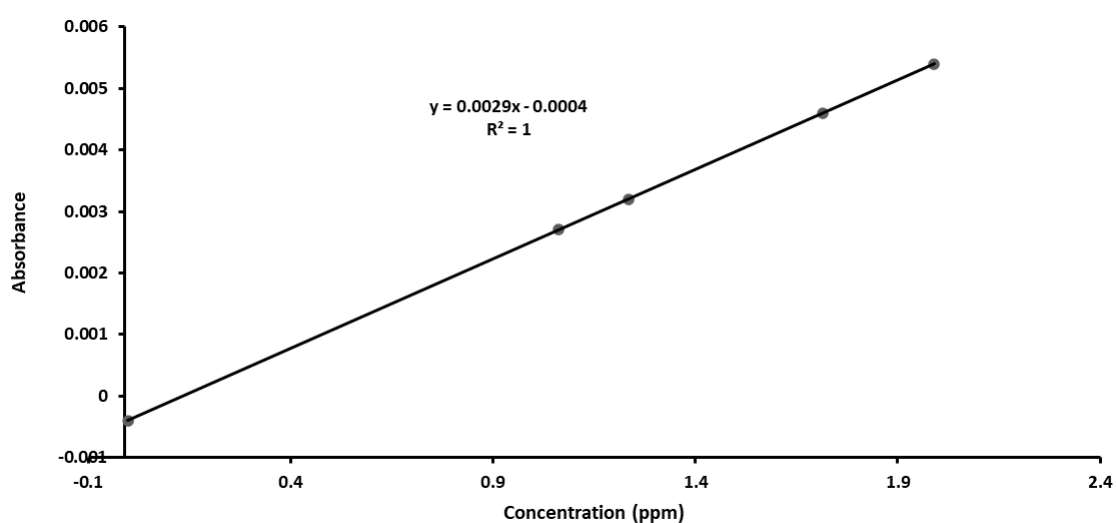


Figure 6. Calibration curve of Hg(II) in %5 HNO₃.

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Table 7. Data for the calibration curve of Hg(II) in H₂O.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank	0	-0.006	
1	0.4	0.004	0.5
2	0.8	0.003	0.4
3	1.2	0.005	1.1
4	1.6	0.006	1.7
5	2.0	0.007	2.2

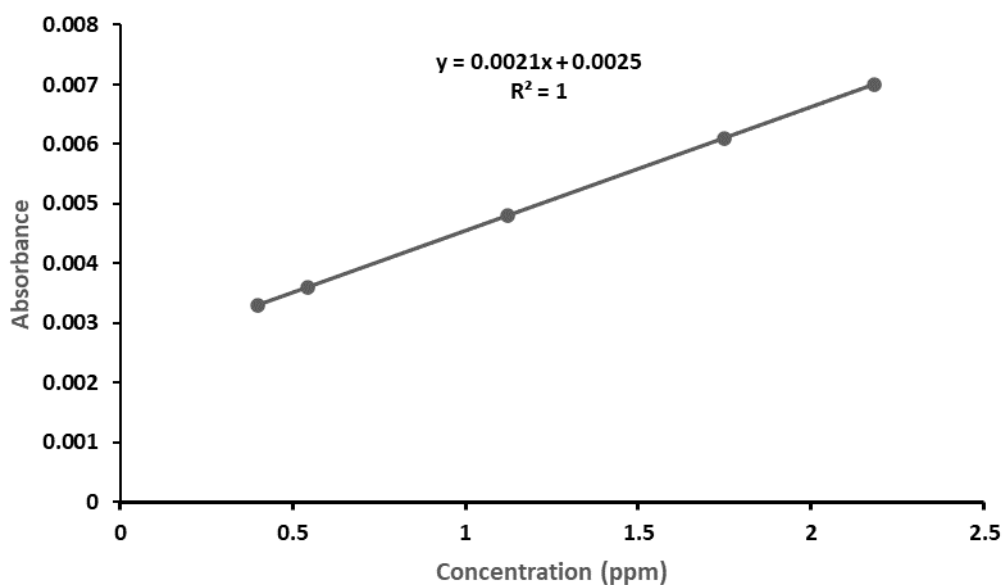


Figure 7. Calibration curve of Hg(II) in H₂O.

Table 8. Data for the calibration curve of Hg (II) in 0.1 M NH₃.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank	0	0.003	
1	0.4	-0.002	0.4
2	0.8	-0.003	0.6
3	1.2	-0.004	1.1
4	2.0	-0.007	1.9
5	2.4	-0.007	2.2

APPENDIX

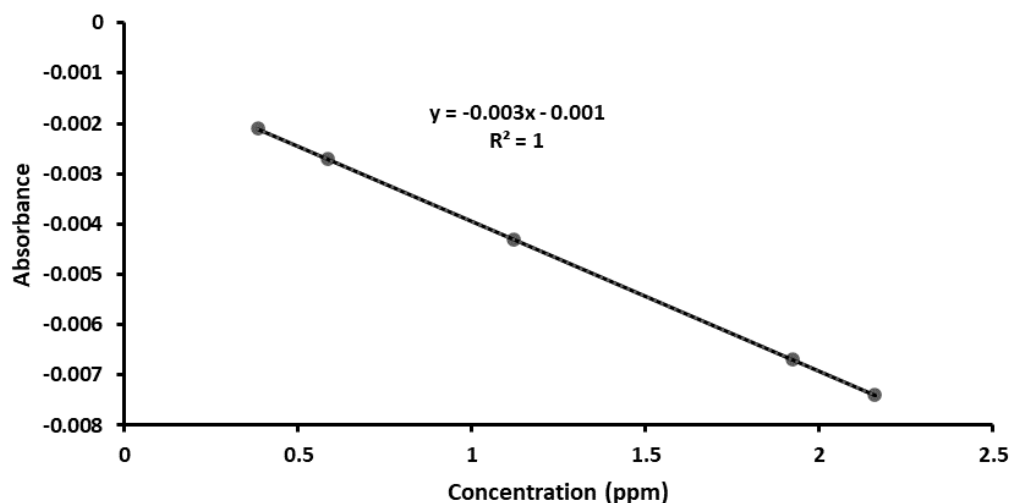


Figure 8. Calibration curve of Hg(II) in 0.1 M NH₃.

Table 9. Data for calibration of Pb(II) in H₂O post-regeneration of the substrate.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank		-0.0198	
1	0.5	0.0001	-0.04
2	1	-0.0022	1.1
3	1.5	-0.0038	2.0
4	2	-0.0042	2.2
5	2.5	-0.0058	3.0

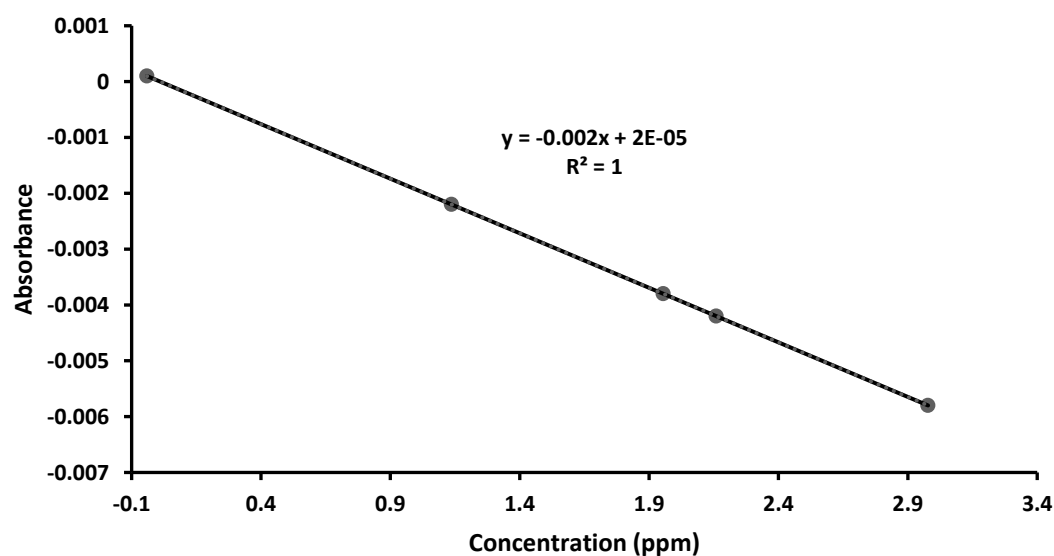


Figure 9. Calibration curve of Pb(II) in H₂O post regeneration.

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Table 10. Data for calibration of Ni(II) in H₂O post regeneration of the substrate.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank	0	0.011	
1	0.5	0.006	0.5
2	1.0	0.011	1.0
3	1.5	0.015	1.5
4	2.0	0.019	1.9
5	2.5	0.024	2.6
6	3.0	0.028	3.0

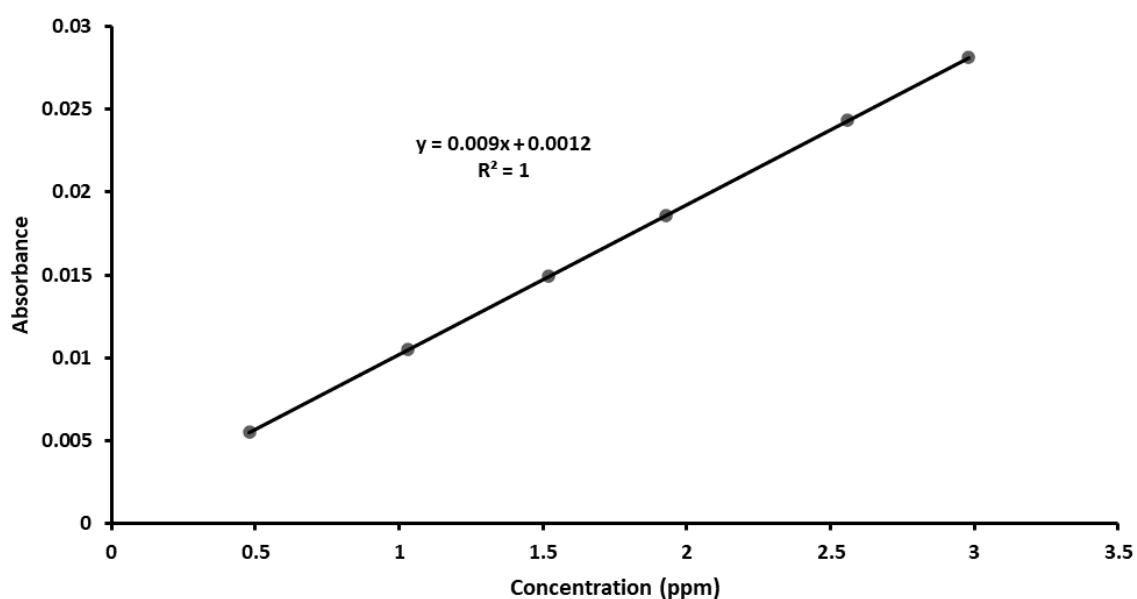


Figure 10. Calibration curve of Ni(II) in H₂O post regeneration.

Table 11. Data for calibration of Hg(II) in H₂O post regeneration of the substrate.

Standard	Input concentration (ppm)	Absorbance	Output concentration (ppm)
Blank	0	0.018	
1	0.5	0.0004	0.8
2	1.0	0.0005	0.8
3	1.5	-0.0003	1.3
4	2.0	-0.001	2.0
5	2.5	-0.002	2.3
6	3.0	-0.003	3.3

APPENDIX

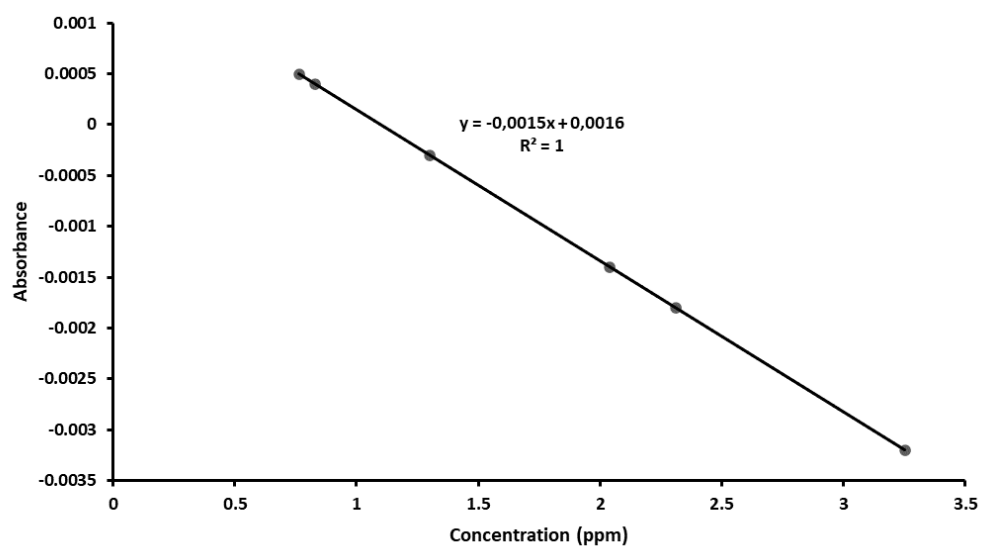


Figure 11. Calibration curve of Hg(II) in H₂O post regeneration.