

Optimization of covalently cross-linked graphene oxide-infused polyamide thin film nanocomposite membrane for treating wastewater containing heavy metallic ions.



Mashau Phanuel Mafamadi

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Declaration

I, Mashau Phanuel Mafamadi, herewith declare in terms of university plagiarism policy that:

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A handwritten signature in black ink, appearing to read 'Mashau', is written over a circular, pixelated graphic element.

Signature

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Date Submitted.

Dedication

This master's thesis pays tribute to my late mother, Mrs. Konanani Constance Mafamadi, and grandmother, Vho Tshinakaho Matamela Mukwevho, for their encouragement and support in my academic endeavours, and for understanding the value of my efforts. To the all-powerful God for providing me with determination, wisdom, and capacity to conduct this study.

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Abstract

The Nanofiltration technology is widely used wastewater treatment to reduce the salt concentration of toxic heavy metallic ions present in drinking waters and acid mine drainage systems containing impurities emanating from commercial and industrial discharge of effluents comprised of heavy metals such as Cobalt, Iron, Sodium, Magnesium, Nickel, and Manganese for reusable application. The best techniques for removing heavy metals from wastewater have been researched using a broad range of strategies comprising membrane separation processes, ion exchange resins, coagulation, and chemical precipitation. The rate of water consumption nationally has led research into considering advanced water treatment technologies into providing safer water treatment technologies which can provide safe water supply in a more energy productive and sustainable manner environmentally. To achieve continual improvement, different methods have been established for removal of the heavy metals present in wastewaters such as adsorption, chemical precipitation, membrane filtration and ion exchange processes.

This study discussed the treatment of heavy metallic ions composed of different concentrations in acid mine wastewater using a thin film nanocomposite (TFN) membrane. This study focused on fabrication of thin film nanocomposite (TFNs) which were utilised for the adsorption of heavy metals and membrane performance was evaluated using different operating parameters which include rejection, flux, and recovery. Response surface methodology (RSM) technique was used to develop mathematical models for the optimization of the nanofiltration separation process by finding the optimum operating conditions of the membrane. The performance of the Graphene Oxide/Polyethersulphone (PES) nanocomposite membranes composed of different PES-GO ratios was measured against permeability and selectivity. However, some of the disadvantages associated with GO membranes are their extremely hydrophobic nature causing them to become unstable in water, and the weak interaction between GO sheets also leads to low mechanical strength of the GO membranes. To resolve the above-mentioned challenges, chemical bonding can be induced between GO sheets to improve the mechanical strength properties and prevent dispersion in water. In this study, the chemical crosslinking of the GO sheets involved the comparison of three dicarboxylic acids in Glutaric acid, Pimelic acid and hexanedioic acid. The aim of using the three different carbon chain dicarboxylic acids as crosslinking solutions was to evaluate the effect which the increasing chain length will have on the intersheet spacing, permeation flux, membrane selectivity, and elastic moduli of the GO-PES membrane.

The objective of this research study was to fabricate and improve the efficiency of a PES/GO nanocomposite membrane for the removal of heavy metals from wastewater. Three different types of PES/GO membranes were constructed based on different functional groups added onto the GO material and were analyzed for their membrane composition, characteristics as well as performance in the removal of the Iron, Manganese, Sodium, Magnesium, Nickel, and Cobalt and was compared to the primary PES commercial membrane. The ideal membrane suitable for the above-mentioned quality standards was found to be the one composed of PES membrane infused with Pimelic acid. The fabricated TFN membrane could separate inorganic pollutants without undergoing severe fouling or clogging during membrane operation and was found to be chemically stable, physically durable, and chemically resistant. The PES GO-Pimelic acid functionalized membrane performed better when compared to the other two TFN membranes synthesized utilizing glutaric and adipic dicarboxylic acids. The membrane surface morphologies of the three different membranes were vastly altered with the addition of different crosslinkers and such observations were caused by the different functional groups added onto the GO surface. The effective crosslinking reactions between the polyamide layers formed onto the TFC composite membrane and GO functionalised with different dicarboxylic acids was instrumental in formulating adequate stability between the charges, spacing of GO sheets and functionality when dispersed within the water environment to such an extent that the TFN membrane was found to be physically durable in overcoming GO leaching during the separation process. The Glutaric and Adipic functionalised GO material was faced with the challenge of unbonded GO layers which contributed to achieving low nanofiltration performance targets in removal heavy metals and that compromised the accuracy of the models used in fitting the experimental data to obtain the optimal solution from their respective experiments.

In most research studies conducted regarding the optimization for preparation conditions was not done, and therefore such research gap was filled within this research study. The optimization of concentration of crosslinker, reaction time as well as temperature was conducted for pimelic acid functionalised infused PES thin film membrane and the reaction time was reduced from 48 hours to 30 minutes. The performance for the PES membrane and Pimelic functionalised GO-PES infused membranes was studied, and the commercial PES membrane revealed great permeability of 65.74 L/m².hr as well as mean rejection of low concentration of heavy metals at 96 % removal rate. The GO-PES membrane functionalised with pimelic acid was studied for its heavy metal removal rate at low concentrations using

synthetic acid mine drainage, and it showed a rejection rate of 98% with decreased flux of 43.41 L/m².hr. The input variables responsible for changing the nanofiltration process were limited to operating pressure as driving force which had great potential in affecting process performance at different stipulated operating times, with the synthesized TFN membrane responsible for adsorbing the heavy metals. Subsequently, it can be concluded that a well-designed RSM predictive model using Design Expert 12 can be utilised as a feasible tool for the prediction of nanocomposite membrane at different operational conditions. The membranes used in this study showed excellent permeate fluxes and rejection factors like those obtained by other researchers in this field using the same carbon nanostructures in GO embedded into polymer matrix.

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Structure of the dissertation

Chapter 1 -Main focus entails the general background towards the objectives, aims and problem statement. It focusses mainly on introducing the subject of the research study being undertaken.

Chapter 2 - This chapter emphasizes on underlining and providing in-depth overview and description on the subject matter discussed in this report. Description of literature concerning the development of thin film nanocomposite technology via the incorporation of nanofillers into host polymeric membranes for wastewater treatment purposes.

Chapter 3- This chapter emphasizes on the materials as well as the experimental procedure utilised for the synthesis of Graphene Oxide and provides an overview of its functionalization process. Provides a detailed description on the entire fabrication process of the TFN membrane as well as the batch adsorption studies conducted which gives an overview on the heavy metals that were attached to the covalently bonded PES/GO membrane.

Chapter 4 -. This chapter involved the synthesis and characterization of pristine graphene oxide with the use of three different dicarboxylic acids. The change in morphology of the pristine GO was examined using SEM as the structure deformed to new morphology once treated with different dicarboxylic acid. These changes were also noted when the sample underwent characterization using other characterization techniques mentioned in the chapter as well as in the published journal: <https://doi.org/10.1016/j.matpr.2023.08.291>

Chapter 5 –This chapter outlines the stages followed to aminate and bind the functionalised GO into membrane as aid to improve the membranes performance and make it more hydrophilic. The nanocomposite membranes were prepared by the dip coating assembly method, and scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) were used to characterize them. The RSM modelling technique was used through the construction of non-parametric simulative models known as “black -box” or Box-Behnken model to verify the relationship between the stipulated design variables with the response or output of the process in performing the limited number of experiments.

Chapter 6 - Conclusion and Recommendations.

References

Appendix A – The experimental results used to calculate the permeate flux and heavy metal removal rates was stipulated in this section of the report. The Atomic Adsorption (AA) equipment was used to obtain the metal compositions before and after filtration. X-Ray diffraction (XRD) equipment was used to calculate the interlayer spacing for the different functionalised GO materials.

Appendix B – The picture of the covalently bonded pimelic functionalised GO/PES TFN membrane was provided in this section after filtration to provide evidence of the study that was undertaken together with other experimental results obtained to fulfil the calculations required to conclude this thesis document.

Chapter 1

Introduction

This Chapter provides the general background towards achieving the aim and objectives of the study, as well as the identified problem and significance of the study. Focus entails the general background towards the objectives, aims and problem statement. It focusses mainly on introducing the subject of the research study being undertaken.

1. Introduction

1.1 Background and Motivation

The tremendous volume of effluent wastewater flows into rivers, oceans, soil and the environment are a result of the world's rapid industrial expansion. Water quality is declining globally because of rapid industrialization, erratic use of water resources, and the rate of increase in the world's population (12). According to Prabhu *et al* (13) the availability of water supply in both quality and quantity is paramount for human survival. In wastewater treatment industry, the water contaminants comprise of organic and inorganic pollutants (14). The organic pollutants include food processing waste, detergents, fats, and grease as well as insecticides, whereas the inorganic pollutants include heavy metals (14).

According to Maher *et al.* (1), while heavy metals are not biodegradable and instead grow in living things before becoming destructive to the entire food chain and ecological chain process, organic pollutants can naturally degrade in a way that is not harmful to the environment.

This practice of releasing inadequately treated wastewater laden with heavy metals into the environment leads to the degradation of aquatic ecosystems, contamination of underground water resources, adverse health effects to human and plants (1). Most developing countries such as South Africa are faced with huge dilemma due to moderate and high tensions regarding the freshwater resource's availability, as well as the major inequalities which exist in the quantity and quality of portable drinking water available to rural areas and urban areas (13). Due to high clean water demands from both industrial and domestic users, wastewater treatment and management require stringent policies and regulations regarding the discharge of contaminated water into the environment and the use of water sources (15). Agarwal *et al* (16) has found that when most commercial and industrial processes produce contaminated wastewater consisting of one or more trace quantities of heavy metals, the environment tends to degrade. The governments of several nations across the world have established the maximum contaminant limit (MCL) heavy metals in wastewater and portable drinking water to protect aquatic life, plants, and human health from heavy metal wastewater contamination. The maximum contaminant level (MCL) for heavy metals in industrial and portable drinking water in South Africa are 0.1 and 0.001 mg/L, respectively (8).

There are several approaches to the treatment of wastewater contaminated with heavy metals. They include ion exchange resins, conventional coagulation, chemical precipitations, membrane separation processes, softening of lime and adsorption (16). However, a few factors,

such as operational and start-up (capital) costs as well as the discharge of residual metal sludge, are considered before any method is used.

Reverse osmosis, ultrafiltration, and nanofiltration are a few efficient physicochemical separation techniques that can be utilised to remove a high level of contaminants from wastewater using membrane techniques (8). Membrane technology is relatively easy to operate when compared to the other conventional wastewater treatment methods (5). Traditional membranes employed for the removal of water contaminants are PVDF, PSF, and PES (8). To achieve enhanced performance from membrane separation processes, there are quite numerous quality parameters regarding the membrane material produced. According to Nasser *et al* (8), assessment of the physical and chemical properties serves as an important indicator defining the performance of the membrane material. The ideal membrane is one with a high permeate flux, high selectivity, low fouling propensity, physically indestructible, cost-effective, chemically stable, and resistant. Traditional membranes, such as PSF and PVDF are still faced with several limitations such as inability to control membrane thickness, pore size distribution, low chlorine resistance, low permeability, low selectivity, and inability to prevent fouling (7). The low permeate flux and fouling of the traditional membranes are caused by low porosity and surface hydrophobicity (17). Global research on heavy metal removal from wastewater is currently focused on developing membranes with improved permeability and selectivity premised on enhanced hydrophilicity (7).

1.2 Research Aim

The primary goal of this work was to synthesize and optimize the production of thin-film nanocomposite membranes made of graphene oxide that are embedded in polyamide (PA) layers to remove heavy metal ion from wastewater.

1.3 Research Questions

- (1) Will embedding graphene oxide (GO) inside Polyethersulphone membrane enhance its separation performance for the removal of metallic ion when compared to that of the pure/ pristine Polyethersulphone membrane?
- (2) What effect will the cross-linked agents like dicarboxylic acids (e.g., Glutaric acid, Pimelic acid and hexanedioic acid) have on the morphology (e.g., intersheet spacing, porosity, etc.) and separation performance of the GO-infused membranes in (1)?
- (3) Will changing the process variables during the separation using empirical modelling approach (e.g., response surface methodology approach, artificial neural network, etc.) enhance the separation performance of the best performing synthesized membranes in (2) towards achieving the permissible discharge limit of 0.1 ppm for heavy metallic ions concentrations such as Nickel, Cobalt, Iron and manganese as set by the National drinking water guidelines?

1.4 Research Objectives.

- (1) To synthesize GO and embed them into PES membrane forming GO-PES. Make PES membrane using similar condition. Then characterize these membranes and evaluate their removal efficiency for removal of heavy metallic ions from wastewater. Finally compare their performance and conclude.
- (2) To functionalize the GO-PES membrane in (1) using the cross-linked agents like dicarboxylic acids (e.g., Glutaric acid, Pimelic acid and hexanedioic acid), characterize the membranes and evaluate them for removal of heavy metallic ions from wastewater. Compare the results and conclude on the performance.
- (3) To optimize and investigate the effect of process variables on the separation performance of the best separation performance of the best performing membrane in the removal of heavy metallic ions based on the results obtained in (2). Develop a statistical model to explain the parametric effect and cross-validate the development of the model.

Chapter 2

Literature Review

This chapter emphasizes on underlining and providing in-depth overview and description on the subject matter discussed in this report. Description of literature concerning the development of thin film nanocomposite technology via the incorporation of nanofillers into host polymeric membranes for wastewater treatment purposes.

2. Literature Review

2.1 Introduction

The search for better and faster ways to develop effective separation processes such as nanofiltration (NF) and reverse osmosis (RO) have been widely researched area of study in response of the global challenges of water reclamation, desalination, and removal of contaminated water in a more environmentally sustainable way (18). Further improvement projects aimed towards the enhancement of membrane separation processes is vital for achieving better separation performance (19). Evaluating the thin film composite (TFC) polyamide membranes' quality is the aim of the membrane-based separation procedure. Modern wastewater treatment systems with advanced qualities are essential to preventing the tragic and potentially catastrophic issue of water body pollution brought on by the toxicity of heavy metals to aquatic life and subsequently humans (20). In the last few years, the notion of continually improving the nanotechnology systems has been intensified through research and new improvements which led to the emergence of thin film technology (21). The major improvements in thin film technology stems from the challenges, which polymeric membranes have faced regarding permeability and solute rejection (22). One significant technical issue with polymeric membrane is membrane fouling, which is brought on by the accumulation of retained materials on the membrane surface and/or inside the membrane pores, which involves heavy metallic ions, colloidal and suspended particles, and inorganic and organic matter. This ultimately results in a decline in the membrane performance (8). The driving force towards developments of such membrane processes can be attributed towards its promising technological advancement processes for heavy metal removal based on various benefits such as less need for addition of chemicals, ease of system capacity development and simplicity of membrane process integration with other processes (23). The most fundamental aspect for conducting this research study was to address the membrane restrictions that caused various challenges such as limited pore size availability as well as the economic challenge of high capital and operating costs. According to Rezaei *et al* (23) other technical drawbacks involving membrane separation technology is that of low water recovery, concentration polarization and membrane fouling and high energy usage (24). In addressing such technical drawbacks, this report emphasized on the incorporation of nanofillers into traditional host PES membrane with the aim of improving the matrix structure of the thin film membranes as well as optimizing performance (7). To achieve the goal of this research study, it is crucial to incorporate inorganic nanoparticles such as titanium dioxide (TiO₂), zinc oxide (ZnO), silica, and GO to

remove the portions of the polymeric membrane structure that were flawed and produced technical restrictions. Their outstanding properties have been reported by many researchers to enhance the hydrophilicity, durability, permeability, and antifouling of the polymer nanocomposite membranes (7).

2.2 Nanocomposite membranes

Nanomaterials constitute of composite materials which are formulated in solid structure format at nanometer scale (1- 100 nm) dimensional spaces between the different phases (25). These materials are usually made-up of organic solid (host polymer matrix) containing inorganic components or vice versa (25). These membrane reinforcements comprise of a combination of two or more materials or phases, whereby one phase is constructed within the nanometer range. The nanocomposite membrane development had its roots in early 1990's. During that time nanocomposite membranes were fabricated for use in gas separation processes. To ensure that good quality nanocomposite membranes were developed, selective zeolites were filled into the polymer matrix to improve both selectivity and permeability (26). Nanocomposite membranes possess unique properties superior to their counterpart conventional membranes, such as PES or PSF. These membranes boost greater advantage over conventional membranes based on unmatched characteristics such as high durability, ability to resist being corroded, low density, gas-blockade features, heat resistance and high membrane stiffness (27).

There is a common phrase which says that "quality is an ever-changing state", and hence the drive for continual improvements efforts aimed at enhancing nanocomposite membranes is a legitimate one, so is the utilization of nanofillers such as carbon nanotubes (CNTs), metal nanocomposite, titanium oxide, silica and GO (25). The incorporation of inorganic nanofillers as nanocomposite membrane reinforcements is to improve membrane flux, selectivity, permeation, and other desirable characteristics which contributes to fabrication of nanocomposite membrane meeting most of technical specifications which will enable good separation performance of contaminants.

The infusion of nanofillers affects the membrane performance in following ways:

- Ability to prevent membrane fouling, loss of product quality and flux decline
- Ability to improve hydrophilicity of membranes, i.e., water loving nature of membranes
- Ability to improve solute rejection and selectivity efficiency of the membrane
- Ability to produce defect free membranes that are more durable and meet technical specifications

2.3 Synthesis of Nanocomposite membranes

The traditional conventional membranes had its shortcomings in terms of its make-up and in the membrane's ability to achieve greater separation performances (25). To combat most of the technical limitations posed by the conventional membranes, nanocomposite membranes were recognized as suitable alternatives which can be customized to suit the required water treatment quality standards set to achieve high contamination rejection rates

(25). To fabricate a nanocomposite membrane of such superior quality (28), research studies have examined and took cognizant of the fact that the synthesis methods of such membranes will play a major role in preserving the structural properties of materials. Making changes to the synthesis methods produced different types of morphologies as well as the thermal, optical, and electrical properties of nanomaterials, according to a detailed study of the fabrication process of nanocomposites by Tewari (2015) (25), and it was noted that understanding the structure-property relationships of nanocomposites relies deeply on the surface area per volume of the reinforcement materials applied in their preparation (25,29).

2.3.1 Different types of nanocomposite membranes synthesized.

The search for a highly durable, corrosion resistance and good separation performance nanocomposites membranes has resulted in the creation of nanocomposites that are categorized based on the kind of matrix and reinforcing components that were utilized throughout the synthesis process. Several different kinds of nanocomposites have been developed because of the above-mentioned innovation strategy, which largely depends on the kind of matrix materials utilized (25)

- Ceramic matrix nanocomposites (CMNCs)
- Polymer matrix nanocomposites (PMNCs)
- Metal matrix nanocomposites (MMNCs)

2.3.2 The predominance impact possessed by nanocomposite membranes.

The underlying trade-off which exists for modern day use polymeric membranes is between the rate of permeation as well as its salt rejection efficiencies (25). The effective means of exploiting the flourishing opportunities in the field of liquid/gas separation including its application in other fields such as medicine and energy sectors provide greater interest within the research and scientific communities to put more efforts in the identification of technological breakthrough membrane materials that will adhere to the current requirements and future potential in terms of providing superior service within the wastewater treatment markets. The

emphasis is on the technical objectives which these innovated membranes will achieve rather than its traditional role of separating gas or liquid ions (25). With growing interest in membranes that have been fabricated from less traditional methods, assessing the impact brought by such membrane types becomes vital. A special class of such innovated membranes is the ceramic membranes which are microporous type of membrane used in the ultrafiltration and microfiltration solicitation. The conceptual design should phase in the trade-off between solute rejection and filtration capacity of the nanocomposite membrane to be fabricated (22). The mechanically robust and durable nanocomposite membrane should be able to overcome technical limitations during operation such as concentration polarization, compaction, and antifouling characteristics (25). To achieve such high-quality parameters, nanocomposite membranes are composed of inorganic matrix components embedded within organic phase solutions to form rigid ceramic structures hosted by traditional polymer membranes (25,27). The main advantage of such materials lies in their predominant degree of uniqueness which renders their application suitable for improving structural properties of the conventional membranes (17,30).

2.3.3 The major challenges faced during the fabrication of nanocomposite membranes.

The refinements made to ensure that nanocomposite membranes achieve high heavy metallic ions removal rates and high permeations, however, are coupled with major shortcomings. The uncertainties associated with innovation makes it difficult to accomplish the set objectives for such membranes. During the assembly of these membranes, interface defects are likely to occur due to weak polymer-particle adhesion (25). The defects could in turn affect the fabricated nanocomposite membrane surface properties. Such defects have ability to create voids and form agglomerated particles on the host polymer membranes leading to poor surface morphologies and deficient separation performance (25,31). The degree to which the nanofiller material interacts with the polymer matrix greatly influences the separation performance of composite materials (25). Therefore, weak formation of amide bonds to couple with the aromatic rings within the formation of nanoparticles will bring about decline in the properties of the nanocomposite membrane, as well as create pore blockages amongst the nanochannels meant to transport water (31).

2.4 Thin film nanocomposite (TFNs) membrane

One of the most important performance gains from customized innovation on membrane technology lies in the fabrication of ultra-thin barrier layer membrane that has the capacity of separating organic and inorganic pollutants from wastewater without undergoing extreme fouling on the surface of the membrane (32). Thin film nanocomposite (TFNs) membranes are amongst the most productive membrane technologies (32). TFNs membranes comprises of ultra-thin barrier layer, usually fabricated with PA (polyamide) serving as a more porous supportive layer (25). These membranes are tailored via three components system whereby a polyester non-woven web consisting of hard and smooth surfaces as well as a bolstered polymeric asymmetric support, which is fabricated in a phase-separation process (33). To overcome the technical challenges this membrane, possess; surface polymer is cast onto the polymeric membrane's surface; that is often accomplished by creating a thin active skin layer of TFC membrane, which is strengthened by adding sulfonic acid groups. This helps to improve the TFN membrane's mechanical stability (34). The membrane is interfacial tailored NF and RO membrane utilized for removing impurities in wastewater such as seawater, heavy metals, and organic micro pollutants such as pesticides (25). Throughout the past 30 years, numerous attempts have been made to improve TFC membranes' water flux, solute rejection, and antifouling qualities. The intention was to design TFN membrane that will suitably select or change the supporting layer, that would serve as an aid in improving the polymeric membrane properties (35–37). This might be accomplished by applying chemical and physical changes, modifying the barrier layers, adjusting the interfacial polymerization (IP) settings, and changing the monomers (34). The inherent trade-off between adsorptive capacity and selectivity undoubtedly limits the separation performance system's results (34).

2.4.1 The improvement strategy for mitigating chlorine attack on TFC membrane.

One of the keys to obtaining better performance from the nanocomposite membrane is the elimination and reduction thereof of the likelihood of degradation by strong oxidants such as chlorine (25). The lifespan of the TFN membranes needs to be sustained and therefore it becomes paramount to anticipate the situation whereby undesired deterioration of the surface properties of the membrane could occur (33,38). The continuously improved membrane technology for TFNs is renowned for its superior quality in terms of enhancing separation performance, achieving high solute rejection rates and good permeation rates (7). The complex matrix membrane should thereof mitigate the risk of chlorine attacks which according to

research is likely to occur within the amide linkage in PA-TFC membranes (25). To create a scalable and ideal separation membrane structure, the improvement method used in the TFN design should overcome membrane chlorination and fouling of polyamide membrane layers (7). Among the strategies deployed by several researchers to aid chlorine resistance of polyamide nanofiltration, the establishment of nanomaterials onto polyamide structure will exhibit new features to design chlorine-resistant membranes (25). The addition of specific functional groups to the amide structure will create a compatible thin film nanocomposite membrane which will be stable while reacting with chlorine (25). The emphasis is mainly on the amide bond formed during the interfacial polymerization stage in creating a well-balanced thin film layer, mainly because it is the main target for chlorination. It is vital to introduce new amino groups as an improvement strategy to protect the polyamide structure, because active chlorine possess the potential to deteriorate the PA membrane structure and decrease its performance and ultimately reducing the service life of the membrane severely (39). Protecting the PA film's chlorine-sensitive areas, like the amide nitrogen and aromatic rings, is the hallmark of ongoing modification for the PA thin film layers (39).

2.4.2 The effects of antibacterial properties on TFN membranes

Developing a mixed matrix thin film membrane with high-strength, non-toxic smooth surfaces, channels, and the capacity to hold onto contaminated materials was the aim of having researchers decide to work on membrane separation technology (21). Worldwide, researchers are working on continually improving the membrane lifespan by ensuring that it contains finely balanced characteristics (5). Using antibacterial and biocidal compounds to boost the biofouling capabilities in nanocomposite membranes was used another creative approach (25). Many factors contribute to the creation of biofouling such as the presence of surplus organic, inorganic colloidal and biological particles in the feed (33). Based on membrane fouling, the degree to which contaminants assembles on the membrane surface gives rise to multiple problems regarding the retention and capture of organic and inorganic compounds (33). The challenge imposed by such level of biofouling can be mitigated and resolved via cleaning as well as application of strong shear force towards foulants on membrane surfaces (40). High concentration of inorganic contaminants, pore blocking, cake formation and biomacromolecules formation on the membrane surface has been reported to result in huge decline in water flux, selectivity, and entire performance of nanocomposite membranes (41). The reconstruction of thin film nanocomposite membranes in a framework that minimizes bacterial adhesion, inorganic precipitation, and pore blocking was crucial (33).

2.4.3 The improvement of TFN membranes' thermal stability.

Another advanced manufacturing technique for increasing the thermal stability of the TFN membrane involves the insertion of silica nanoparticles into the PA thin-film layer (42). Stronger electrostatic and steric reactions between the silica and PA in the changed polymer network structure will be the outcome of this modification technique, according to research work done by Tewari (2015) (25). The rate of thermal decomposition has been noted to decrease with an increase in the doping quantities of inorganic nanofillers (42). The introduction of nanofillers increases the heating capacity of the TFN as well as restricting movement from the polyamide macromolecular chains due to stronger bonds formed in the process (25). To improve efficiency as well as reducing the pore blockages of TFN membranes, researchers have noted that manipulating the membrane to adopt a much robust structure with improved properties, the insertion of zeolite (NaX) into the polymer matrix will enhance filtration performance as well as improve its thermal stability (25). An advanced understanding of nanofiller and PA structure with different polymer matrices, illustrating new material combinations for the much-improved state-of-the-art polymer membranes.

2.4.4 Effect of antifouling properties

It is necessary to consistently improve the quality of the TFN membranes to provide superior value within the wastewater treatment industry. As the complexity and different types of wastewater contaminants emerge, the need for continually improved thin film membranes becomes paramount. Polymeric membrane fouling has consistently been the bottleneck that restricts wastewater system efficiency by decreasing water penetration flux, negatively affecting the water quality as well as elevating energy usage (43). In practice, the fouling is caused by pore blocking, organic adsorption as well as the cake formation, which could eventually lead to everlasting flux decline (34). The emphasis is on building a technology that will enable formation of strong hydration layer onto the polyamide layer with the goal of minimizing direct adsorption of the foulants onto the polymer surface during the heavy metal ion separation process (35,36).

2.4.5 Consequences of the trade-off between selectivity and permeability.

Producing the membrane's physicochemical characteristics such as its hydrophilicity, porosity, cross-linking and charge density – to meet the membrane quality standards is the most crucial part of the entire nanofiltration process to achieve great separation (30). Advances in separation efficiency of the TFN membranes is extraordinarily impacted by the structure and chemistry of selected nanofillers (33,37,44). Despite the exceptional separation performance and stable

structures, the PA TFC membrane continue to be associated with the trade-off between permeability and salt rejection. A stable bonding between the nanofillers and TFN must be orchestrated to improve the membrane's separation efficiency as well as inhibiting fouling which can cause low salt rejection (21). In addition to improving the physicochemical properties of TFN membranes, various strategies aimed at improving permeability needs to be implemented. The strategy should have the potential to combat the trade-off relationship between permeability and selectivity. The underlying value system of trade-off relationship observed for polymeric membranes is to overcome the selectivity and permeability ratio. The work in process should result in solute rejection rate remaining abt equal to ratio when the water permeability is improved (33,38).

2.5 Graphene – oxide TFNs

The continual improvement of Graphene has become the cutting-edge addition used in the design and development of nanocomposite membrane systems to increase their hydrophilicity and antifouling membrane characteristics (25). According to Jia & Wang (4), GO embedded thin film nanocomposite membranes are potentially used for a wide variety of application such as water purification, gas separation, and polymer composites. GO is made up of epoxy and hydroxyl functional groups on the basement planes of the membrane, in inclusion to the carboxyl and carbonyl groups which are situated at sheet edges, and it provides breakthrough innovation, which is mechanically strong, good selectivity, high-flux, ultrathin, and fouling resistant membranes (25). Research has shown that such scientific developments of embedding GO thin film nanocomposite into polyamide layer (PA) has yielded great impact within wastewater treatment technology as the innovation has led to increased water permeability, chlorine resistance without incurring salt losses as well as anti-biofouling property (45).

2.5.1 Background of Graphene Oxide and Graphite oxide.

The discovery process concerning the overall study of graphite and its derivative graphene oxide emerged through intensive research studies conducted by chemist B.C Brodie in the year 1859 (46). The research focused mainly on the reactivity side of the flaky raw graphite material with the pioneering work regarding the treatment of graphitic powder in the presence of concentrated HNO_3 and KClO_3 which eventually led to the high overall mass yield of flake graphite producing graphitic oxide composed of elements such as carbon, oxygen, and hydrogen (47). The traditional view focused on studying the reactivity mechanism of graphite, identifying its structure as well as examining its crystal lattice form. The first innovation began when Staudenmaier commenced with optimization work on the method utilized by Brodie (47).

The major improvement on Brodie's work was the introduction of concentrated sulfuric acid as extra additive on the oxidizing agents used by Brodie (47,48). The shortcoming on the synthesis method introduced by Brodie had major drawbacks that resulted in lengthy reaction times coupled with environmental hazards in the release of heavily contaminated toxic gases (47). The quality of the product formed from Brodie's method was dispersible in pure or basic water however not soluble in acidic media, therefore negatively impacting the nature of the reaction and material formed (49). Staudenmaier work emphasized on suppressing the side effects of the Brodie's reaction mechanism by reducing the release of toxic gases (46). This was a structured improvement method where concentrated sulphuric acid was added into reaction mixture of potassium chlorate and multiple aliquots solution with the aim to increase the acidity of the mixture (47). After such innovation, in 1909 researcher Charpy revealed his work where graphite oxide was assembled in one step procedure (46). The overall work done by Staudenmaier and Charpy had an impact on the extent of oxidation and the structure of the product formed. The disadvantages of the above-mentioned methods were that they were time consuming and hazardous (50). Renowned researcher Hofmann worked on some major adjustments regarding the graphite synthesis procedure to improve on the major drawbacks encountered by the earliest research work done on the subject. In the year 1937, Hofmann used concentrated sulphuric acid blended with mixture of Potassium chlorate (KClO_3) and nitric acid to form graphite oxide via the oxidation of graphite (47). This research output from Hoffman gained a bit of acknowledgement and was therefore implemented by several researchers for different applications (50). Proceeding all these stages of research development regarding the synthesis of GO by different researchers, a much improved and well innovated synthesis procedure was examined and published by well-known author in this field of study known as Hummers (46). The earliest conceptual phases for developing successful GO synthesis methods were hindered by the side effects such as air pollution and hazardous impact on environment (46,51). The revolutionized Hummers method for synthesizing GO took cognizance of the disadvantages which other methods had and accomplished great advantages over the previous techniques. With the adjustments that Hummers introduced, the reaction completion time was reduced as compared to other methods, as well as achievement of high reaction efficiency and safety (46). The hummers synthesis method resulted in the replacement of KClO_3 with the use of potassium permanganate that was employed to improve the reaction safety as well as avoiding the modification of explosive ClO_2 (47,52).

2.5.2 Structure of Graphene Oxide.

The construction of GO is highly irregular, and the absolute structure is dependent on the preparation conditions (47). The morphological pattern for the GO structure cannot be attributed to any molecular formula and its assembly does not conform to any given form or structure (53,54). A structure in which no unambiguous model has been formulated, the operative oxidative mechanism for manufacturing GO throughout the years has been refined to produce the same product which displays highly variable morphologies (47). However, for the most part, the motivation behind the variability in GO construction lies in the complexity of the material based upon its amorphous, berthollide character (55). The level of technical complexity regarding the formation of GO can be attributed to its nonstoichiometric atomic composition, amongst others being the lack of explicit analytical techniques for characterizing such materials (47). It is important to understand the distinction amongst different types of GO (49). The distinction could be well explained via the type of functional groups present (47). The carbon nanostructure has been greatly examined owing to its unique properties, such as adsorption of organic dyes and metals, degeneration of organic and inorganic molecules as well eliminating microbes. The functional groups present on this carbon nanomaterial namely hydroxyl, carboxyl and epoxide functional groups located on the edges and basal planes as indicated in figure 1 below presents a remarkable opportunity to create functional nanocomposite materials with improved hydrophilicity, antifouling qualities, and great chemical stability; all which could resolve the technical limitations when exploited within the water treatment processes (18).

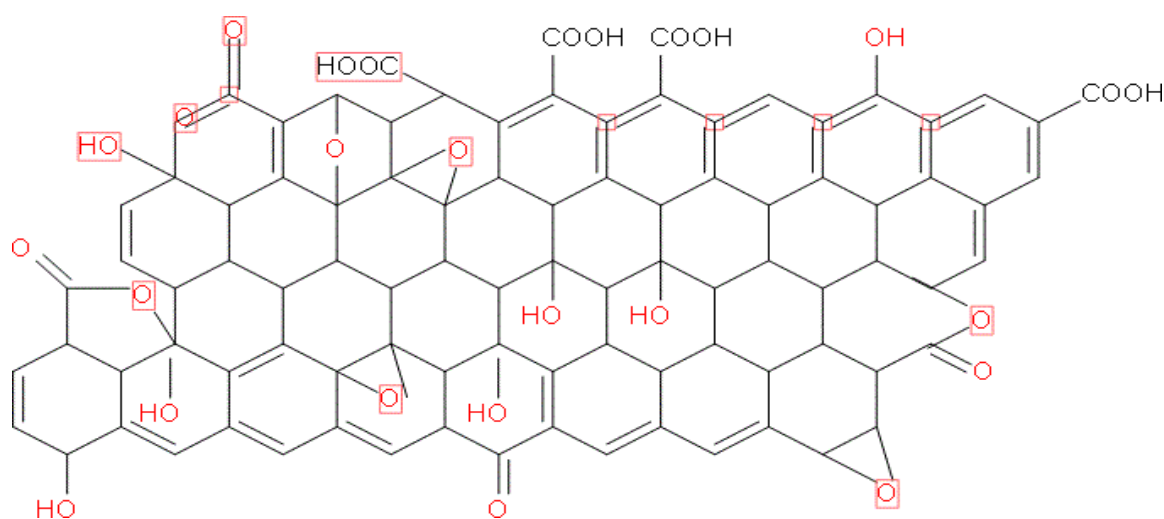


Figure 1 Structure of oxidized GO: Reproduced from this source (56).

2.6 Examining the separation performance of GO membranes.

The complexity of the separation mechanism for membrane technology encompasses the need to assess the control aspect of multi-layered GO membranes (7). The procedure for contaminant separation is associated to Donnan exclusion principles and molecular sieving which operate as same principle as traditional nanofiltration membranes (7). The objective is to achieve good permeability rates while maintaining high solute rejection efficiencies (21). The laminar channels as well as their charge properties determine the selectivity procedure of the thin film membranes (7,57). There have been tremendous changes towards the membrane structural benefits for separation performance, as it has been noted via experimentation that via vacuum filtration, higher salt rejection was obtained as opposed pressure filtrated and evaporation assembly methods (58). The uninhibited interpenetration of water molecules in multi-layered membranes are mostly linked to the functional groups in charge of preserving the non-oxidized areas and the wide distances between the GO laminates (7).

2.6.1 Modifying the thickness of multi-layered GO membranes.

The permeability of the thin film modified membranes is largely influenced by the thickness of the coated layer (7). It has been noted through numerous research work conducted that the material's chemical and physical characteristics strongly influences membrane performance (8). The rate of water flux is very slow in membranes, which have been assembled with greater thickness of GO laminates. The elements influencing the thickness of the membrane are very complex for thin film membranes assembled via layer-to-layer method as well as vacuum filtration (7), in general, however, an increase in the number of inorganic particle layers has substantial ability to enhance the penetration resistance and selectivity of the cations and anions which are being adsorbed in the nanofiltration process. The main objective for adjusting the thickness of GO membrane is to increase the ratio of separation for various ions and molecules. According to thorough research studies conducted by Jia & Wang (59), it was found out that this could only be achieved through continuously altering the quantity of stacked GO sheets during the preparation process.

2.6.2 The effect of crosslinking on multi-layered GO membranes

The justification for functionalizing GO before proceeding to the development of multi-layered membrane lies in providing quality and superior performance modified nanocomposite membranes (7,60). The main advantage of adding nanoparticles is to improve the membrane hydrophilicity, permeability, selectivity of contaminants as well as antifouling characteristics (23). There are different ranges of monomers being utilized to bring about great effect to the d-

spacing or laminar channels created within the network of interlayer nanocapillaries (61). The different sizes of the crosslinking agents bring about different innovative separation capacities and efficiencies regarding adsorption of contaminants (7). Therefore, the degree of crosslinking not only provides greater surface area for adsorption sites but however control the flow of molecules and ions across the multi-layered membranes (7). The enormous discrete surface area and two-dimensional multi-layered structure of GO are claimed to give a quick mass transfer property as well as high adsorption capacity (62).

2.6.3 Alteration of GO nanosheets to tailor-suite the multi-layered GO membranes.

The most fundamental aspect concerning the alteration of GO nanosheets lies in the complexity of the pore formation as well as the nano-channels created whilst fabricating the multi-layered GO nanocomposite membranes (7,21). The balance between the pore formation formed by the added GO nanoparticles onto host membrane as well as the nano-channels created will thus bring forward the greater permeability to separation ratio of the solutes contained in the wastewater solution. The GO dispersed onto the polymeric membrane surface is negatively charged due to the presence of carboxylic groups, which gives the membrane hydrophilic properties. One of the better ways to induce hydrophilicity and higher chargeability, which according to researchers has higher chances of improving permeation and separation performance of GO membranes (7). Many factors contribute towards the accomplishment of nanofiltration separation performance-oriented goals includes addition of other functional groups, such as sulfonic groups (7,21).

2.7 Membrane Separation Process Technologies

2.7.1 Microfiltration

To control the problem caused by effluent discharge emanating from municipal and industrial wastewaters, microfiltration membranes are utilized to eliminate impurities, viruses and colloidal substances that falls under size range of 0,1 -10 μ m contained within solvents present in wastewater (12,63). This type of membranes operates via a sieving mechanism effect where particles are separated based on their sizes (64). The process separation technology mechanism is built to control the pore size, thickness, and porosity of the membrane via manipulation and functionalization of the organic solution embedded within the polymer matrix to help achieve better permeate fluxes and heavy metal retention (63). In such operation, most of the contained species are mostly colossal by several magnitudes when compared to the filtrated species. The microfiltration membrane module was first commercially developed in 1960 by scientist Bechold and was tested within the biological and pharmaceutical industries. Micro porous

pressure driven membranes are used to separate particles from solution by size exclusion mechanism. The pore sizes range from 0.1 to 3 microns as shown in figure 2 below (64). The operating pressure ranges from 0.2 to 3.5 bars. Microfiltration is affected mainly by flux decline that occur because of fouling and concentration polarization (65). Despite the disadvantages of the membrane which owes to its configuration which permits the accumulation of the particles within the inner side of the microchannels, forming a deposited cake layer of retentates which prohibits greater volume of permeate flux (65). The average flux is greater than $200 \text{ Lm}^{-2}\text{h}^{-1}$ and it does not depend on the membrane type but on nature of the feed (65). This membrane type is made from synthetic polymers such as cellulose acetate, polyvinylidene difluoride (PVDF) and polycarbonates (64). The porosity of the membrane varies significantly with the addition of different loadings for cellulose acetate and its derivatives such as diacetate and triacetate (64). However, before 1960's the membrane microfilters were largely fabricated using nitro-cellulose and cellulose esters. The cellulose rich type of membrane is composed of polysaccharides that has regular repeating structure that can create strong intermolecular hydrogen bonds between the hydroxy groups. The different methods used in the synthesis of microfiltration membranes includes stretching, phase inversion technique, sintering and track-etching (Hakami *et al*,2020). The process capabilities possessed by such membrane type renders it a more versatile membrane as it can reject a wide array of large-scale contaminants (64).

2.7.1.1 Application for Microfiltration

Microfiltration is a technique of choice and highly regarded separation process for industrial applications where particles of a size greater than 0,1microns are removed from wastewater solution using microfiltration membrane (65). The advent of these membranes type dates to the 1960's, where the technological breakthroughs were salient, but application was limited to small scale industries. Scientific developments have led to commercialization of this membrane technologies into other fields such as biomass sedimentation using membrane bioreactor and tertiary treatment of municipal wastewater for reuse, as well as the recovery of inks, textile sizing and electro deposition of paints (66). Sterilization and clarification of all kinds of beverages and pharmaceuticals (66).

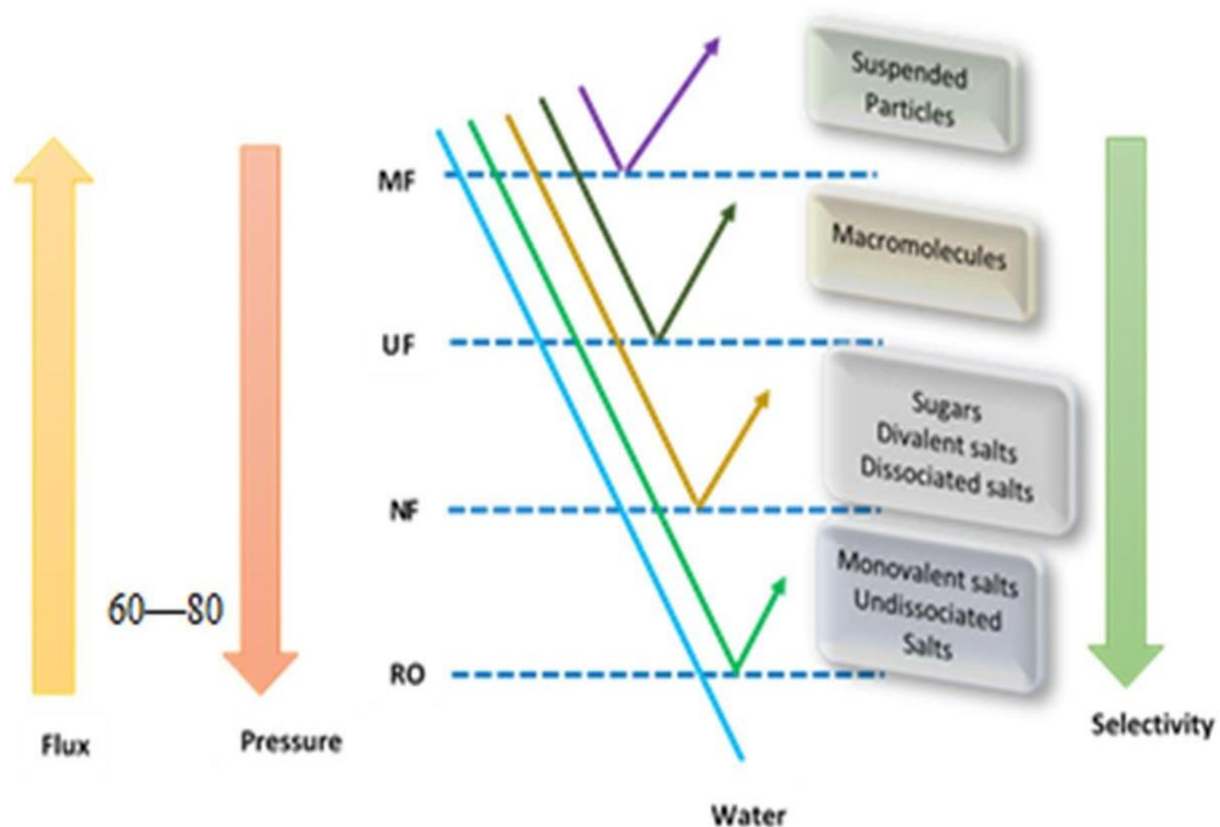


Figure 2 Size range for filtration separation processes (67)

2.7.2 Ultrafiltration

It is a membrane process that lies between nanofiltration and microfiltration. It separates particles and high molecular weight soluble species from solution using pressure driven micro porous membranes. The pore sizes range from 0.005 to 0.1 microns as shown in figure 2 above. The operating pressure ranges from 30 to 150 psi with optimum pressure ranges from 30 to 75 psi. The pore sizes are small results in high rejection of solids and bacteria. Ultrafiltration (UF) in a tubular module is used for bulk removal of suspended solids prior to RO treatment (65). High-grade PES was used to make UF membrane (68). A hollow fiber membrane that is very stable and less susceptible to breakage is made from seven-pore membrane fibers material (68). The membrane's strength is increased by the thick layer of skin that forms a double layer on the inside and exterior (65). The membranes are assembled in one bundle firmly rooted onto potting resins and is protected by PVC housing (65). The ultrafiltration membranes' fouling resistance is enhanced by the hydrophilic nature of their surface. Uniform pore size and inside-out flow of UF membrane creates a barrier without sacrificing membrane performances (65). The double walled hollow fiber membrane of UF membrane with very small pore diameter

effectively removes the particulate matter, bacteria, colloids, and some viruses. High membrane porosity results in stabilized flux like that of NF despite the small-pore diameter. The permeate flow rate is constant while the trans membrane pressure (TMP) increase over time and front and back flushing is used for module cleaning (65).

2.7.3 Nanofiltration

The function of the nanofiltration fabricated membranes is to provide exceptional separation of inorganic pollutants ions contained in wastewater. The nanofiltration process dates to the late 1980's where it was introduced to permit some ionic solutes selectively and purposefully in feed water to permeate through (19). The process, however, had significant drawbacks concerning its mechanics and structural properties of materials used to fabricate the nanofiltration membranes (58). The relentless improvement movement began after the disadvantages of nanofiltration system had been examined. Several factors can inhibit the productivity of the nanofiltration process, including the archetype of solute being used, pH value and temperature (7).

One of the greatest obstacles faced by the nanofiltration membrane process is the pollutants rejection rates which affects the quality of the permeate solution (7). The effectiveness of the nanofiltration membrane is measured on the amount of solute rejection per amount of solvent being filtered. Nanofiltration membranes typically consist of MWCOs of 200-1000 Da for dissolved organic solutes and sodium chloride (NaCl) rejections between 20% and 80% (27). Nanofiltration entails the molecular separation method that takes place within the separation ranges of ultrafiltration and reverse osmosis ((65). Furthermore, the pressure driven membranes are either negatively or positively charged, which influences the membranes separation mechanisms that are governed by Donnan exclusion (charge repulsion) principles and size exclusion (7). Substantial research done on the nanofiltration process was to precisely select the areas of improvement to which most development and optimization requirements was to be met. The strategy was to refine the material composition and structural properties of the existing nanofiltration membranes as those factors strongly affects membrane performance (69). Numerous different processes have been utilised to improve the nanofiltration process, possessing state of the art thin film composite structure (TFC) structure (70). The improved process establishes starting point for system improvement in the configuration of a thin rejection polyamide layer, as well as the key element in process being the porous substrate layer (membrane), as well as non-woven fabric support (37). The objective is to produce a nanofiltration membrane of exceptionally high performance (34). It is very important to design

a process that will meet the performance requirements in terms of what it is meant to do (34). It is imperative to determine the correlation between the process capability and its optimization standards. The TFC membrane structure is designed in a format which allows for independent optimization of rejection and support layers, which in turn provides greater flexibility regarding the design of high performance of nanofiltration membranes (70,71).

The application of the above-mentioned filtration process takes center stage within the separation of heavy metallic ions, the withdrawal of natural organic matter, the softening of water as well as organic solvent separation processes. The performance of this nanofiltration process system which utilizes GO membrane is influenced by varying process parameters such as pH, solute concentration as well as temperature of the solution being treated. A change in any of these parameters has been reported to bring about changes to the performance of the membrane system. Research has outlined that higher pH solutions being treated incurred lower rejection rates whilst utilizing nanofiltration induced membranes (72).

2.7.3.1 Nanofiltration polymeric membranes

When assessing the produced nanofiltration membranes capacity for metallic ions separation processes, the strength of the polyamide layer is critical factor assessed in terms of its durability, quality, and ability to adsorb heavy metallic ions (70). Regardless of the evaluation of the thin layer formed on the polymeric membrane, another factor which should be considered is the limited trade-off between membrane permeability and selectivity (5). It is therefore necessary to identify areas which would require significant quality improvements for polymeric nanofiltration membranes, and certain mechanisms are investigated to improve the efficiency of the polymeric process. To achieve the quality standards for polymeric nanofiltration membrane, the mechanism employed involves the multi-step interfacial reaction between the nanomaterial used GO and its addition into the aqueous/organic phase solution to form thin film nanocomposite polymeric membrane (19). The main aim is to develop improved nanofiltration membranes for efficient heavy metal removal contained in wastewater, and therefore the integration of nanomaterials in the surface grafting of the polymeric NF membrane being fabricated has beneficial functions such as creation of vast nanochannels for water transport, as well as antimicrobial properties (2). Strategies in this stage are implemented to add value and improve process capability of the fabricated polymeric nanofiltration membranes via the construction of the interlayer which occurs within the host (substrate) membrane. In this interlayer region, water shows dynamics, which involves the rotational and transactional motions that get reduced within the grafted polar surfaces of the host membrane

as it encounters the strong interaction of the attached functional groups (73). The rationale for construction the interlayer space before the Interfacial polymerization stage was to produce a good fit separation membrane. Before the nanofiltration membrane process could be improved, its major challenges were understood and technical limitations were identified as factors that could cause special causes of variations regarding permeability and selectivity, therefore the incorporation of these polyamide layer via surface grafting process can be deemed viable solution strategy. The use of this solution strategy ensures better-quality polyamide rejection layer as well as optimized conditions for nanofiller utilized which would ensure improvement in permeate flux of the synthesized membrane and improvement in the antifouling properties (8,23). It is desirable to increase the rejection of solutes contained in wastewater during the membrane separation process, and this newly improved thin film membrane are engineered to break the longstanding perm-selectivity trade-off effects (74). Consequently, the emphasis placed on the TFN structure also highlights the importance of the addition of sulfonated groups during the coating of the polymeric membrane (75). The negatively formed charged thin film membrane has been reported to add superior value in terms of solute retention because of electrostatic repulsion during filtration (76,77).

2.7.3.2 Nanofiltration ceramic membranes

The heart of nanofiltration is to fabricate superior quality membranes which possesses robust structure, average pore size dimension which will not affect membrane porosity and its permeability as well as the percentage of volume of voids compared to total volume of membrane (23). Non -polymeric membranes (ceramic membranes), contains superior physical and chemical properties as compared to polymeric membranes (70). The actual format for this type of membranes doesn't differ much when compared to polymeric membrane in terms of the mechanics and structural compositions. The ceramic membrane has an average pore size dimension ranging from 1 – 2nm which is the standardized dimension to achieve high removal of contaminants (78). The novel nanofillers used in the fabrication process of ceramic nanofiltration membranes has drawn huge interest in the membrane separation industry (19). The promising ventures possessed by this nanofillers is their ability to create interlocked layered structures whilst grafted on polymeric membrane surface, leading to a dynamic and improving nanochannel spacing within the fabricated thin film membranes with controllable thickness which will in turn help the industry in its drive to achieve high solute retention and clean water (79). However, ceramic membranes mostly suffer from poor separation, chlorine resistance and other technical drawbacks such as fouling. Several research studies conducted

on numerous nanomaterials such as metal organic frameworks (MOF), zeolites and carbon-based materials have been demonstrated to contribute towards continual improvement of physicochemical membrane properties (79). The 2D nanomaterials, such as GO, the nanofiller utilized in this research, possess vastly large surface area and is rich in oxygen containing functional groups within its peripheral and basal edges (56). It is necessary to further explore the advantages of this nanomaterial as it has been examined to have a remarkable effect on the adsorption of cationic compounds (56). The TFN problems could be addressed via the incorporation of those nanomaterials onto the PA layer as its likely to improve both water flux and rejection of heavy metallic compounds contained in wastewater (80). The most difficult challenge posed with the incorporation of carbon-based materials such as GO, is the challenge of disseminating them homogenously onto the substrate membrane surface (80,81). During the coating stage of nanofiller onto the substrate membrane and polyamide layer, the GO based on its properties tends to agglomerate due to high concentration of the material used or inability to achieve uniform distribution above the surface area of the membrane (82). This process deficiency tends to cause breakdown in membrane performance and eventually bring about discrepancies in expected results such as decreased hydrophilicity and water flux (80,83). A problem of such nature may cause havoc to the entire fabrication of nanofiltration membrane, and it becomes pivotal to reduce the agglomeration of nanomaterials via the attachment of functional groups which will permit for successful dispersion of the GO and carbon-based nanomaterials. The three different classes of ceramic membranes are discussed below:

2.7.3.2.1 The sol-gel method to fabricate metal oxide membranes.

This type of membranes possess similar structural composition as reverse osmosis metal oxide however contains no selective top layer (25). The following steps are utilized during the preparation for ceramic membranes, as stipulated in figure 3.

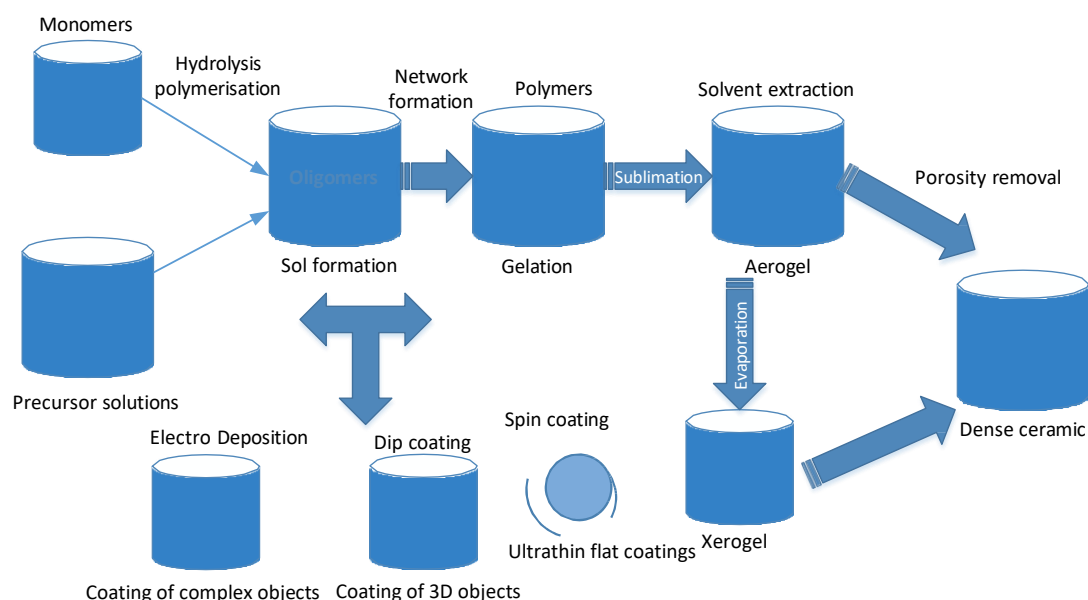


Figure 3 The different techniques utilised in the sol-gel process (84).

2.7.3.2.2 The layer – by – layer (LbL) fabrication technique to fabricate carbon based ceramic membranes.

This assembly technique is one of key improvement strategies applied to nanofiltration membranes and it involves the bonding of multiple layers onto the membrane surface. Numerous research work done recently is focused mainly on achieving finely balanced characteristics for nanofiltration membranes (5). This fabrication technique involves immersing nanoparticles into organic solution which either contains positively charged ions or negatively charged ions. The mixture undergoes sonication prior to assembling it onto coated host polymer conventional membrane to create a much-improved nanofiltration membrane as illustrated in figure 4. This technique can assemble thin film membranes charged at molecular level (57). The typical nanomaterials utilised in this process are polyanions and polycations which can be hoarded onto the substrate through electrostatic interactions.

GO is a suitable material for layer-to-layer self-assembly technology based on the existence of laminar structure and charged oxygen- containing functional groups. In this research study, the layer-by-layer self-assembly approach was utilised.

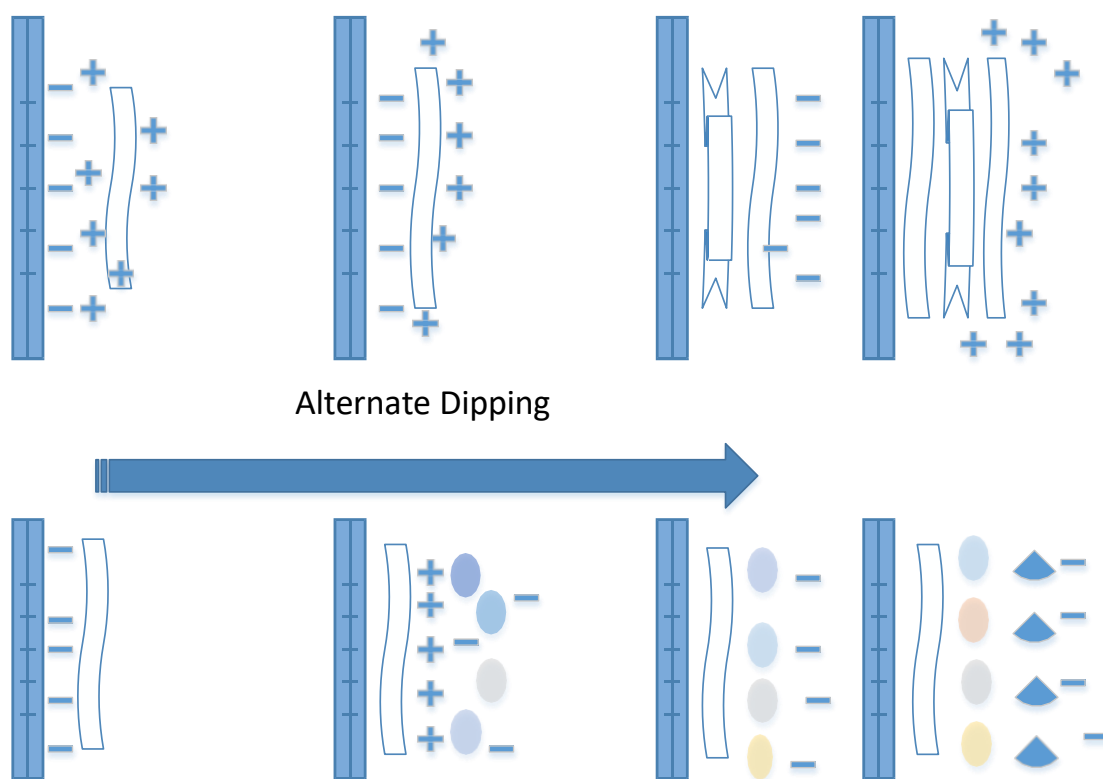


Figure 4 Schematic diagram of the layer by layer (LBL) assembly. Adsorption process for polyanions and polycations.

2.7.3.2.3 The dip Coating assembly method.

This type of membrane fabrication method is amongst the least utilised by researchers however it is still technically feasible to assess its advantages and disadvantages. According to Wei *et al* (7), the precipitation process is simple and direct. When compared to the other two preparation methods, the casting and dip coating assembly method possesses a broader range of substrate choices, especially in cases where the GO membranes are not going to be supported by any host polymer membrane. (2) synthesized GO exfoliates on copper foils via coating technique and engraved them to obtain a freestanding GO.

2.7.3.3 The impact of fouling in nanofiltration membranes

To attempt assessing the separation performance of nanofiltration membranes without considering the effects of fouling is to invite failure (85). After the advent of membranes, fouling has been a congenial bottleneck that inhibited the nanofiltration process efficiency via the reduction of water permeation flux, causing deterioration in the quality of permeates achieved as well as increasing energy consumption (25). One of the main goals for fabricating nanofiltration membranes is to achieve high separation efficiencies, however, severe fouling is a detractor as it leads to high hydraulic resistance during separation process due to blockages caused by foulants contained in wastewater feed which sticks on the surface of the membrane leading to an increase in operational pressure as well as decrease in solutes rejection (70). Much emphasis is directed on the causes for fouling which are namely, cake formation deposits on membrane surface, pore blockages that occurs, organic and inorganic precipitation and biological fouling which leads to huge decrease in flux of the permeate stream. In analyzing the nanofiltration process, the fouling dilemma is not an easy one to eradicate due to the complexity of the membrane surface structure. The incorporation of a coated layer onto membrane surface during the construction of thin film membrane becomes beneficial in terms increasing the membrane antifouling properties (86). The procedure involves the usage of typical surface coating materials such as polydopamine, sulfonated group linkages with amide bonds and polyvinyl alcohols to implicitly enhance the membrane surface hydrophilicity, which will in turn help in repelling hydrophobic foulants on causing pore blockages on membrane surface (87). The efficient fabrication of TFN membrane using nanomaterials such as GO has reported to produce strong hydration layer together with the coated polyamide layer and help minimize the unswerving adsorption of foulants onto the polymer surface during heavy metallic ions filtration process (79).

2.7.3.4 The impact of concentration polarization on membranes used in nanofiltration (NF).

The accumulation of solutes on the membrane surface has a significant influence on the decrease in nanofiltration membrane performance (19). This prompts a greater need to examine the effect that concentration polarization would cause onto membrane surface (25). The emergence of concentration gradients as shown in figure 5, accrues on the membrane surface. This phenomenon occurs as a common consequence caused by the semi-permeability and selectivity capacity of the nanofiltration membrane resulting in compilation of rejected particles in a mass transfer boundary layer adjacent to the membrane surface (19). The greatest

impact arises when the flow of permeate, and solvent molecules passes through the membrane with larger metallic ions being rejected and retained within the semi-permeable thin film nanocomposite layer (25,73). Consequently, the rejected ionic molecules remain reinforced within the pore dimensions of the polyamide layers of membrane causing a concentration gradient incline. The weaknesses associated with this phenomenon is the creation of osmotic back pressure which in turn reduces the transmembrane pressure (TMP) of the NF system.

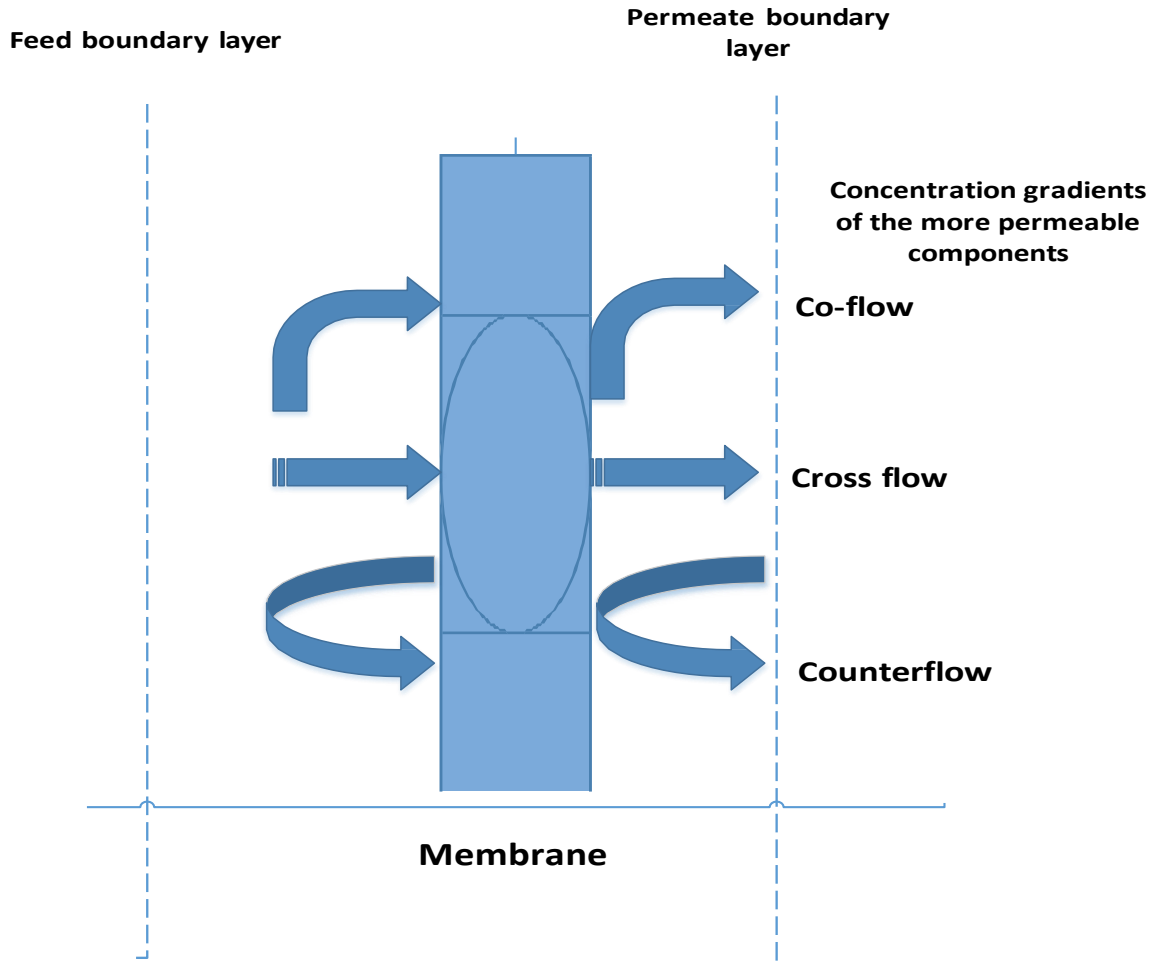


Figure 5. Different types of flow arrangements in typical membrane setting displaying the changes in concentration gradients.

2.7.3.5 The structural integrity of NF membranes.

One other critical aspect which needs proper evaluation is the membrane integrity in concerning the removal of pathogens, inorganic and organic contaminants. The nanofiltration membrane integrity is also an important aspect to consider which has tremendous influence in membrane separation performance (19). The membrane's integrity is improved via the optimization of the nanofiltration surface coating and manufacturing process, as well as establishing viable methods for monitoring the success in terms of membrane's performance (70,83). The aim for continuously assessing the defects contained in these membranes is to put counter measures in place to avoid unsatisfactory results stemming from the filtration process (88). The detrimental effect of not evaluating the structural integrity of nanofiltration membranes at the conceptual (fabrication) stage is that further along the developmental cycle, it would become very costly to repair defects. Typically, most of the operating parameters such as rate of heavy metallic ions recovery, permeate flux as well as feed pressure gets affected by

poor structural integrity of nanofiltration membranes (35,70). In the need for new approaches to resolve the nanosized defects, the regions within the polyamide layers of the membrane are regulated via interfacial polymerization reactions by adding surfactants into aqueous amine solutions, as well as incorporation of inhibitors via controlling diffusion of monomers and addition of interlayers connecting the polyamide rejection layer with the substrate (89). The membrane surface charges are key factor in forecasting the mechanics of separation performance for membranes (19). The functional groups present within the surface is pH sensitive, the existence of carboxyl and amine groups on active layer making the membranes susceptible to ionization as pH of the solution changes (89). The anticipated results are to have stronger electrostatic interactions between dissociated functional groups from materials surface creating a negative zeta potential surface which will withstand change in operating parameters such as pH, concentration of feed solution and feed pressure (19).

2.7.3.6 Nanofiltration membrane selectivity stage.

The severe impact caused by poor membrane performance has adverse effects not only pertaining to lower rejection of heavy metallic ions and severe concentration polarization effects, however, there is a health consequence which arises when there is a degrade in the standard of drinking water produced from deficient nanofiltration membrane (19). The optimization of the NF membrane surface properties such as charge, pore size and hydrophilicity are paramount in the upscaling and fine tuning of the membrane surface. This in turn helps to minimize the partition of pollutants into membrane thereby improving their rejections (19). The traditional adversarial relationship between fouling and concentration polarization yields inconsistent selectivity rates for such membrane types (90). The selectivity process becomes unstable due to the calamity of solvent build-up causing narrow nanochannels created within the nanocomposite membranes (19). Great research effort is pivotal in great need to construct a succinct and implicit chassis to conduct the optimization of nanofiltration membranes targeting for highly selective removal of contaminants found in wastewater (19).

2.7.4 Reverse Osmosis

Reis and his colleagues' whole dedication to improvement of the membrane separation process resulted in the development of reverse osmosis (RO) membranes in 1957 (65). Technological innovations developed rapidly through the 1960's when Loeb and Sourirajan fabricated an asymmetric cellulose diacetate membrane which refined the quality of the separation mechanism process (91). At that stage, the technological commercialization of component innovation that was taking centre stage began to diffuse into industry with the aim to resolve wastewater challenges (65). Reverse osmosis was then ranked amongst the fastest developing desalination technologies in the world with custom-built technological advances (65). The creation of thin films has been great part of the ongoing innovative research, which has taken centre stage in the advancement of membrane-based separation technologies filtration capacity (92). Recent RO membranes have advanced in similar fashion as nanofiltration membranes with differences being that RO has more compact structure and consumes less energy (65). The most obvious problem faced with all this membrane separation technologies is the accumulation of solutes on active layer of polyamide membrane causing a flux deterioration during operation altering the flow rate of the permeate due to pressure build-up (93). One of the many reasons why fouling and concentration polarization occurs on such membranes is due to the nature of the contaminants found in the wastewater feed which forms deposits within the porous structure and on membrane surface (25). Regardless of the technical challenges the membranes are inebrated with, the modified versions of reverse osmosis membrane cater for greater improvement in electro catalytic activity while retaining its hydrophilicity and selectivity capacity. This helps ensure a continual improvement in salt rejection on the one hand and improved selectivity and permeability on the other hand with greater impact resolving the environmental and energy issues (64). Reverse osmosis is the movement of molecules against the concentration gradient (65). A micro porous membrane was used to separate dissolved ions from a solution. The most fundamental aspect of this process, which utilizes semi-permeable spiral wound type of membranes to orchestrate the separation of dissolved solids in wastewater contaminants (94). To continually improve the filtration process used during reverse osmosis, the design technology has been suited for the elimination of both inorganic and organic pollutants simultaneously (94). The pivotal advantages of this technology reduction of effluent discharges and minimization of contaminants in wastewater, improvement in economics, safety, and easy recycling (91). The filtration application of RO and NF separation processes has attracted industrial interest and research studies owing to their superior performance when compared to conventional membranes as they are deemed to have

high capacity of metal and salt retention (95). The filtration efficiencies of both membrane processes have been a subject of study by many researchers, and it has been noted that nanofiltration membranes had higher permeate flux and adequate solutes sustentation efficiency than reverse osmosis membranes. The permeation technique was evaluated in terms of the free-volume theory of polymers or hydrodynamic flow of water through the micropores (96). The different filtration methods applied to achieve such objectives have been discussed below.

2.7.4.1 Types of filtrations.

2.7.4.1.1 Dead end filtration

There are numerous different definitions for this process, however it's the highly regarded fundamental filtration format where the inlet contaminated feed flow undergoes separation based on mechanics of the membrane utilized for filtration. This filtering procedure is carried out in batch mode, using a membrane-based filter to filter the feed water while trapping the solids behind the membrane. The residue accumulates on the membrane during filtration process resulting in pore blocking to an extent that only about 1ml of water will pass through the nanochannels or furrows formed within the functionalized permselective layer of the membranes. The advantage of such filtration system is that it follows a useful procedure for concentrating compounds (97).

2.8The importance of assessing how well nanofiltration membranes remove heavy metal ions from wastewater.

The presence of heavy metals in wastewaters has been escalating with the ever-growing expansion of industries such as mineral separation industries, metal plating facilities, fertilizer, and paper industries (98). Humans, aquatic life and the ecosystem as a whole are all seriously threatened by the concentration and spread of these heavy metals into their ecosystem and environment (1). The basic problem is to sort out the influences of these various sources of inorganic contaminants. The detrimental effect such toxic contaminants poses has led to breakthrough innovations utilized to eliminate the heavy metals from wastewaters ((98). The adoption of advanced innovation systems such as the fabricated state of the art nanocomposite membranes has led to greater certainty towards conserving humans, aquatic life and environment from deterioration and homicides (99). The toxic heavy metals of great concern include cadmium, copper, lead, cobalt, mercury, gold, manganese, iron, magnesium, and nickel. Even though these metals are found in trace amounts in the wastewater, it is paramount to remove them using this newly fabricated membranes (16). The legal requirements require

organizations to implement rapid changes regarding the disposal of such toxic contaminants and that will include the installation of effective wastewater treatment systems.

Table 1. Discharge limits standards set for each heavy metal ions.

Heavy metal ion	Typical sources	Health hazards & impact	Acceptable amounts (mg/L) Drinking and wastewater limits.
Mercury (Hg)	Landfill effluent wastewater.	Impotency for humans. Second most toxic element in the world. Affects the immune system, alters genetic and enzyme systems.	0,001(16)
Magnesium (Mg)	Reprocessing paper industries.	Taints household sink. Prohibits effective heat conduction.	
Manganese (Mn)	Paper and pulp industries as well as metal refineries.	Lung cancer.	0,4 (100)
Copper (Cu)	Worn down plumbing system, cables as electronic industry.	Affects brain problems and hematological system.	1,5 (101)

Calcium (Ca)	Paper recycling companies, Landfill leachates and citric acid production plants.	Scaling of industrial pipes and reactor vessels.	9 (101)
Silicon (Si)	Blended nickel production companies and from stainless steel plants.	Pulmonary fibrosis as well as skin problems.	0,2
Iron (Fe)	Acid mine drainage	Carcinogen to aquatic life.	2 (100)
Cadmium (Cd)	This transpires naturally in lead, zinc, copper, and other ores which emanate from surface and ground waters. Emanates from corroded invigorated plumbing and water main pipe material.	The negative impact of cadmium comprises of interferences of important body systems which could potentially lead to long- and short-term disorders.	0,003 (101)

Nickel (Ni)	This originates from the addition of chemicals into the wastewater treatment plants and released from metal cockware during cleaning.	The side effects of nickel may include dermatitis and allergies.	0,07 (101)
Lead (Pb)	Metal production is one of the main ways that lead enters the environment. Paint and Pesticides industry.	Humans who are exposed to lead on a regular basis may experience changes in their physiological processes.	0,01(101)
Cobalt (Co)	Seldom does this scattered metal element exist as a separate mineral.	The side effects of this mineral include cancer related diseases.	0,05 (102)

2.9 Adsorption of heavy metals to protect environment.

The environmental laws enacted by governments regarding disposal of inorganic contaminants mentioned in Table 1 compels industries to manage wastewater containing heavy metals to minimize their concentration to acceptable levels. The solution strategy is to recuperate the valuable materials, metals and water and obviate environmental degradation (103). The process description regarding the recovery of inorganic pollutants contained in wastewater like the heavy metals mentioned in Table 1 from acid mine drainage is known as adsorption. Over the past decades the adsorption process has evolved to a stage where it became a very important industrial separation modus operandi (103). The study of adsorption involves the distribution

of molecules between two phases, one of which is a solid albeit the other may be a liquid or gas (103). The distinction between absorption and adsorption lies in medium utilized for molecular diffusion of solutes, in absorption the solute molecules diffuse from the bulk of the gas phase to liquid phase, whereas in adsorption, the molecules are dispersed from the bulk of the fluid to the surface of the solid adsorbent resulting in a definite adsorbed phase (104).

2.9.1 The different ranges of adsorbents utilised and their impact on adsorption capacity.

The distinct types of adsorbents utilised for treatment of heavy metallic ions come in non-uniform granules, exuded pellets and formed spheres (103). The adsorbent surfaces fabricated from various materials such as graphene oxide, activated carbon and zeolites are composed of several features which entails:

- The adsorbent should possess greater surface area and have accessible pores able to permit molecules which must be adsorbed.
- The lifespan of the adsorbent is very key in sustaining its regeneration capacity.
- Another crucial component for guaranteeing the bulk handling and vibration of adsorption in industrial units is the adsorbent's mechanical toughness.

2.9.2 The nanomaterials rate of adsorption and desorption.

Adsorption provides a versatile and cheaper option, permitting for the tailoring of heavy metal ion removal to different reaction conditions with the use of wide array of materials as adsorbents (105). This process is essential in eliminating small quantities of metallic components from a liquid phase and could also be utilised either to recover the component or via complete removal of the noxious substance from industrial effluent (103). The Adsorption process is proportionally a recently developed process and is materializing as the preferred alternative regarding the removal of heavy metallic ions since it offers great flexibility in design, high-quality treated effluent and is reversible and the adsorbent can be regenerated (63). However, adsorbents with beneficial properties, for instance, fast sorption kinetics, selectivity and high capacity are instrumental for the adsorption process (6). The equilibrium capacity, or rather the rate at which desorption and adsorption of adsorbate occurs on the surface of the adsorbent concerning different molecules is amongst the main factors which affects selectivity (103). The dynamic concept involving adsorption equilibrium can be accomplished when the rate at which the ions adsorb onto the surface equals the rate at which they desorb (103). The other factors which affect selectivity is the arrangement of pores which filter through the adsorbent.

2.10 The structured Design of Experiments (DoE) method for conducting experiments.

The design of experiments is a very complicated method for experimenting with processes with the purpose of optimizing them. If you deal with complicated processes that have multiple factors affecting them, design of experiments strategy could provide the only viable practical way of bringing about improvement (106). However, the advancement of mathematical models expressing the process and how it is influenced by its variables is a seemingly difficult challenge (107). The factors which influence the process interacts with one another, however, the best strategy to understand the complexity behind the influence each factor or a combination of factors have on the outcome of any given process is to design experiments stating the different factors at given coded levels with their related outcomes (108). This methodology allows for a minimum number of experimental runs to extract significant information on the studied process. The traditional optimization approach which involved the usage of one variable at a time suffer quite a lot of disadvantages (109). Firstly, it hardly exhibits the optimal conditions in large part since the results from One variable at a time (OVAT) are hardly dependent on the starting point. Another disadvantage which arises from this methodology is its inability to set apart the inherent run to run variations of a system of a particular reaction

from actual improvement unless a huge number of experimental runs are highly repeated utilizing similar conditions (110). Whereas the DOE approach ensures there is a reduction in the numerical runs from hundreds to tens as a rule, or by an order of magnitude. This means that process experimentation allows multiple factor adjustment simultaneously, shortening the total process, but as equally as important, exhibiting complex interactions amid the design factors (106). Unlike OVAT, DoE intends to examine, plot, and design the behavior of the response within a given reaction space across numerous factors concurrently via changing all variables at once according to a predefined experimental matrix. The multilinear linear regression modelling technique is used to examine the DoE data regarding error analysis without much use of replicate experiments as opposed to OVAT time consuming and consuming process (110). The concurrent variation of process parameters save time, effort as well as precision. The number of DoE runs are defined from the onset as opposed to the traditional OVAT approach, to such an extent that quality and meticulousness of the information obtained exceed the effort placed in performing the long experiments (110).

2.10.1 Different types of Design of Experiment (DoE) models.

2.10.1.1 Full-factorial design

This type of design of experiments is easy to operate, widely systematic and structured to run, simple to analyze. It is composed of all feasible combinations of asset of factors. The drawback is that it is quite costly in experimental resources, but it is the full proof design approach.

2.10.1.2 Response surface design

This type of design is utilised to improve a complex process by setting up improved DoE techniques which provides better interpretation between the independent variables factored in the design setup. The response surface technique is widely used to process models after important factors using screening designs or factorial designs have been setup (109). The distinction between response surface design equations and factorial equations is the incorporation of the quadratic terms which allow the model curvature in the response. The design equations exhibit critical factors and reveal changes in process variables that affect the response of interest, as well as helping in establishing the levels at which the variables will have major impact regarding meeting the design outcome specifications targeted by the stated objective function from the given process. Box Behnken designs and central composite designs are the two main categories of response surface designs.

2.10.1.2.1 Box Behnken design (BBD).

The Box-Behnken design (BBD) was originated by Box and Behnken in 1980. Since its advent, BBD has been widely accepted and used by the scientific community as a functional method for expanding second-order response surface models. This is a type of response surface design without installation of factorial or fractional factorial design. It contains fewer design points when compared to central composite designs making them quite adaptable and cheaper to utilize. The Box Behnken design (BBD) contains 3-levels for each factor to be assessed unlike central composite designs (CCD) which have up to 5. It is largely established via the construction of balanced incomplete block designs and it's compelled for use with minimum of three levels for each factor. Within the experimental design setup using BBD, one factor is fixed whereas other combinations are factor levels are applied (110). The BBD design is composed of an equal number of replicates with all possible combinations of sets being tested.

2.10.1.2.2 Central composite design (CCD).

This is the most utilized response surface design, and it is a factorial or fractional factorial design with centre points, supplemented with a group of axial points which helps in estimating curvature. This response design process can approximate first, and second order terms and significantly models response variable with curvatures through the addition of focus and axial points. In the process optimization and discovering the best possible response from the independent variables or factors, the central composite design (CCD) utilizes the three-level factorial experiment to construct second order regression model (107,111). The main advantage for this type of model is the distinct level of accuracy for sequential experiments. The different types of CCD designs based on the constraints are faced central design (CCF), Inscribed central composite design (ICF) as well as Circumscribed central composite design (CCCD). This different design matrix is good over the complete design space and central subset. CCD confirms that the prediction error is similar at any point within the same distance located from the centre of the design (109).

2.10.2 Response Surface Methodology (RSM).

This type of modelling technique is utilised to resolve linear and non-linear multivariate regression models. The methodology works on empirical models and does not necessarily confirm to any given fundamental equations; however, the collection of mathematical and statistical approach is utilised to analyze the influence of combination of factors within the independent variable set has on the outcome of the process under evaluation. The relationship between the design variables as well as the response (output function) of the process is verified

by the coded model using a limited number of experimental runs. The supremacy of empirical modelling techniques over theoretical models dwells in its prospects to rapidly generate the objective function which will be deployed for process optimization. The RSM model's purpose lies in simulation and process optimization on membrane systems paramount to productive and economical designs of membrane separation processes. The manifested approach of experimentation as illustrated in figure 6 commences with standard two-level fractional factorial design. The traditional approach for experimentation states that screening designs should not incorporate factors that are known to have major influence in the system. These designs might be setup by determining half the experimental runs of the original design (109). During this phase, the investigator seeks to determine the important few factors which generates statistically significant effects of practical importance for the goal of process improvement (112,113). After the screening stage, the non-important factors are eliminated from the experimental program prior to the characterization stage. The characterization phase makes use of the full factorial design resolutions, meaning all combination of factors will be assessed for their effects on the dependent variable.

2.10.2.1 The prognostic approach to modelling using RSM.

This refers to the optimization approach that allows to influence the combination of factors which minimize or maximize a given objective function. The second order polynomial regression models.

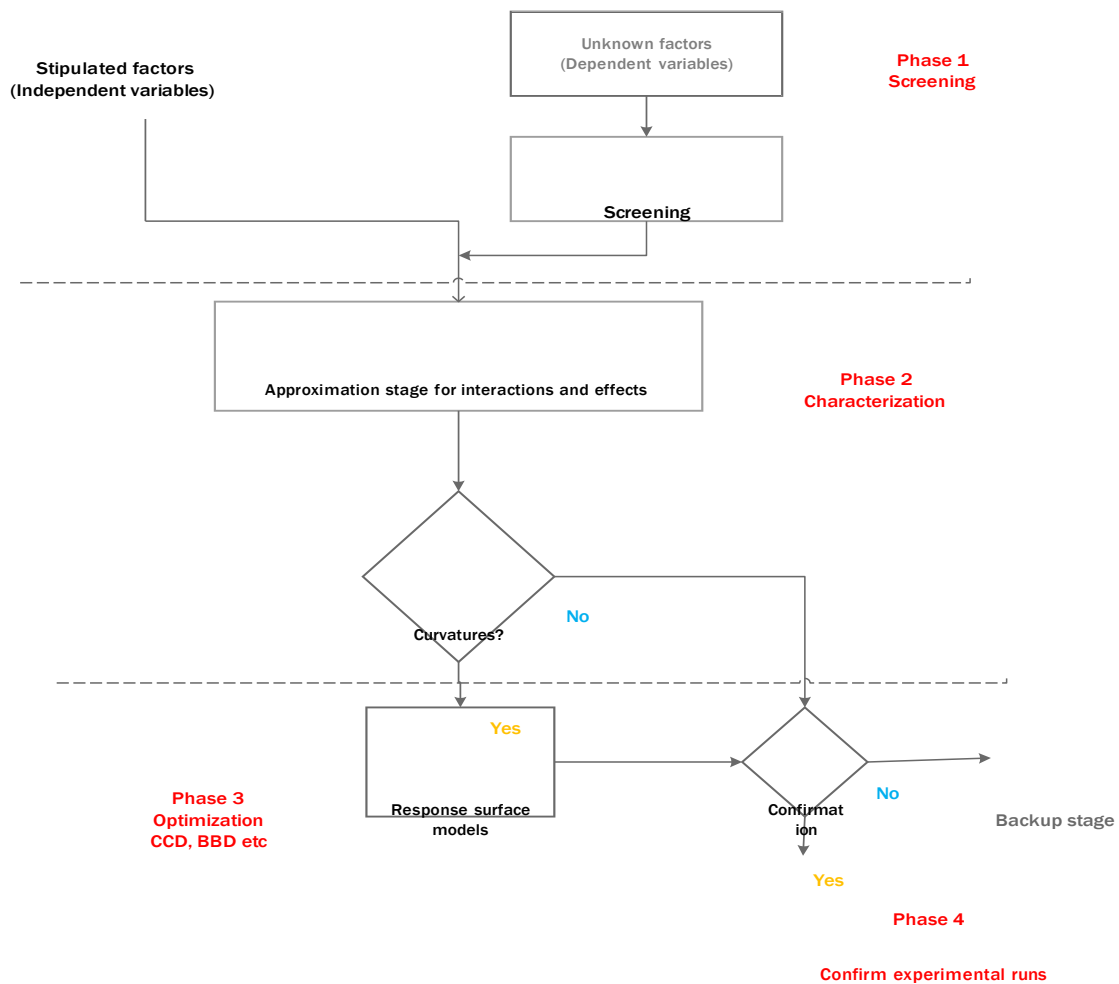


Figure 6 Response surface methodology algorithm applied when constructing models for experiment (110).

2.11 Conclusion

The degree of novelty regarding separation processes has prompted huge interest from global researchers to thoroughly examine the innovative materials which will combat the major technical challenges faced by such processes. The literature study concerning the development of nanocomposite membranes that will offer superior value in terms of performance was investigated. The emergence of thin film nanocomposite membranes has led to quantum technological change era in the field of nanotechnology. Numerous research studies have discussed on the likelihood of quantum changes in technology which entailed the development of ultra-thin barrier layers which according to produced research, possessed the capacity to aid filtration processes in removing foulants contained in wastewater. The embattled conventional ultrafiltration membranes had persisting fouling problems as reported by literature, despite their great separation performance in removing organic and inorganic pollutants. The membranes fouling problems caused researchers to come up with new assembly approaches utilizing advanced polymer additives aimed at enhancing the structures of the laden PES and PVDF membranes. GO, a monolayer of carbon atoms which are tightly arranged within the two-dimensional crystal carbon framework was chosen material under evaluation to improve the surface properties of the composite membranes. Exploration efforts was intensified for this novel two-dimensional carbon allotrope with regards to its potential applicability for water treatment. The flexible manufacturing technology process for this material was examined and employed by researchers such as Brodie, Staudenmaier, and Hummers. The revolutionized Hummers method for synthesizing GO from graphite using concentrated acids took centre stage in the 1960's.

Chapter 3

Synthesis and characterization of Graphene Oxide

This chapter emphasizes on the materials as well as the experimental procedure utilised for the synthesis of Graphene Oxide and provides an overview of its functionalization process.

3 Materials

3.1 Laboratory equipment's and Glassware utilized.

The laboratory equipment and glassware employed in this work was thoroughly washed with detergents, successfully soaked with appropriate chemicals, and subsequently rinsed with deionised water.

Table 3.1 The Laboratory equipment models and operating conditions.

Laboratory equipment	Operating condition	Equipment model	Analysis	Location
X-ray powder diffraction (XRD)	The D2 Bruker diffractometer used a Cu tube with a wavelength of 1.5418Å in the 2θ range	Bruker D2 phaser diffractometer.	Examine the crystal phase or arrangement of GO atoms and investigate interlayer spacing.	University of the Witwatersrand, Johannesburg
FTIR spectroscopy	Vibrational excitation of molecular bonds by absorption of infrared light energy in form of wavelength from 4000cm ⁻¹ to 500cm ⁻¹	Spectrum two FTIR spectrometer, Perkin Elmer.	Analyze the presence of functional groups attached to synthesized GO material composite.	University of the Witwatersrand, Johannesburg
Scanning electron microscopy (SEM)	The synthesized samples were placed on stubs, taken to	Sigma 300VP scanning electron microscope (Zeiss,	To explore the morphology and composition of the GO	University of the Witwatersrand, Johannesburg

	MMU for coating, and analyzed using SEM at different magnifications ranging from 1000 X with voltage of 15KV	Germany)	structure.	
Brunauer-Emmett-Teller (BET) surface area analyzer	The analyzer operated at 77K, within the device using nitrogen gas.	Quantachrome Instruments, United States.	Used to examine the surface structure of GO in terms of its influence on adsorption-desorption process.	University of the Witwatersrand, Johannesburg
Transmission electron microscopy (TEM)	Produces morphology and images of sample under vacuum at accelerating voltage of 120KV	FEI Tecnai 120KV TEM	Validates the thickness of GO formed.	University of the Witwatersrand, Johannesburg
Atomic absorption spectroscopy (AAS)	Dissolve certain mass of reference sample in water and	200 Series AA Perkin Elmer Analyst 240FS	Used to estimate the concentration of metal element	University of the Witwatersrand, Johannesburg

	dilute to 1 Liter to give microgram concentration		present in a sample.	
Zeta Potential analyzer	Sample dissolved in solution, electric field from Zetasizer applied to determine the ionic charges	Malvern instruments Zetasizer Nano ZS90	Measures the electrical conductivity of the ions present the formed product.	University of the Witwatersrand, Johannesburg.
Atomic Force Microscopy (AFM)	Utilizes a laser beam directed towards sample to produce 3- dimensional map of sample surface at nanometer range	Eza AFM controller Nanomagnetic	To examine the thickness of the nanomaterial formed.	University of the Witwatersrand

3.2 Laboratory consumables and Chemicals

The chemicals used for this research experiments includes H_2SO_4 , H_3PO_4 , H_2O_2 , hydrochloric acid, KMnO_4 , Adipic acid, Pimelic acid, Glutaric acid, as well as Graphite powder were purchased from Sigma- Aldrich (Schnelldorf, Germany). Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), Ethyl- 3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC). All chemicals utilised are of analytical grade.

3.3 Fabrication and characterization of Graphene Oxide and its derivatives.

3.3.1 Synthesis of Graphene Oxide

The product development process for Graphene Oxide was synthesized using the modified Hummers method (105). The process involved a reaction mixture containing 120mL of 98% concentrated H_2SO_4 and 13mL of 90% concentrated H_3PO_4 by volume. The mixture was prepared in a 500mL beaker at a volume ratio of 9:1. The chemical process objective was to ensure complete conversion of graphite powder into graphene oxide (GO) within an acidic medium utilizing potassium permanganate as a catalyst. To maximize the synthesis of GO, the oxidation reaction involved the addition of 1 gram of graphite powder into cooled mixture of sulphuric and phosphoric acids. The reaction acidic solution in the 500mL beaker was allowed to react for 15 minutes with graphite powder, where the concentrated sulphuric acid protonates the graphite powder as the reaction produces 2H^+ and SO_4^- , while the other reactant in phosphoric acid H_3PO_4 ensuring the oxidation reaction constancy or making sure it reaches equilibrium Marcano *et al* (52). With 6 grams of Potassium permanganate added slowly into the reaction mixture, the reaction was to be allowed to form the GO product faster within 12 hours interval, as KMnO_4 was used as a catalyst in the process.

The mixture was then left to stir in an oil bath for 12 hours under controlled temperature of 50°C until the solution turned dark green. The GO product formed was then cooled at room temperature at 25°C . The prepared concentration of 0.83 g/L of ice and hydrogen peroxide (H_2O_2), solution make-up of 1mL of 30% H_2O_2 and 400mL of ice was used in attempt to terminate the oxidation reaction. The synthesis of GO described above involved the usage of strong oxidizing agents in the combination of H_2SO_4 and KMnO_4 , and as described by Tiliakos *et al* (50), where the reactivity of the MnO_4^- ions gets activated in an acidic solution to form Mn_2O_7 , which in turn helps to oxidize the graphite. The addition of H_3PO_4 has been explained to be advantageous towards the formation of intact 6-membered rings on the basal planes of the GO product synthesized. The mixture underwent a washing step with 10% hydrochloric acid and deionized water, and eventually got centrifuged for 60 minutes at 4000 rpm. The supernatant, composed of the nitrate will then be discarded, and precipitate obtained will undergo drying at controlled temperature.

3.3.1.1 Characterization of the synthesized GO sample.

To verify the successful synthesis of the GO product formed, the physicochemical properties of the nanomaterial was evaluated such as its morphology to indicate the presence of oxygen containing functional groups. and having to also take into account the physical properties regarding the thickness of the GO membrane measured by the use of Atomic force microscopy, and calculated the intersheet spacing of the synthesized GO using Braggs Law equation with the data obtained from the D2 Bruker diffractometer used a Cu tube with a wavelength of $1.5418\text{\AA}$ in the 2θ range to quantify the possibility of creation of pores within the nanomaterial structure that will allow for both hydrophilicity of GO with water and transport and rejection of solutes (contaminants). The Spectrum two FTIR spectrometer, Perkin Elmer instrument was used to analyze the quality of the produced GO in terms of assessing the extent at which the oxidation reaction occurred from the stipulated method in 3.3.1 by verifying the addition of functional groups present which are stipulated in figure 8. The presence of these functional groups has been reported to enhance the chemical properties of the GO by making it more hydrophilic in water. The FTIR analyzed the presence of the functional groups at wavelength ranging between $4000 - 500\text{ cm}^{-1}$, with each formation of functional group denoted by the different peaks revealing the formation of those functional groups after reaction time of 12 hours. The SEM instrument was used to examine the morphology and structure of the fabricated GO at magnification of 45 KX, aperture size of 30 μm , The accelerating voltage applied to the electron beam was at a n electron high tension (EHT) of 8.0 KV, signifying the kinetic energy that was applied in analyzing the sample structure. The thickness of the GO formed was analyzed using ezaAFM controller nanomagnetics instrument (Banbury, UK) was utilised to obtain high-resolution imaging from range between 1-6 μm to obtain atomic-level description for samples like the single layer graphene stipulated in Figure 10. The Field emission instruments (FEI) Tecnai transmission electron microscopy (TEM) operating at an accelerating voltage of 120KV was used to validate the thickness and morphology of the formed GO nanosheet.

3.3.2 Functionalization of Graphene Oxide using dicarboxylic acids

The experimental process regarding the functionalization of synthesized GO material composite as explained in 3.3.1 commenced with the addition of 50ml of deionized water. To form a GO solution, 500 mg was dissolved in deionized water and allowed to be sonicated to break up any GO aggregates due to their higher hydrophilicity. The sonication process took place within a time of 2 hours (4). The sonicator utilizes high frequency sound waves to achieve reaction mechanism for evenly distribution of GO particles to form GO colloidal solution. The three different dicarboxylic acids were reacted with GO prepared at a concentration of 10 g/L or 1% w/v as explained above. 1 g of Glutaric, Adipic and Pimelic was added into 100 mL solution make-up of deionized water to make up 1% of crosslinker solution. After that, 50 ml of crosslinker solution was added into GO colloidal suspension, and the mixture was stirred for 2 days at room temperature (114). It has been reported that GO nanosheets are hydrophilic and instable in water, so changing their functional groups, chain length and intersheet spacing would be beneficial for improved separation of ions and molecules. The covalent modification reaction process mechanism occurring between the dicarboxylic acids at prepared concentration of 10 g/L and 10 g/L of GO solution was to be studied in terms of analyzing the bonding of different functional groups added and substituted within the GO structure. The mixture was then filtered with a PP microfiltration (Filter paper) to obtain the GO composite. After the termination of the reaction progress, 0,2 mL of hydrochloric acid, concentration make-up of 9,6 mol/L was filtered through the GO membrane. The GO membrane deposited onto the filter paper was then placed in oven for drying, with 0,3 mL of hydrochloric acid added. The membrane was washed with deionized water to remove excess hydrochloric acid and crosslinkers before it was dried for 24 hrs at room temperature.

3.4 Experimental Procedure for the surface modification procedure of the PES sheets to activate it for binding with functionalized Graphene Oxide.

The amino functional groups are mostly attached to the Polyethersulphone (PES) sheets via two -step process. The procedure for attaching the electrophilic amine groups onto the polymer chain of PES is very efficient since the groups are very reactive and easily used to covalently bond with so many functional groups. Aminated Polyethersulphone (NH_2 – PES) could be generated from the reduction of nitro Polyethersulphone ($\text{PES} - \text{NO}_2$).

3.4.1 Preparation of the Polyethersulphone- graphene oxide infused nanocomposite membranes.

The PES membrane sheet was cut into smaller sizes, in preparation for dipping into acidic solution of nitric and sulphuric acids. For the amination of membrane sheet, the PES membrane was dipped into the solution with reaction being monitored within different set of times, as well as concentration of acids being varied at 0,001, 0,01 and 0.02M. Mixture proportion was 1:4(5ml: 20 ml) of $\text{H}_2\text{SO}_4 - \text{HNO}_3$. The reaction was carried out within nitrogen atmosphere, to avoid oxidization taking place and to allow for reduction process proceeding this stage to occur. The generation of aminated Polyethersulphone (PES- NH_2) from the reduction of nitro Polyethersulphone (PES- NO_2). Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) solution with concentration of 0,5 mol was prepared. The PES- NO_2 membrane sheet was dipped onto the prepared solution, with reaction being monitored and allowed to occur at different time frames, to allow for maximum amination (attachment of amino groups) to take place. The unattached solution was drained and washed off from membrane surface with de-ionized water. To study and evaluate the effect of changing the acidic solution mixture concentration of sulphuric acid (H_2SO_4) and nitric acid HNO_3 by changing the membrane dip coating times from 5 – 30 minutes, SEM and FTIR instruments were used to analyze the change in the morphology of the dipped PES membrane as well as the attached functional groups during the reaction process. The parameters that were being checked was the morphological changes with changes in PES membrane structure with change in concentration of acidic mixture versus dipping time. The three different acidic concentrations were prepared as explained above in different quantities, whereas the dipping time was assessed from 5 minutes to 15 minutes and 30 minutes. The objective of this process was to add amine groups using acidic mixture onto the PES membrane before the membrane was attached or bonded with the synthesized GO membrane. The membrane amination technique was applied to improve the robustness of the adhesion and structure-property relationship between the synthesized GO and PES membrane to avoid GO leaching during filtration process. The amine groups would be needed to substitute or replace the carboxylic functional groups from the synthesized GO structure to form a highly reactive intermediate between the PES membrane surface and the fabricated GO sample with the use of a crosslinker solution in N-(3-Dimethylaminopropyl)-N-ethyl-carbodiimide hydrochloride (EDC solution). So, the process, as defined in 3.4.2 involved the depositing of synthesized GO nanosheets via the layer-by-layer (LbL) method described in the literature review section on an acidic solution ($\text{H}_2\text{SO}_4 - \text{HNO}_3$) coated PES membrane and then crosslinked using N-(3-

Dimethylaminopropyl)-N-ethyl-carbodiimide hydrochloride solution. The physicochemical properties of the coated PES membrane using acidic solutions and LBL method to attach GO was analyzed using the SEM and FTIR. The structure and surface morphologies of these membranes were evaluated using Sigma 300VP scanning electron microscope (Zeiss, Germany) at magnification of 500 X and accelerating voltage of 8.00KV. The FTIR was operated from ranges varying between 4000 - 500 cm^{-1} to illustrate the addition of amine functional groups as illustrated in Figure ...! The purpose of this analysis was to understand the distribution of the coated acidic solution onto the PES membrane surface.

3.4.2 Stage three – activation of functionalised GO and attachment onto the aminated PES- NH₂ membrane

To activate the GO, 0.1 grams of functionalised GO was mixed with EDC. To allow for the amidation reaction to occur, the aminated PES membrane was dipped into the mixture solution for an observed maximum reaction time. A concentration solution of 2% N-(3-Dimethylaminopropyl)-N-ethyl carbodiimide hydrochloride was prepared (EDC). The aminated PES membrane was reacted with sonicated functionalised graphene oxide solution in a petri dish. The 2% EDC solution was added as a crosslinker and for creation of strong amide bonds. Each set of membrane was reacted with crosslinker and GO solution for a period of 24 hrs and left to dry at room temperature for another 24 hours allowing for covalent bond attachment to occur.

3.4.3 Evaluation of membrane performance.

The performance of the two synthesized membranes was calculated by examining the permeation flux and using the equation below to determine heavy metallic ions rejection rates prior to simulating the two responses regarding membrane performance on Design expert 12 software to analyze the optimized process system. Initially, the pure flux experiments were conducted to acknowledge the water transport behaviour of the plain PES membrane. The three different membranes, Plain PES, PES membrane doped with GO and PES membrane coated with pimelic acid functionalised graphene oxide. The effect of pressure, concentration of feed mixed salt solutions as well as operating time was studied. The permeation experiments were carried out in a dead-end flow cell. The heavy metallic ions rejection was calculated using the following equation.

$$\%Rejection = (1 - \frac{C_p}{C_F}) \times 100$$

The saturation factor for the feed solution is a parameter for establishing the probability of metal hydroxide in the concentrate stream and the definition is as follows:

$$Saturation\ component = \frac{C_M(OH)_2conc}{C_M^{sat}(OH)_2conc}$$

Where the $C_M(OH)_2$ concentration and $C_M^{sat}(OH)_2$ concentrations are molar concentrations of metal hydroxide in the feed solution stream and in the saturated conditions respectively. C_P referred to concentration of the permeate solution after nanofiltration process, and C_F denoted the concentration of the synthetic and real AMD feed solution composed of heavy metals. The pure water flux and rejection experiments were performed using the operation variables stipulated from Design of Experiments simulations. The concentrations of the feed solutions for synthetic AMD wastewater are recorded together with the concentrations after filtrations within the same screenshots. The concentrations for feedstock manganese and iron are in the same spreadsheet denoted membrane validation results, where the feedstock concentration for manganese was recorded as 7.323 mg/L, and that of Iron was 10.414 mg/L. The same pattern can be observed for other metallic ions.

The permeate flux was calculated using the following equation:

$$J_w = \frac{V}{A\Delta t}$$

J_w = Volumetric flowrate in L/m².hr

V = Volume of the permeate stream in litres

A = Area of the membrane (m²)

3.5 The removal of synthetic metallic and Real AMD ions by synthesized GO. The adsorption studies were carried out with the aim of exploring the removal capacity of heavy metallic ions by the synthesized GO within the batch system. The rate at which adsorption was taking place would depend on the adsorption equilibria and reaction kinetics in terms of the Freundlich and Langmuir isotherms. The batch studies were done in this research to examine the effectiveness of GO as an adsorbent under specified conditions. The Graphene oxide nanosheets were tested on acid mine drainage wastewater collected from Mintek research centre in Randburg, South Africa. The experiments were conducted in duplicates to verify the results. In the experiment conducted, 20 mg of the unfunctionalized GO nanosheets were added into 25 mL of synthetic and real AMD water into 50 mL centrifuge tube. The suspensions were shaken using a rotary shaker for 24 hrs at 25°C. The mixture then underwent centrifugation process for a period of 20 minutes to separate the suspension from the solution. The supernatant was discarded, and solution was acidified using 1% HNO₃, and the concentrations of the metallic ions was determined using Atomic Adsorption

spectrophotometer. The spectroscopy method of determining the feedstock concentration as well as the concentrations of the metallic ions after filtration was utilised. The solution technique based on the method involved preparation of a stock solution, where certain mass of Sodium chloride solution was dissolved in water and diluted in 1 Litre bottle to give a final solution concentration of 1000 $\mu\text{g/mL}$ of Na (sodium). The same technique was used for other metallic ions analyzed such as Nickel, manganese, cobalt, iron, and magnesium. To measure the concentration of iron (Fe), the AAS was operated at 372nm, with slit width of 0.2 nm and lamp current at 5.0 mA at acetylene flowrate of 4.40 L/min and air used flowing at 17.56 L/min. The below results summary was obtained from AAS spreadsheet at Richard Ward, University of the Witwatersrand, Johannesburg.

<i>Metallic ion</i>	<i>Wavelength (nm)</i>	<i>Slit width (nm)</i>	<i>Lamp current (mA)</i>	<i>Air flowrate (L/min)</i>	<i>Acetylene flowrate (L/min)</i>
<i>Manganese</i>	403.1	0.2	5.0	16.56	3.97
<i>Magnesium</i>	202.6	1.0	4.0	13.78	4.15
<i>Sodium</i>	330.3	0.2	5.0	15.62	4.51
<i>Nickel</i>	341.5	0.2	4.0	14.18	3.08
<i>Cobalt</i>	304.4	0.5	7.0	14.56	4.15

Chapter 4 – Synthesis and characterization of graphene oxide functionalised with dicarboxylic acids.

This chapter outlines the synthesis procedure used to convert graphite into GO. The functionalization stage proceeding it and comparing the pristine GO with the functionalized GO in terms of the morphology, interlayer spacing, and other quality parameters used to identify the addition of new functional groups. The surface charges of the material were calculated and BET analysis done to verify the surface areas of the pristine and functionalised GO materials.

4 Introduction

GO has been reported as another kind of membrane material. Although the use of GO in TFNs imbues advantages including antibacterial activity, major challenges to this approach include attrition of the GO sheets from the membrane surface and flux reduction where movement between GO sheets is impeded. This study examined the use of dicarboxylic acids for crosslinking GO sheets to prevent attrition and to control the interlayer spacing of GO sheets. GO prepared via the modified Hummers method, was crosslinked using three dicarboxylic acids of varying chain length: Glutaric ($C_5H_8O_4$), Adipic ($C_6H_{10}O_4$) and Pimelic ($C_7H_{12}O_4$) acids. The FTIR spectrum revealed a wider and stronger absorption peak of GO near 3430 cm^{-1} , which could be attributed to the stretching vibration peak of $-OH$. The peak at 1750 cm^{-1} revealed a stretching vibration peak of $C=O$ on the carboxyl group of graphite oxide. The esterification reaction largely occurred at the basal surface area and was shown via the disappearance of epoxy and hydroxyl groups being replaced by an amine group. The spatial XRD analysis showed that interlayer spacing between the GO sheets increased in the order: An increase in the molecular chain of the different crosslinker acids resulted in an increase in the interlayer spacing of the functionalized GO from $7.96\text{\AA}$ - $8.9\text{\AA}$, with the diffraction peaks moving to lower angles. SEM images indicated different surface morphology, attributable to the different effects each dicarboxylic acid has on the initial GO formed.

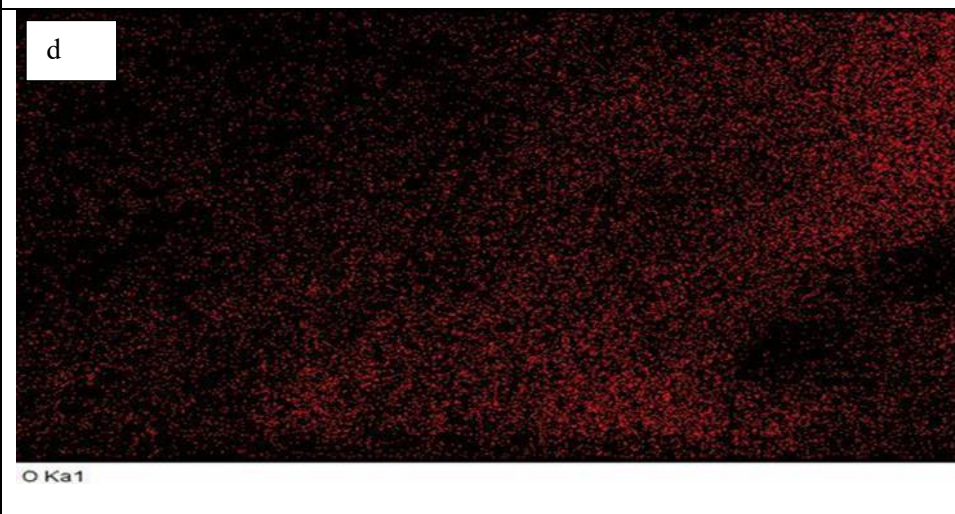
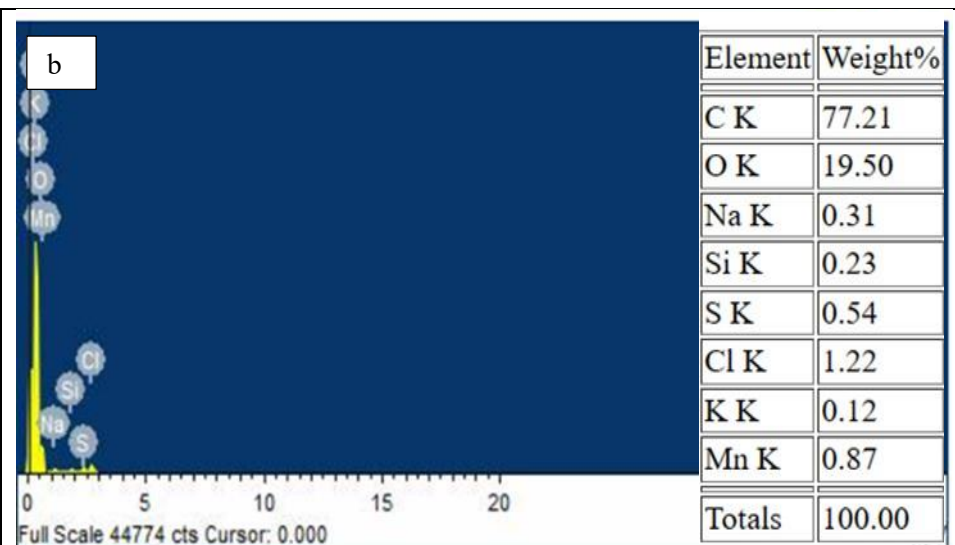
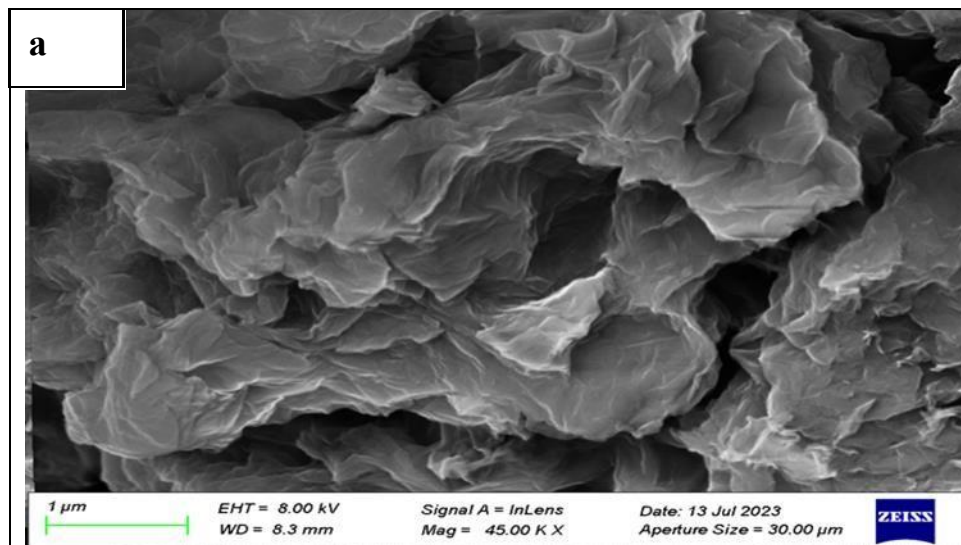
4.1 Results and discussion for the pristine and functionalized process for GO

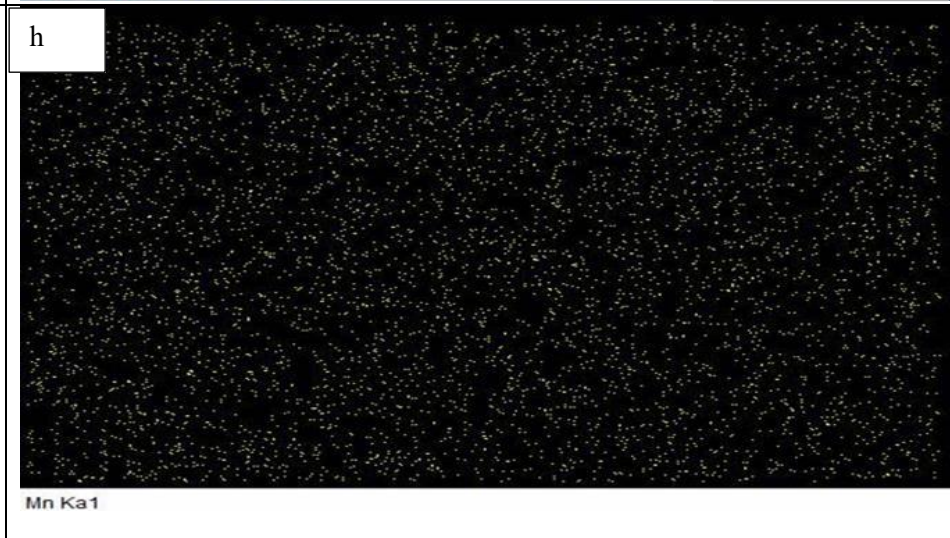
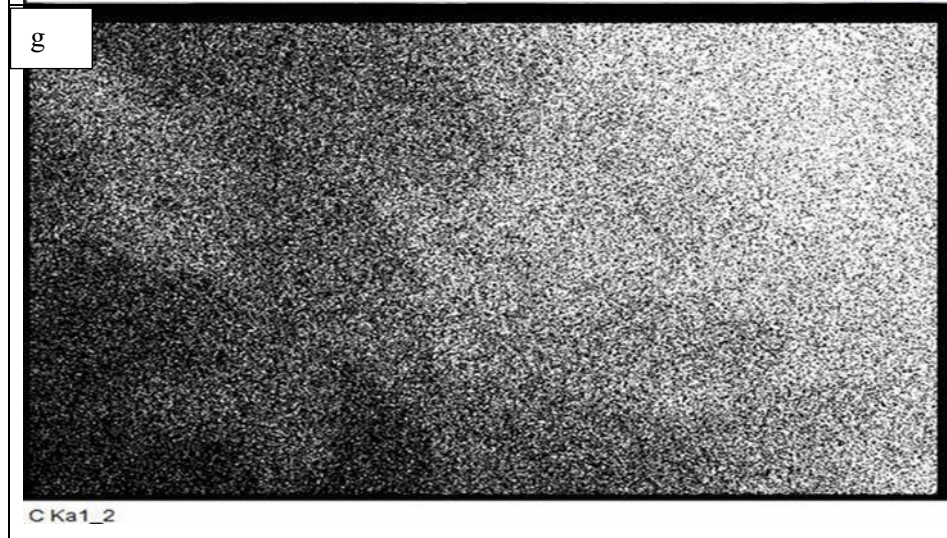
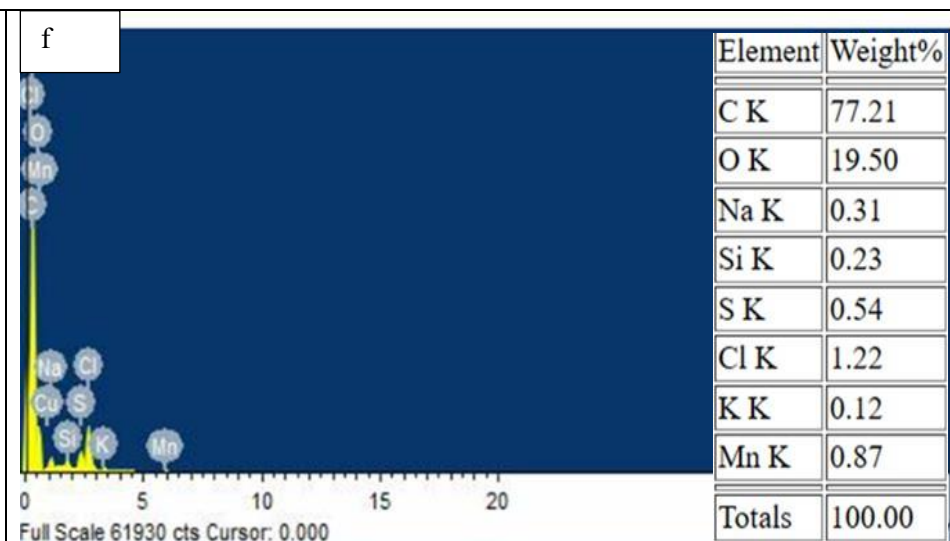
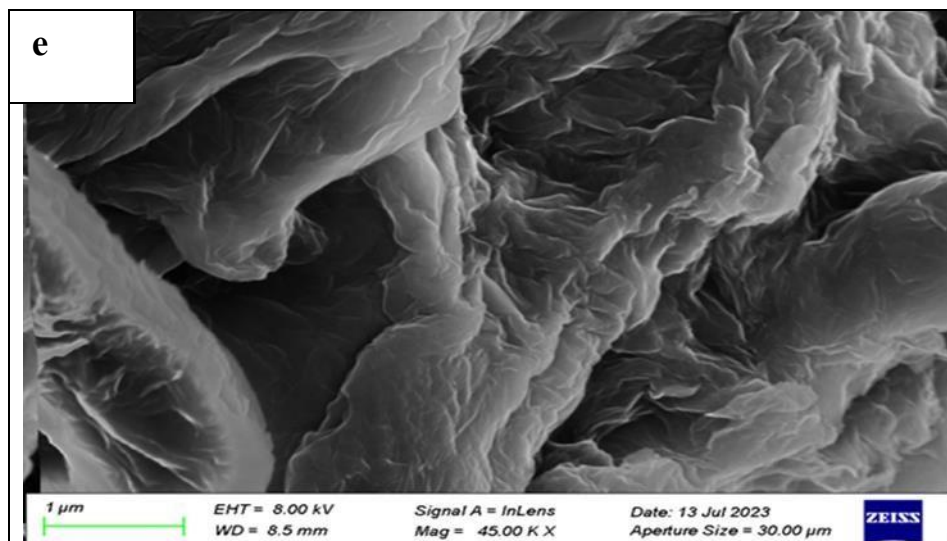
4.1.1 Synthesis and characterization of Graphene Oxide.

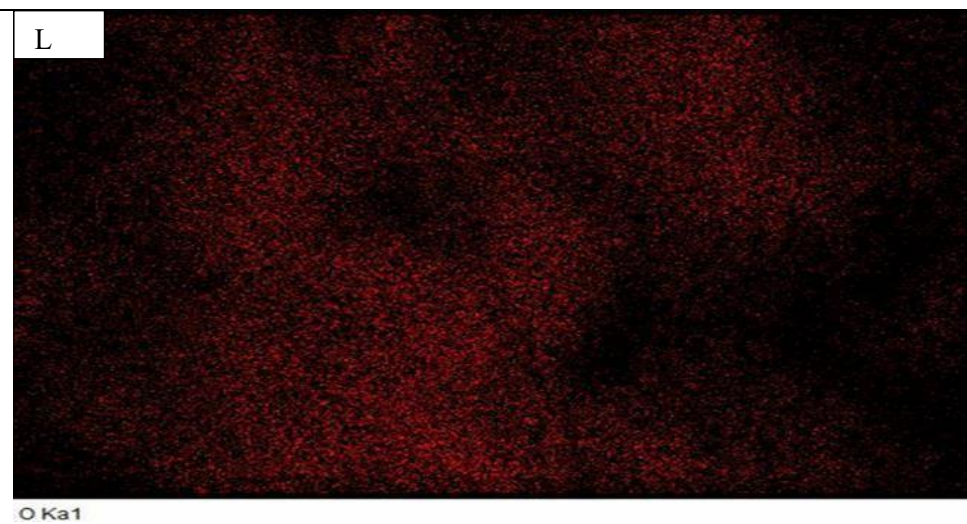
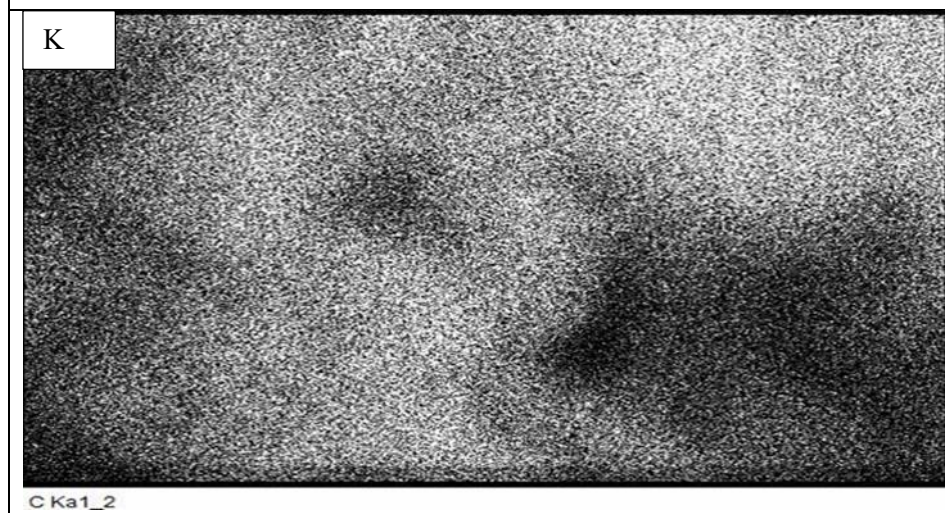
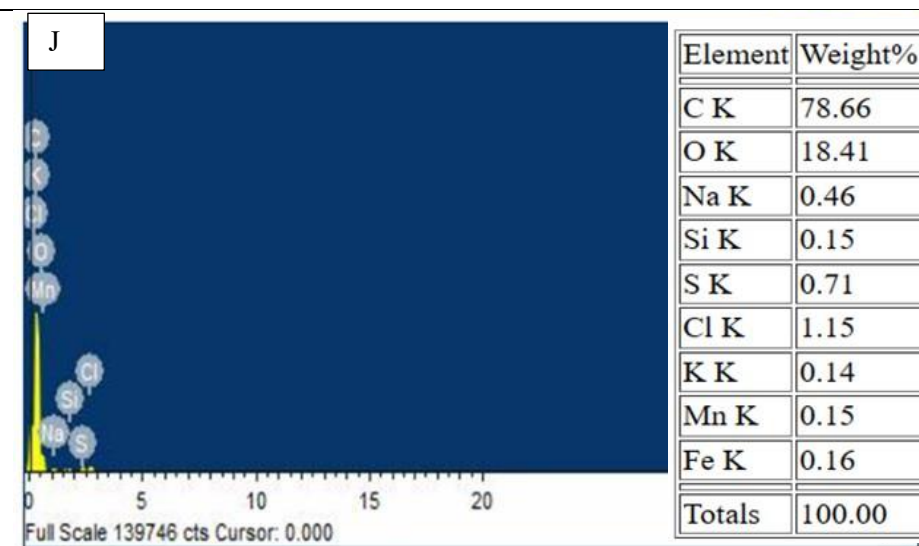
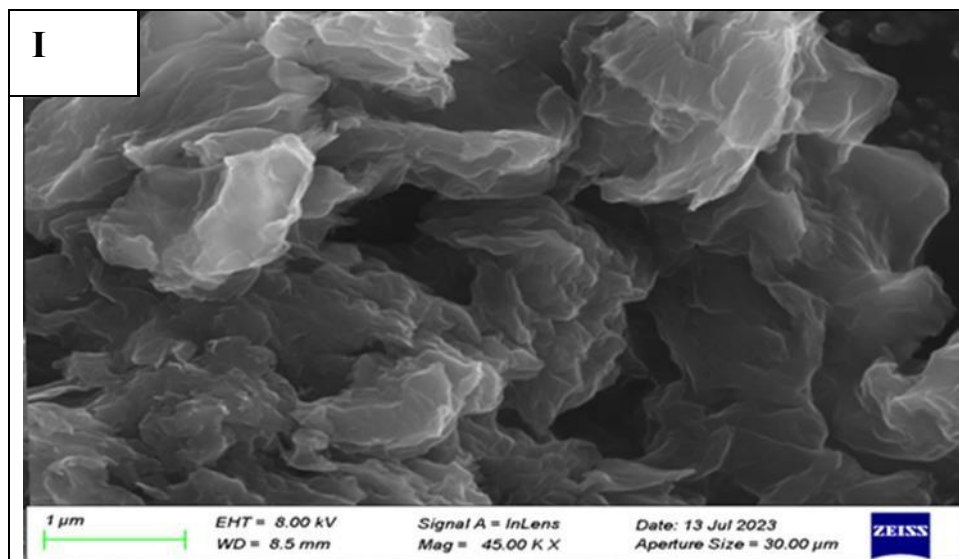
Scanning electron microscopy (SEM) was employed to characterize and depict the morphology of the synthesized GO sample. The SEM images of the morphology of the synthesized GO sample are depicted in Figure 7. GO was yielded via an oxidative reaction process which took place within an acidic medium to form individual graphene sheets which would be ideally suitable to be incorporated into polymeric membranes for the successful separation of heavy metallic ions contained in wastewater. Such GO material offers enormous potential in fabricating functional nanocomposite materials with superior chemical stability, strong hydrophilicity, and excellent antifouling properties (34). The pristine GO image illustrated in Figure 7 (a-d) was generated through an in-Lens detector which provided a clear picture of the actual surface of the sample. The SEM image portrayed in Figure 7(a-d) reveals a wrinkled surface morphology with a well-layered structure. The leafy attached spotted on the basal surface of the wrinkled GO layer can be attributed to the presence of epoxide and hydroxyl groups, the structure reveals the attachment of carbonyl and carboxyl groups located at the graphene sheet edges. The Figure 7 (a-d) image also reveals the randomly aggregated, thick crumpled layer structure of GO with the oxygen-containing functional groups retaining most of the surface area whilst the non-oxidized regions and empty spaces in form of furrows forming channel for permeation of water (4). The presence of flakes entails that the graphene layers were fully oxidized into GO. The morphologies of the synthesized GO were found to be similar with the work reported in (7). The elemental mapping for pristine GO reveals the scattered carbon and oxygen atoms within the specified area where the SEM in-lens detector microscope was focused. The scattered grey area in Figure 7c indicates the presence of carbon atoms for the pristine GO formed, whereas the red area in Figure 7d reveals the abundance of oxygen atoms. Those observations can confirm the successful fabrication of pristine or unfunctionalized GO. The elemental compositions stipulated in Figure 7b confirms the weight percentage of carbon atoms at 77.21%, whereas oxygen atoms were at 19.75 %. The other atoms such as Mn was part of the chemical oxidation reaction, and Na was used as sodium peroxide (Na_2O_2) to balance the GO solution pH before drying during the synthesis process. All functionalised GO images revealed leaf like morphology folded together with spatial distribution within oxidized regions, with the in- Lens magnifications revealing differences in the surface texture of the formed FGO membranes. The modification that has occurred on pristine GO nanosheets via functionalization can clearly provide details regarding the improved

permeability and separation that should be expected on the impermeable pristine GO membranes. The flat structure observed for synthesized GO was modified via the covalent functionalization with dicarboxylic acids. Functionalization with Glutaric acid resulted in graphene sheet folded with nanochannels created between the functionalised GO sheets, as revealed in Figure 7e. The elemental mapping provided in Figure 7 g and Figure 7 h reveals the scattered presence of the carbon and oxygen atoms like the ones from pristine GO, with also minor differences in the elemental composition percentages as depicted in Figure 7f. This observation could be since with functionalization of GO and glutaric acid, the molecular chain of the introduced acid is not if compared to the other dicarboxylic acids, and hence doesn't bring many changes to the composition, however, changes the structure and morphology of the GO sample. The morphology of the pristine GO was altered when functionalized with Glutaric acid, as can be seen in their structural differences in Figure 7a and Figure 7e.

The covalent linkages are visible within the surface morphologies of the adipic acid functionalised GO depicted by the light grey layer on top of the basal functional groups of GO as revealed in Figure 7I. The pristine surface structure from Figure 7a changed to a more rippled furrow like structure morphology as shown by SEM images in Figure 7I, attributed to the presence of esters functional groups, which were substituted during the functionalization reactions. From the crosslinking mechanism described by Jia & Wang (4), it was stipulated that hydroxyl groups on adjoining GO sheets react with the carboxyl of dicarboxylic acids to enable the formation of covalent bond to occur. The elemental mapping shows the greater percentage of carbon and oxygen atoms in Figure 7K and Figure 7L. Similar findings with those other functionalization reactions and could be confirmed with the presence of grey and red areas mapped for indicating the presence of carbon and oxygen atoms. After functionalization with Pimelic acid, the randomly stacked two dimensional flakes were modified into more penetrative surface structure (115). The Pimelic acid functionalized sample revealed a wave like surface morphology resembling the presence of other functional groups present as explained in the FTIR analysis in Figure 8. The carbon atoms in Figure 7O reveals how well scattered the oxygen are within the analyzed area, whereas the electron mapping for Potassium atoms as they were involved in the oxidation reaction reveals less of the scattered atoms. The elemental composition for pimelic acid in Figure 7N differs by larger fraction from pristine in Figure 7B, as well as those found in glutaric and adipic functionalized samples.







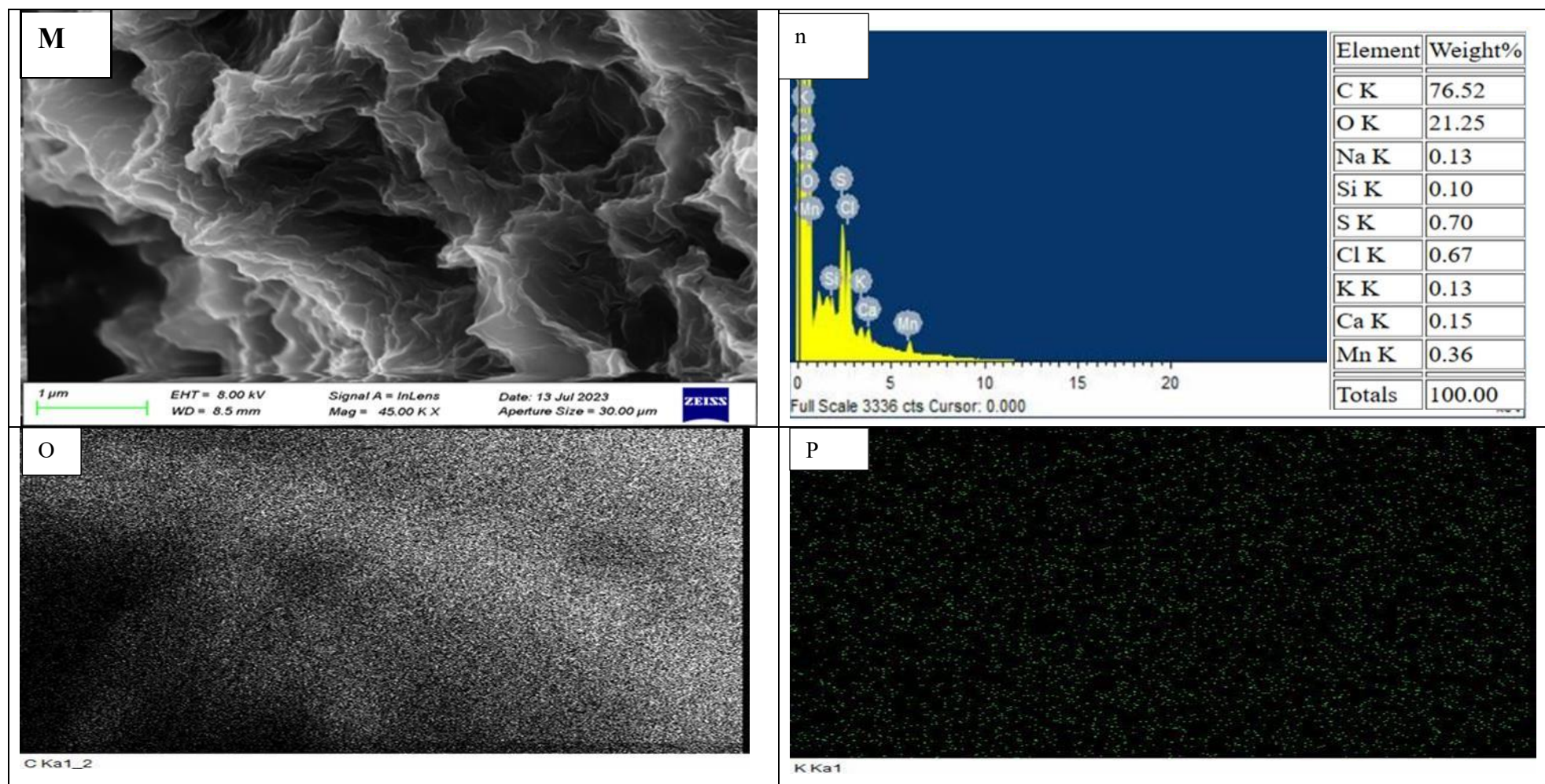


Figure 7 (a-d) SEM micrographs for pristine GO, (e-h) GO functionalised with Glutaric acid, (i-l) GO functionalised with Adipic acid, (m-p) GO functionalised with Pimelic acid and their respective EDS and elemental mapping images.

4.1.3 FTIR analysis for GO.

The functionalization of synthesized graphene is paramount for the improvement of the compatibility with polymers (116). The study conducted for IR spectra was to differentiate the functionalization processes of GO using three different dicarboxylic acids. The semi-quantitative analysis was to provide a detailed investigation of the modification of chemically reactive epoxy and hydroxyl groups within the basal plane site of the graphene oxide surface. The FTIR spectra of pristine GO revealed a broad peak stretching from 3000 – 3700 cm^{-1} with other important groups being the carbonyl and carboxyl groups revealed by the peaks available at 1635 cm^{-1} and 1740 cm^{-1} (7). In this context, the appearance of such stretching vibrations reveals that the sample GO formed is strongly hydrophilic. These results findings were like those reported by Agarwal *et al* (16). The absorption band positioned at 1280 cm^{-1} and 1000 cm^{-1} related to the hydroxyl and epoxy stretches on the basal surface of GO membrane. The desired absorption peaks were observed providing an indication that graphite was successfully oxidized into GO via the chosen Hummers method process. Other researchers as listed in table 1 found the IR spectra results had little variances in the position of absorption bands as well as stretching vibrations when compared to the results found in this research. The aim was to fabricate functionalized GO through esterification reactions, to introduce stronger vibrational interactions. There is a disappearance of peak observed at 980 cm^{-1} within the pristine GO, which was not seen at Pimelic acid FGO; this is evident to the expected outcome of functionalization reactions where other functional groups are being substituted. The results attained in this section could be correlated to those obtained by Jia & Wang (7). After cross-linking, the functionality of esters noted with the small new C-O stretch occurring at range of 1000 – 1300 cm^{-1} in all the functionalized GO plots. Such trends can be attributed to the successful manipulation of the physico-chemical properties of the functionalized GO. According to Guo *et al* (19), the broad peak at the range of 3600 – 2800 cm^{-1} has become flat when GO was functionalized by adipic acid when compared to pristine GO. The new stretch observed in adipic and glutaric acid plots can be attributed to the presence of carboxylic acids functional group in substitution of the alcohol and phenol groups detected in the pristine GO. A new peak stretching in the range 3200 to 3400 cm^{-1} can be ascribed to the functionality of secondary amines when GO is functionalized using Pimelic acid as the disappearance of the O-H stretch bonded to free hydroxyl functional group is observed from pristine GO.

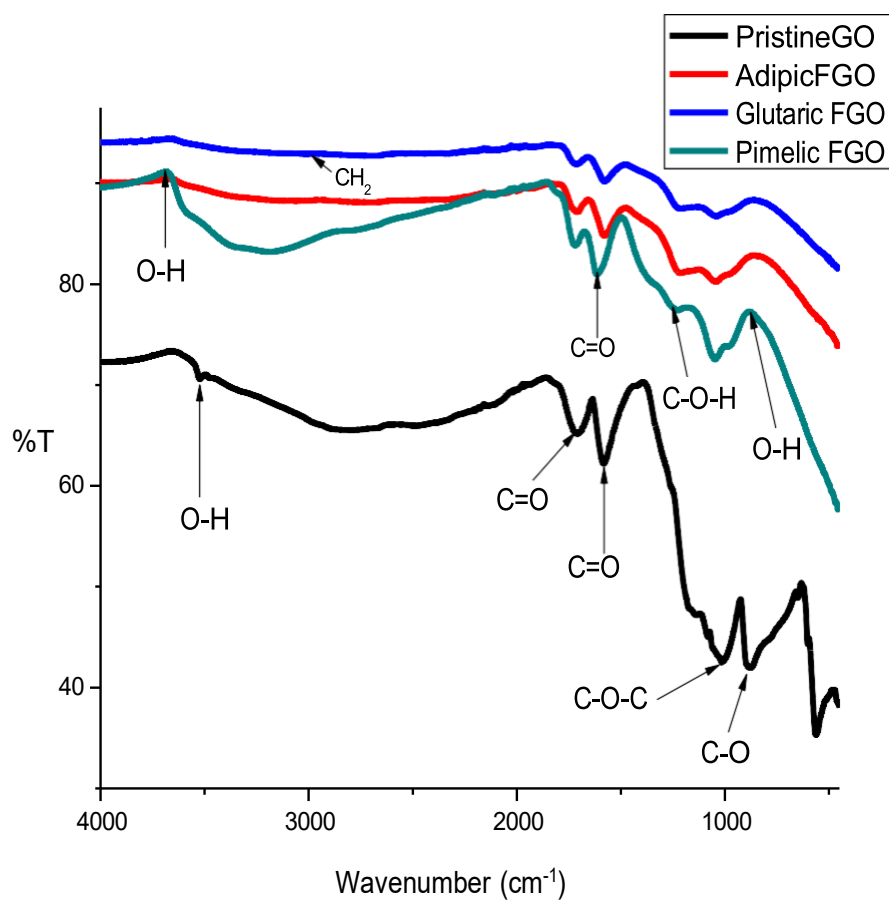


Figure 8 FTIR spectra for Graphene Oxide (GO).

Table 2. FTIR spectra of GO sheets synthesized from literature studies by different researchers.

Researcher	Wavenumber cm ⁻¹	Functional group before <u>crosslinking</u>	Functional groups after <u>crosslinking</u>
Jia & wang (2015)	3214,1720, 1630,1380, 1049	Carbonyl, carboxyl, epoxy, hydroxyl, and O-H groups.	Esters, amino groups, carboxylic, alcoholic, and phenolic groups.
Hidayah <i>et al</i> (2017)	3420,1739, 1226,1015, 3420,1739,1226, 1015	Carboxylic, hydroxyl, epoxide, carbonyl, and Oxygen molecules (O).	Carboxylic, carbonyls, alcohols, and esters.
Kong <i>et al</i> (2017)	3400,1730, 1640,3438, 1722,1259, 1635,1450, 1384, 964.	Alcohols, Carboxylic, carbonyl, and hydroxyl groups.	Esters, amine, alcohols, carboxylic and quaternary amine groups.
Stankovich <i>et al</i> (2007)	1594,1352, 1363	Non- oxygenated ring carbons, carbonyl C and carboxylate carbon groups.	Ring-open epoxides, hydrazine alcohols and hydroxyl oxygen groups.
This study	3200,1740, 1635, 1280, 1000	Epoxy, hydroxyl, carbonyl, carboxylic and O-H groups.	Carboxylic, secondary amines, phenolic, alcohol, free hydroxyl, and ester functional groups.

4.1.3 Interlayer spacing of functionalised GO.

Continual improvement is a key element towards achieving great modification of the synthesized GO. The laminated structure of the GO has been explored to assess the improvement objectives, with strategies including engineering the spacing between GO layers by incorporating different-sized cross-linkers. As revealed in Figure 9, the diffraction peak of the pristine GO membrane is located at $2\theta = 11.2$, correlating to an intersheet spacing of 7.96 Å. The separation procedure of the GO-associated membranes follows that stipulated by Donnan exclusion principles as well as the molecular sieving process (18). Peak performance is a priority for membrane separation processes, and such expectations lead to further enhancement and modifications of the membrane materials used. The output from the functionalization of GO using Adipic, Glutaric, and Pimelic acids as crosslinkers found out that the correlation between molecular chain length and intersheet spacing was linear. An increase in the molecular chain of the acids, from 5C to 7C resulted in an increase in intersheet spacing. The flux behavior of nanocomposite membranes is largely guided by the size, shape, intersheet spacing, and functionality of the GO nanochannels (18). The results obtained from XRD analysis in this study were like that found by Wei *et al* (7), as the trend analysis was similar. The intercalation effects during the esterification reaction mechanism resulted in the formation of GO membranes with greater intersheet spacing as the molecular chain was increased. The functional groups mounted within the peripheral edges of the synthesized GO allow for further functionalization to modify its properties, to achieve better permeation rates and contamination removal efficiencies. After functionalization with the three different acids, the d spacing changed from 7.9 Å to 8.2 – 8.9 Å. In analyzing the XRD plots after functionalization, one could deduce that the reactants used were able to modify the structure of pristine GO by enabling the separation of the lamellae to be able to produce a significantly less compact structure.

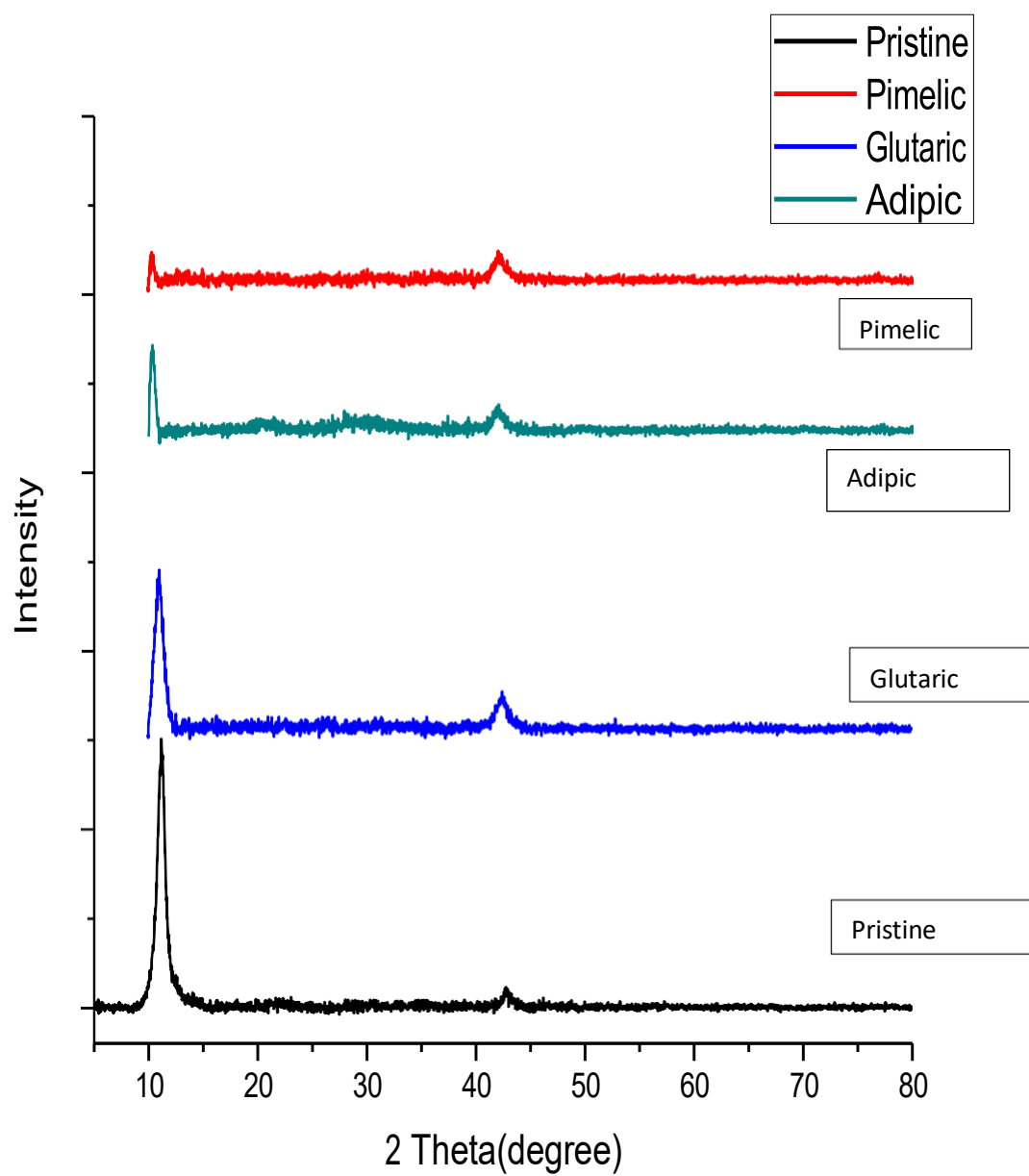


Figure 9 XRD plot depicting the pristine GO and FGO with different crosslinkers.

4.1.4 AFM and TEM analysis for the synthesized GO

The Atomic force microscopy (AFM) characterization method is amongst the principal techniques utilised for precise identification of single-layer graphene. Such evidence is provided in figure 10a where a single-layered graphene sheet has been depicted. Numerous research studies conducted have focused on dispatching one atom thickness graphene sheets as ultimate membrane platform. In its defect free structure, the synthesized graphene can be envisaged to be a perfect barrier property to most molecules and ions (117). The large surface area for this promising material that would be utilised for wastewater treatment applications is depicted in figure 10b with abnormally low thickness ranging between 2nm and 4nm. The carbon atoms present in oxidized graphene are organized in a sp^2 -bonded aromatic structure. Transmission electron microscopy analysis precisely validates the thickness of graphene samples (81). The appearance of stable and translucent graphene sheet depicted in figure 10d demonstrates the presence of single layer graphene (117). The denser surface as studied by Du *et al* (118) has noted that the synthesized GO material has tendency to curl, and glitter depicted TEM images of the material in figure 10c-d. It can also be observed that for monolayer graphene, the one-fold emerges within the dark print as depicted in figure 10c, wherein the electron beam provided high resolution image on how the folded graphene image could be identified.

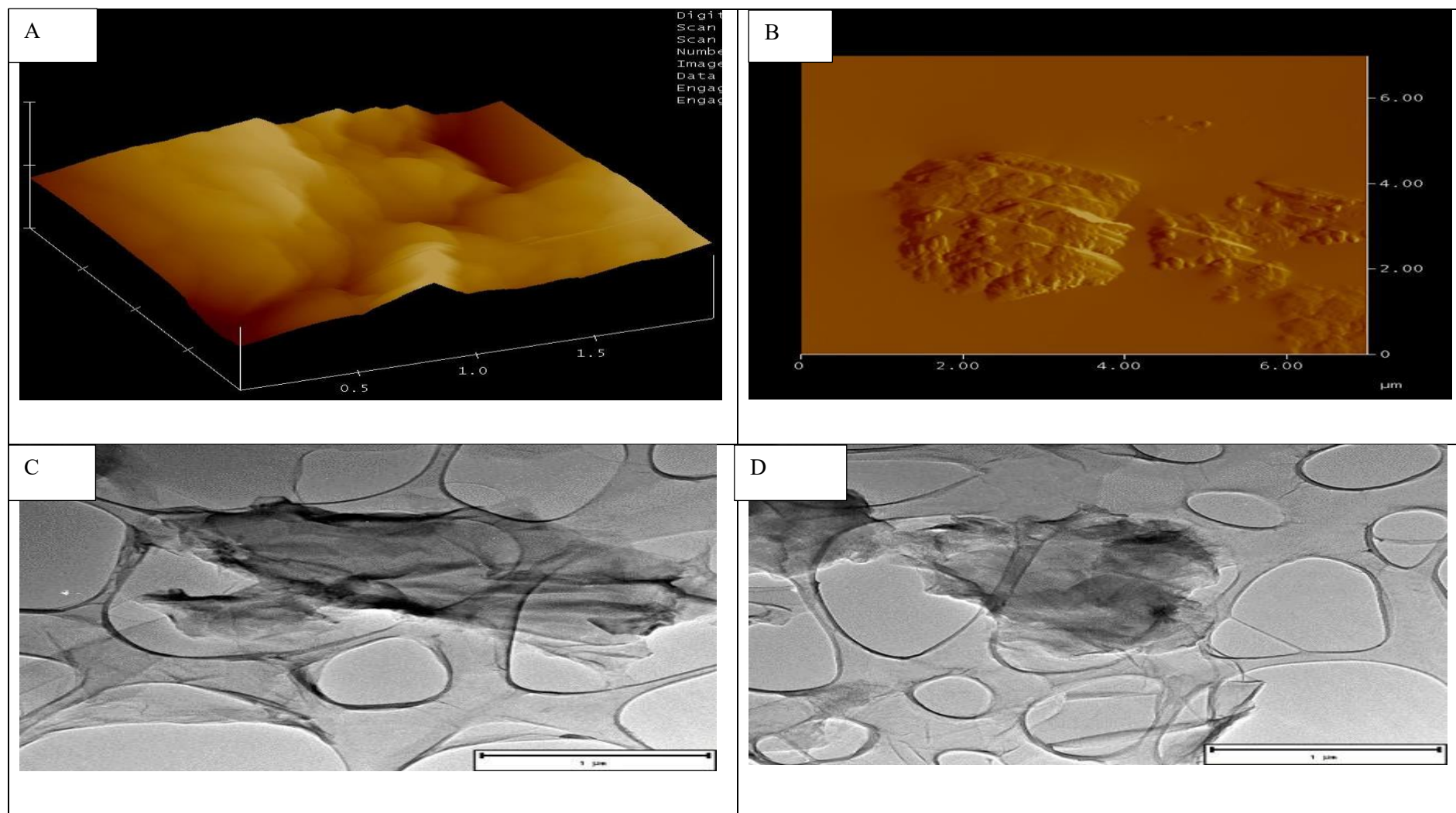


Figure 10 Characterization of the GO nanosheets using atomic force microscopy (AFM).

4.1.5 The GO material surface charges with different crosslinkers.

Chemical functionalization process is one of the main procedures to control the physical and chemical properties of nanomaterials as well as examining the mechanisms of interaction of nanoobjects with their environment. Based on numerous research studies, covalent functionalization yields much stronger changes of electronic and geometric structures of graphene oxide as opposed to non-covalent functionalization. The zeta potential measurements revealed a linear increase in the surface charges with respect to the molecular chain length increase. The increase was due to the deprotonation of carboxylic acid groups and hydroxyl groups present on the surface of the GO sheets during the surface modification where epoxy and amine groups were being introduced. The material surface charges shown in figure 11 in ascending order. Thus, the functionalization process resulted in improved properties such zeta potential charges which according to research studies will improve the interaction between water contaminants and GO material surface charge. The enhanced graphene oxide properties will place GO as a suitable material for achieving high rates of contaminant removal and lead to high performance separation membranes.

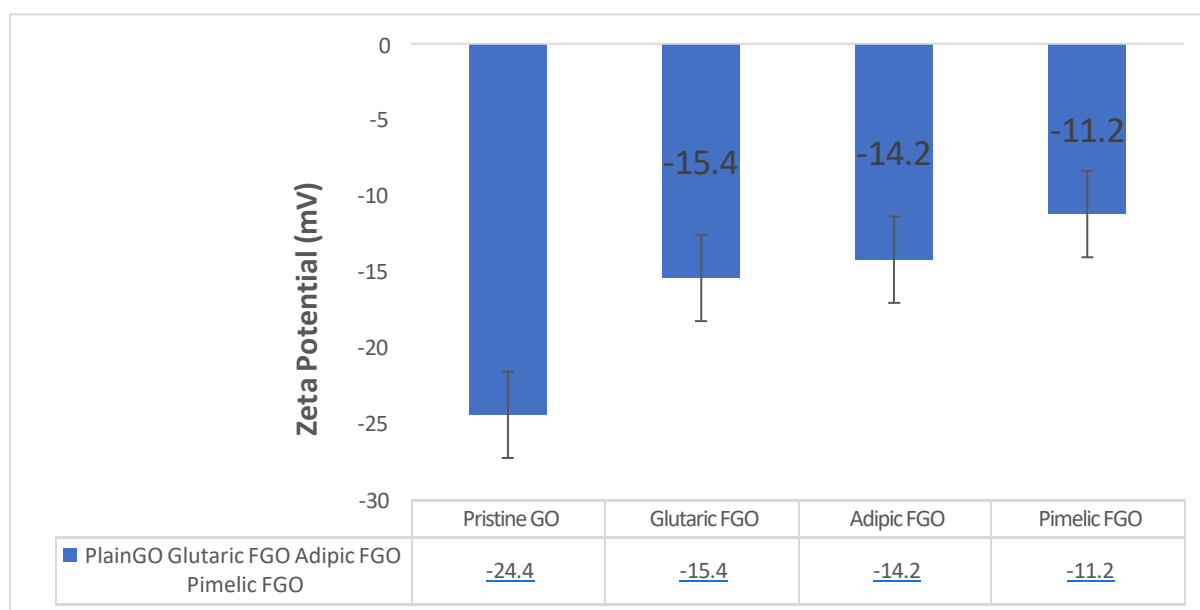


Figure 11 Zeta Potential analysis for (1) pristine, Glutaric FGO, Adipic FGO and Pimelic FGO.

4.1.6 BET analysis.

Most analysis examined with regards to the porous properties of nanomaterials such as GO was acquired from their respective nitrogen adsorption isotherms recorded at 77K. This research study focused mainly on reducing the contamination levels of heavy metallic ions and its very imperative to assess the special characteristics of the nanomaterials used to achieve the optimal goal of obtaining a desirable adsorbent. The surface structure of the synthesized GO was analyzed with the use of the Brunauer, Emmet and Teller (BET) method. The entire aim was to obtain a viable solution towards reaching the project milestone in terms of maintaining a great balance between permeability and selectivity. To get control of the trade-off between permeability and selectivity in polymeric membranes, the nanomaterials utilised should possess higher adsorption selectivity and such properties can be obtained by performing N₂ adsorption-desorption techniques at constant temperature and ideal conditions suitable to analyze the porosity and surface area of the synthesized nanomaterial, in our case being GO. The surface area, pore volume and mean pore diameter of the synthesized GO functionalised with Pimelic acid was found to be 4,837 m²/g, 3,812x10⁻²cc/g and 3.15nm, respectively. The theoretical specific surface area for completely exfoliated graphene sheets was found to be 2,744 m²/g, the pore volume was 1,998x10⁻² cc/g and average pore diameter was 2,93 nm. The BET surface area for synthesized GO by modified Hummer's method was found to be lower than that obtained by Shi, Wang & Liu (119). The researchers found BET surface area to be 8.821 m²/g whereas in this research study it was found to be 2.744 m²/g. The difference in the GO BET surface areas was largely due to partial agglomeration of the graphene sheets as well as the chemical utilised to oxidize the GO material (120). However, research studies conducted by (62), has noted that larger surface areas do not ascribe to greater adsorption capacities of the adsorbent, therefore translating to the fact the higher adsorption capacities can be expected from the GO- Pimelic functionalised material as well as the non-functionalised GO material in terms of removing heavy metallic ions in aqueous solutions. The main reason behind this phenomenon being that the adsorption capacity of an adsorbent does not largely depend on its specific surface area, but a combination of other factors such as the intrinsic properties of the adsorbent, pore distribution and structure and the quantity of functional surface groups present in the adsorbent (62). This research study mainly focused on the two adsorbent materials in terms of studying the reaction kinetics as well as removal of heavy metallic ions from AMD polluted wastewater. The results depicted from the N₂ adsorption-desorption curve figure 12b and c illustrates that the plots are typical type I adsorption-desorption isotherms published by

International Union of Pure and Applied Chemistry (IUPAC), and there is a hysteresis loop phenomenon. The classification of isotherm type is given by microporous solids which possesses approximately small external surfaces (121). For the GO sample functionalised with Adipic and Glutaric acids, within the low-pressure region, at P/P_0 (0.1 – 0.2), the isotherm revealed a sharp adsorption trend, depicting the presence of micropores present within the functionalised GO. According to research studies conducted by Schwertfeger, Frank & Schmidt (121), the steep uptake at very low P/P_0 is mainly due to the improved adsorbent-adsorptive relationship in narrow micropores of molecular proportions. Similar trends were obtained by other researchers, where within the low-pressure regions ($P/P_0 = 0 - 0.01$), the isotherm displays a sharp adsorption trend, providing information regarding the presence of micropores in the functionalised GO samples (122,123).

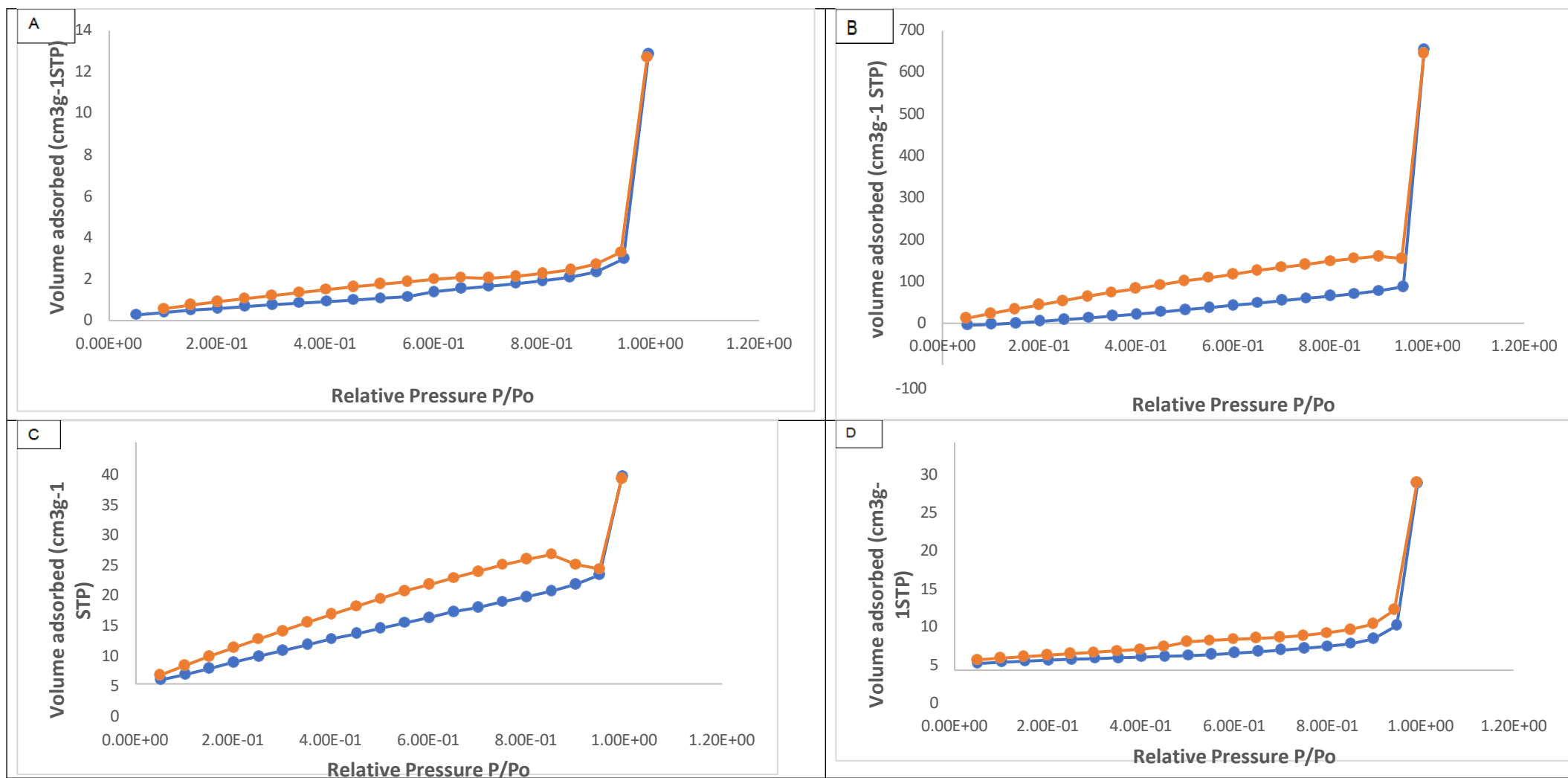


Figure 12 The N₂ adsorption isotherms for (a)pristine GO sample, (b) Glutaric acid functionalised sample, (c) Adipic acid functionalised sample and (d) Pimelic acid functionalised sample.

Table 3 reveals the result of the experiment. The BET-specific surface area of GO as functionalised with Glutaric acid content showed a trend of increase. The oxidized GO was 2.26 m²/g surface area with SEM images resembling interlinked layered structure. As revealed via the surface morphology stipulated in figure 7a, the oxidized regions of the GO were inclined to cluster together creating room for the non - oxidized regions to form a two-dimensional network of nanocapillaries as noted by Jia & Wang (4). The functionalization process which occurred between the glutaric acid and oxidized GO resulted in the formation covalent coupling of native functional groups of synthesized GO with the introduced functional groups from the dicarboxylic acid (124). The esterification reaction which occurred between the carboxyl groups and different crosslinkers resulted in much improved interaction between the graphene oxide sheets, as depicted in Figure 7b where the structural modification was visible through the in-Lens SEM showing the crosslinked GO surface with the added functional groups bonded together creating a compacted wrinkled structure. The BET specific surface area reached its highest when functionalised with Glutaric acid with an area of 61,24 m²/g, ascribing to the short molecular chain length whereby the carboxylic groups of the crosslinkers did not completely link up within the entire network of the oxidized GO as other functional groups were being introduced, therefore creating a polymer like shape of GO material validating the likelihood of large specific surface area (4). The closely packed graphene layers were changed drastically after reacting with Adipic and Pimelic acids. The introduction of increased chain length and functional groups resulted in the surface modification of the GO resulting from the nucleophilic substitution of the hydroxyl groups with the ester functional groups and such was revealed through SEM images depicted in figure 7c and d. According to Wei *et al* (7), the introduction of the esters and charged functional groups is sufficient to enhance the permeability and adsorption capacities of the GO leading to much improved separation performance. The results depicted in Table 3 regarding the adsorption cumulative volume corresponds to their respective surface area whereby the ratio of adsorption is equivalent to the threshold area where the functionalization reaction has occurred. The greater surface area provides higher adsorption volume; however, it has been stipulated that adsorption is not only subjected to high surface area but also dependent on other factors such as the active functional groups present in the material which will be responsible for the binding with the metallic ions (62). We can thus conclude that based on the different pore width of the four different adsorbents being analyzed, the glutaric acid adsorbent with higher surface area and adsorption volume could result in lower

adsorption capacities when compared to that of synthesized GO and GO functionalised with Pimelic and Adipic acids. The increase in the surface area can be assessed in terms the number of pairs of functional groups combined between the carboxyl and hydroxyl groups as discussed earlier in this section which results in efficient ion exchange and van der Waals forces of adsorption occurring within the surface of the inner and outer layers of the GO composites materials. The increase in the molecular chain of the crosslinkers resulting in the addition of huge amounts of functional groups has been reported to cause clogging in the structure of the functionalised GO as seen in Figure 7, where there was complete change which resulted in the decrease in surface area, this observation was noted by Zhao *et al* (122). The detailed knowledge regarding the properties of the porous structure was outlined from their respective nitrogen adsorption isotherms and depicted in figure 12 where the experiment was conducted at 77K. The surface areas, median pore sizes, and adsorption volume of all samples were shown in Table 3. Combined with the results from different adsorption-desorption plots in figure 12, it indicated that there was a typical type IV H3 adsorption desorption isotherm issued by IUPAC, there was a hysteresis loop phenomenon (122). The results have revealed that the sample is composed of flap-like grain cavity structure, where the process of capillary condensation was taking place (125).

Table 3. Table stipulating the BET surface area, BJH adsorption volume and median pore width for GO functionalised with dicarboxylic acids.

Sample	Specific surface BET (m ² /g)	BJH Adsorption cumulative volume (m ² /g)	BJH median pore width (nm)
GO	2.262	0.02	4.90
GO - Glutaric	61.24	0.99	4.913
GO - Adipic	18.34	0.052	3.06
GO - Pimelic	3.28	0.04	4.92

4.2 Conclusion.

In summary, graphite powder was oxidized using the modified hummer's method to synthesize Graphene Oxide using KMnO_4 as catalyst. The synthesized GO underwent various schemes of post-synthesis methods to remove impurities and acidic residues. The composition, morphology, crystal structure, and surface structure of the functionalized and pristine GO were observed in the spectra. The FTIR results confirmed the introduction of hydrophilic functional groups such as the carboxylic acids, alcohols, epoxy, and hydroxy functional groups through the major peaks that were observed in conducting FTIR analysis. The objective was to enhance GO in its use as a performance modifier once blended in thin film nanocomposite membranes. Covalent functionalization on the GO was then implemented with the aim of improving the chemical, mechanical and electronic properties of GO. The increase in molecular length of crosslinkers has resulted in an increase in the intersheet spacing of the functionalized GO membranes. This result suggests that functionalized GO can be further utilized to enhance the separation performance of traditional polymer.

Chapter 5 – Process Optimization for the prediction of the synthesized GO-infused thin film membranes permeate flux and heavy metallic ions removal rates.

After synthesis of Graphene Oxide and functionalizing it, it is paramount to assess its quality in terms of application in wastewater treatment. This chapter outlines the stages followed to aminate and bind the functionalised GO into polymer Polyethersulphone (PES) ultrafiltration membrane to improve the membranes performance and make it more hydrophilic. The nanocomposite membranes were prepared by the dip coating Layer by Layer (LbL) assembly technique and characterized using Fourier transform infrared, X-ray diffraction and scanning electron microscope. The prepared membranes were used for the separation of heavy metallic ions from acid-mine drainage.

5 Introduction

Polysulfone-based materials such as PES have been applied within wastewater treatment applications for many years. Numerous research efforts have noted the technical drawbacks associated with these conventional membranes, such as biofouling and low selectivity rates regarding pollutants contained in wastewater. Another bottleneck that hampered the quality of the functionality of conventional membrane was their intrinsic hydrophobic nature, which contributed to the poor separation performance (56). Research work conducted by Rahimpour *et al* (126) have discovered that the doping of GO into polymer matrix has yielded improved hydrophilicity, heavy metallic ion rejection as well as lead to improved permeability rates defining how well the nanofiltration process works with the innovated membrane system. In the adoption of nanocomposite membrane improvement strategies, Nasser *et al* (8) explored the performance of graphene oxide infused Polysulfone membranes for the purification of Bisphenol A (BPA) containing wastewater. The approach used to fabricate the membranes was the phase inversion technique via blending N, N – Dimethylformamide (DMF) 85% with small weight ratios of GO nanoparticles and subsequently dissolving solvent mixture 15% PSF with 3% polyvinylpyrrolidone (PVP). The results of effects on GO loading on pure water flux at different operating pressures (1-2 bars) for pure PSF, PSF/GO (containing 4%), PSF/GO (containing 1%) were 220, 450 and 510 L/m².hr respectively. Other research work done by Hu&Mi (18) reported GO surface deposited Polysulfone membrane for the rejection of methylene blue. In contrast with the monovalent and divalent salts and Rhodamine-WT, the Polysulfone membrane prepared via the dip coating technique has shown a moderate rejection within range of 46 – 66% of methylene blue. The fabrication of Polysulfone-infused GO mixed matrix membranes was reported by Ganesh *et al* (5) to examine Na₂SO₄ rejection. Performance was improved through the addition of GO nanoparticles as surface modifier to a maximum of 72% Na₂SO₄ rejection (56). However, research work done by Rahimpour *et al* (126,127) has noted that in most studies concerning the performance of ultrafiltration and nanofiltration membranes, the optimization of preparation conditions such as hydrophilic additives, coagulation bath temperature of mixture of GO solution with crosslinkers and concentration of crosslinkers was trivialized. In this study, PES was, therefore used as a polymer matrix to prepare nanofiltration membrane via the layer-by-layer (LBL) self-assembly method. The preparation conditions for the hydrophilic additive, GO, was optimized via functionalization process. It was a complicated and tedious process using Box Behnken design simulation with the response variable being the interlayer distance and independent variables assessed being

concentration of crosslinkers (Glutaric, Adipic and Pimelic acids), reaction time and temperature of the solution mixtures of crosslinker solution and GO colloidal suspensions. The global research network is working around developing nanocomposite infused membranes with finely balanced characteristics (5,21). The membrane separation technology field requires enhanced membranes which possess high strength, well-ordered surfaces, and creation of well-defined nanochannels with the ability to retain organic and inorganic pollutants (21). Based on the past research studies, GO has reported prominent performance in the fabrication of nanocomposite membranes (8). The purpose of this research was to fabricate PES/GO nanocomposite membrane for the removal of heavy metallic ions

5.1 Results and discussion

5.1.1 To examine the effect of reaction time, temperature, and concentration of crosslinkers

The purpose for conducting the crosslinking experiments using different conditions was to improve the robustness of the GO membranes (60). The utilization of graphene oxide as membrane material has great and rewarding advantages as they cater a stronger support force and its sheet spacing can be adjustable to permit for the passage of water molecules while resisting passage for heavy metallic ions and other contaminants contained in wastewater. Overcoming these technical-related challenges, chemical bonding can be created between the GO sheets to prevent its instability in water as well as improving its mechanical properties (4). GO is oxidized form of graphite oxide composed of the carboxyl and carbonyl functional groups which are located within the sheet edges and having hydroxyl and epoxide groups on the basal edges (4). The emphasis surrounding the crosslinking degree lies in the extent to which additional functional groups will be added on top of the synthesized GO. The d-spacing (intersheet spacing) is a measure which defines the channels created within the GO multilayered membrane (7). By concentrating on improving the separation performance of multi-layered GO membranes, the effect of temperature, reaction time and crosslinker concentration needs to be assessed and evaluated. The epoxy and carboxyl groups, which are the sites of chemical reactions, are primarily where the functionalization of GO occurs. (7). The vital step in the functionalization is the integration of both hydrophilic and charged functional groups, which will emanate from addition of dicarboxylic acid groups through covalent crosslinking with GO membranes (4). From the experimental results obtained, assessing all the parameters chosen from the Box-Behnken design (BBD), the functionalization with Glutaric acid, it was found out that reaction time of 12hrs, temperature at 60°C and concentration of 0,0175M, with d-spacing of 8,75 nm was the optimal operating conditions for the system under study based on the lower and upper limit design variables chosen. The optimal reaction conditions for covalent esterification reactions between GO and adipic acid was found to be 12hrs, 25°C and 0,005M with d-spacing of 8,86nm, whereas the one functionalized with Pimelic acid was found to be 30 minutes, 60°C and 0.0175M with d-spacing of 7,82nm. The optimum response was located within those above-mentioned operating parameters with regards to crosslinker concentration, reaction time and reaction temperature. What was deduced from the optimization of the functionalization process was that through the box Behnken

design, the addition of functional groups onto the basal plane of the GO was achieved at minimal reaction time and medium concentration, although reaction temperature was higher.

Table 4. BBD design for Glutaric acid functionalization experiments.

Glutaric acid			
Concentration (M)	Reaction time(minutes)	Temperature (°C)	d-spacing(nm)
0.02	1440	42.5	8.61
0.005	1440	60	8.74
0.0175	1440	60	8.75
0.008	30	42.5	8.07
0.025	30	60	8.19
0.0175	1440	25	7.82
0.03	1440	42.5	7.49

Table 5. BBD design for Adipic acid functionalization experiments.

Adipic acid			
Concentration(M)	Reaction time (minutes)	Temperature (°C)	d-spacing (nm)
0.0175	30	42.5	8.84
0.005	1440	25	8.86
0.003	1440	42.5	8.38
0.008	1440	42.5	7.69
0.02	1440	60	7.96
0.025	30	25	7.75
0.0175	1440	60	8.49

Table 6. BBD design for pimelic acid functionalization experiments.

Pimelic acid			
Concentration (M)	Reaction time (minutes)	Temperature (°C)	d-spacing (nm)
0.03	1440	25	7.49
0.02	1440	60	7.49
0.003	1440	60	7.62
0.0175	30	60	7.82
0.005	1440	42.5	7.25
0.025	1440	25	6.91
0.01	1440	42.5	6.75
0.008	1440	60	7.31

5.1.2 Examining the Surface Morphology of commercial PES membrane.

To better comprehend the difference in ions separation technology processes between the use of commercial ultrafiltration membranes and coated membranes, thorough studies were conducted through performing SEM analysis and examining the surface morphologies of polymeric and nano porous membranes. The membrane desalination process has become pivotal throughout the years as it serves as an aid to solve global water related challenges. This was made feasible through the innovative production of nano porous membranes which was compatible enough to remove microparticles, colloids, salts, metal ions and low molecular substances from polluted wastewater (21). The images are depicted in figure 13a-d, with SEM results being similar the ones obtained by (128). In many research settings, the traditional approach is to understand the physical properties of the materials under study. One such materials are the polymeric membranes, namely the PES, cellulose based membranes and PSF membranes. The structure and membrane morphology influences the adsorption characteristics of the membrane. Establishing a balance of control between selectivity and flux can be daunting for such type of membrane to handle. It has been reported by Khayet *et al* (129), that the membrane application within the wastewater treatment industry becomes susceptible to fouling after long hours of operation. The motivation behind this being that the membrane undergoes attachment of hydrophobic organic substances on the membrane surface. It is thus imperative to examine the surface morphology, roughness and cross-sectional area of the membranes using scanning electron microscopy (SEM). It can be clearly observed through the SEM images in figure 13 a-d, the surface of the unmodified PES membrane is very smooth. The structural integrity of the membrane is intact as there are no visible pores on the active side and flip side of the unmodified PES membranes. The upper part of the membrane is a thin smooth fragile layer supported by interlocked fibrous networked materials. There are no visible pores, and the surface of the membrane is dense, resembling propitious platform for treatment of wastewater (56). The performance of such types of membrane materials have been reported to possess many technical shortcomings such as the designed minimal thickness of the membrane required for membrane to achieve maximum water flux, its ability to retain maximum achievable solutes and improving selectivity as well as its robustness when exposed to conditions of high pressures and temperatures.

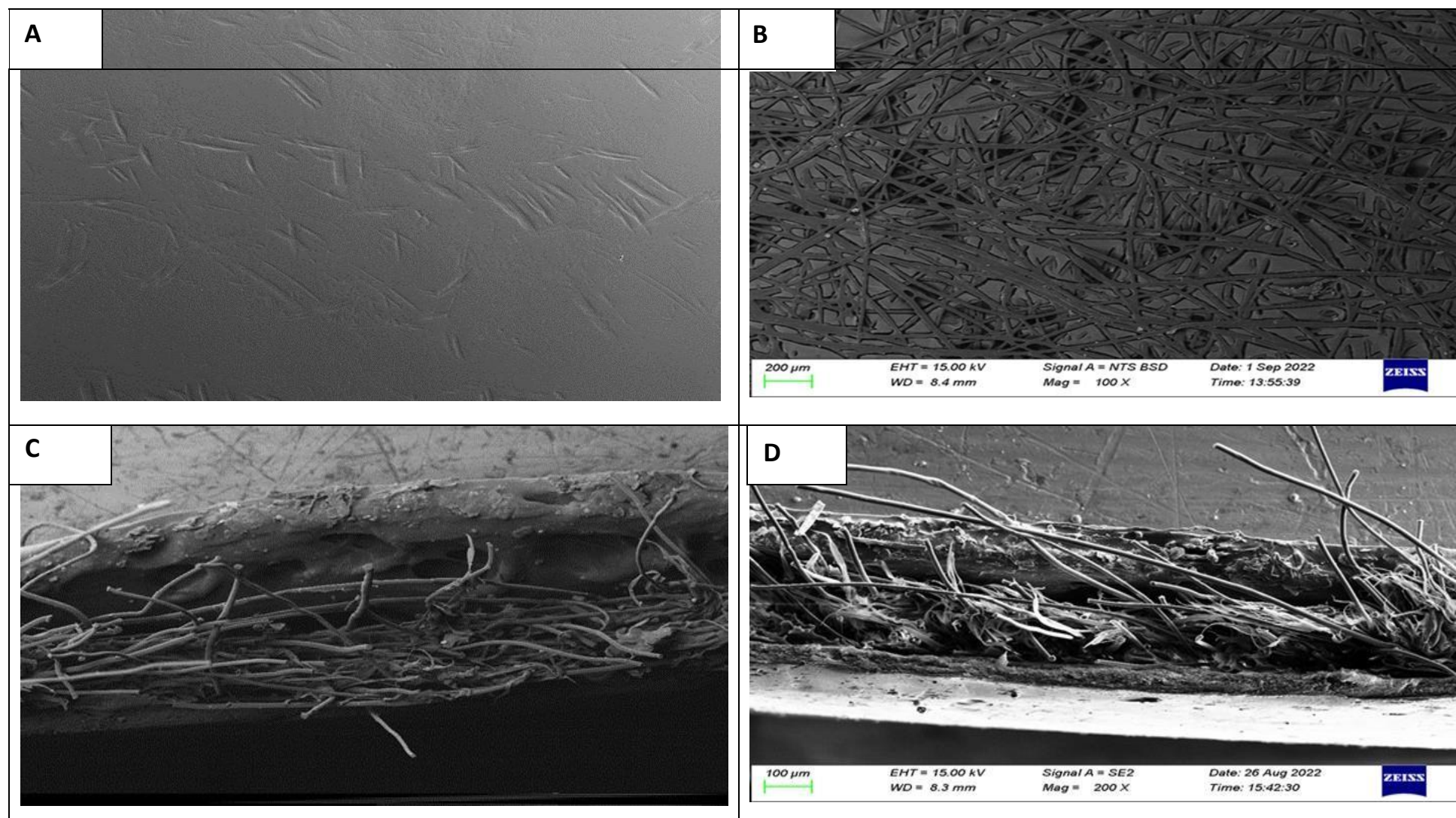


Figure 13 SEM images of (a) the Polyethersulphone membrane support, (b) the non-reactive side of the membrane and (c, d).

5.1.3 The functionalization process for PES membrane.

During the distinct polymeric membranes, PES and PSF have been considerably utilized within the wastewater purification and protein separation industries (130). This was largely due the membrane outstanding properties of being thermally resistant, as well as its magnificent hydrolytic stability and their ability to retain strong mechanical properties within different membrane operating conditions which renders them viable for their suitable use in wastewater treatment. The above-mentioned properties are acceptable factors for various applications of PES in terms of fabricating asymmetric membranes with different pore sizes. Based on the low hydrophilic properties of the PES among others nanofiltration membrane materials such as polyamides and cellulose acetate infused membranes, the PES membrane has been regarded to be the most prominent regarding its susceptibility to membrane fouling. When compared with the PSF membrane, it was found that the PES membrane revealed had much greater hydrophilicity, an increased permeation rates profile as well as improved antifouling properties of the membranes (131). In contrast, the fundamental hydrophobic characteristics of these PES membranes has led to very weak interactions between the solute's in-feed solutions and the membranes (131), leading to non-specific adsorption between heavy metallic ions on the membrane surface as well as within the matrix dimensions. The consequences of the above-mentioned adverse effects of the PES membrane are decline in permeation flux and increased membrane fouling. The decline in membrane performance caused by membrane fouling can be seen as the most pertinent problem in membrane filtration processes. The consequence of fouling makes the membrane processes to be one of the most energy consuming processes, leading to shorter membrane lifetime and unpredictable separation performance (132). However, several research outputs have noted that they can substantially improve on the above-mentioned technical complexity regarding membrane technology through the application of modification techniques. This innovation principle could be achieved through the introduction of hydrophilic functional groups and surface modification of the commercial PES polymers by utilizing approaches such as surface coating, grafting, and blending with nanoparticles as demonstrated in literature with the aim to improve the antifouling characteristics and permeation rates of membranes (131). However, it has been reported that the structured usage of carbon nanotubes (CNTs) and PES in composite applications largely influenced on the ability to distribute the solvents homogenously throughout the matrix and assess its affinity between the matrix and the

polymeric membranes, with the illustration given in Figure 14 and 15. Researchers have established optimized procedures regarding the reduction of membrane fouling and that involves the modification of membrane surface using polyelectrolytes solutions as well as organic coatings (129). During the experimental phase of this study, investigations went underway to study which different concentrations of acids will be effective for attachment of different functional groups during graphene oxide activation process. The process involved amination of Polyethersulphone (NH₂-PES). The subsequent reduction reaction of the nitro Polyethersulphone (NO₂ – PES) that takes place during the process is fabricated by the nitric and sulphuric acid, HNO₃ + H₂SO₄ or rather labelled nitration mixture (129). The SEM images depicted on the figure 14a-b, revealed that the attachment of the electrophilic amine groups on the polymer host membrane was successful. The different concentrations resembled different effects onto the surface of the polymer matrix, as depicted on the SEM images. The introduction of the amine functional groups was more when the concentration of the solution as can be seen in figure 14c-d. The functional groups were attached onto the PES membrane via the dip coating technique in nitrogen environment, guiding to the polymerization of allyamines to occur within the surface of the membrane. Numerous studies conducted by researchers has outlined the amination process as nucleophilic- substitution reaction to be a difficult process whereby the NH₂-amine groups replace the hydrogen atoms within the surface of charged PES membrane. The degree of grafting of the primary amine group onto the surface of membrane₄ increased with an increase in the concentration of the nitration mixture. Figure15a -c shows the stability of the amino group attached onto the host polymer. The dissociation of the SO⁻ occurs during the amination reaction resulting in the introduction of negatively charged sulphonic groups grafted to membrane alongside with the amines (129,135). The introduction of -SO₃H for membrane refitting purposes was applied to improve the surface properties of the ultrafiltration PES membrane. The degree of sulphonation also varied according to the concentration of the acids added into the host membrane. The reaction mechanism involves the electrophilic attack from sulphonic group onto the hydrogen atom within the aromatic polymer chain within the ortho location which is linked to the PES chains. Fourier transform infrared spectroscopy was utilised to examine the interactivity amongst the PES chains and mixed acid solutions composed of H₂SO₄ and HNO₃. As anticipated, it was found that the absorption band located at 1170.92 cm⁻¹ could be attributed to the etheric stretching vibration between the oxygen atoms and aromatic rings of

the PES/ PSf chains (56). The other absorption bands of PES such as aromatic bands at 1578 cm^{-1} from the benzene ring as well as 1485 cm^{-1} attributed to the C-C stretch with the aromatic ether band located around 1250 cm^{-1} , while the asymmetrical and symmetrical vibrations representing the sulphone groups located within wavelength ranging from $1150 - 1300\text{ cm}^{-1}$ (133). It has been well studied that the amine- functional groups are highly reactive with polymer substances and contains a wealth of chemistry with the ability to react with many chemicals, with the most prominent peaks for amide groups located at around 3400 cm^{-1} and was endowed to the NH_2 stretching vibration and the absorption. From the FTIR analyses, it can thus be assumed that the amine functional groups were established on the surface of the commercial PES membrane. In this research study, novel functionalised PES membrane coated with a mixture of HNO_3 and H_2SO_4 , where the different concentration of the acids and their effects on the host polymer membrane was assessed on their impact regarding improving the surface properties and ultimately the performance of the ultrafiltration membranes. The conventional method utilised to functionalize the membranes with the amine functional groups was a process involving the coupling of reagents (SOCL_2), whereas in this study the sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), was used as the crosslinker solution responsible to introduce the amine functional groups as they were being coated on the polyether sulphone membrane support (18). Therefore, as stipulated on the experimental procedure, through changing the coating time and being able to manipulate the supplanting of amines, and sulphonic functional groups with the aim of obtaining the desired functional groups coverage and desired coating thickness on the membrane support.

The results revealed in figures 14 and 15 were the same as those obtained by (128,133), indicating how effective the surface graft polymerization process was in endeavor to enlarge the surface hydrophilicity of the membranes. The FTIR analysis conducted was to assess the formation of hydroxyl, carboxyl, and amide groups on the PES membrane, it is a flexible system to indicate the type of functional groups and demonstrating the formation of polymer restructured PES membrane. Through the surface grafting method applied in this section of research was effective in terms of bringing about effective changes in membrane morphology, altering the surface composition which will in turn improve the hydrophilicity as well as the antifouling properties(132).Research work done by Ganesh *et al*(5), have worked on projects aimed at improving hydrophilicity and enhancing salt rejection was achieved through the Polysulfone membrane support with modified polyisobutylene-alt-

maleic anhydride. This surface grafted functional groups can function as ion-selective operational coatings, which can lessen the co-ions expulsion effect and increase the membrane charge efficiencies. The goal for this improvement process was to mitigate the risk of chlorine attack likely to attack the membrane PA-TFC structure.

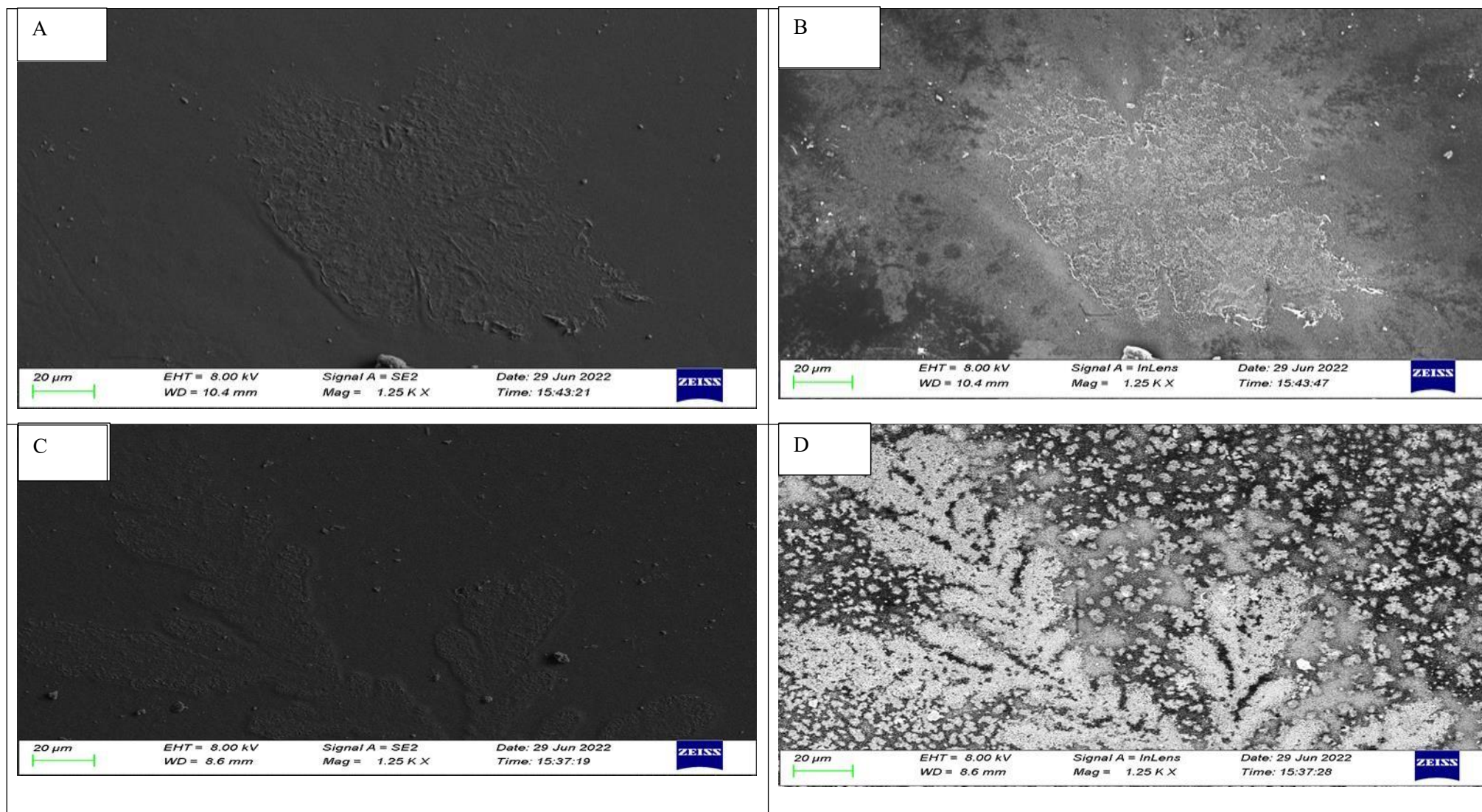


Figure 14. Analysis of the effect of concentration and varying coating times using (a, b) 0,01M oleum mixture, (c, d) 1M oleum mixture onto the PES membrane support.

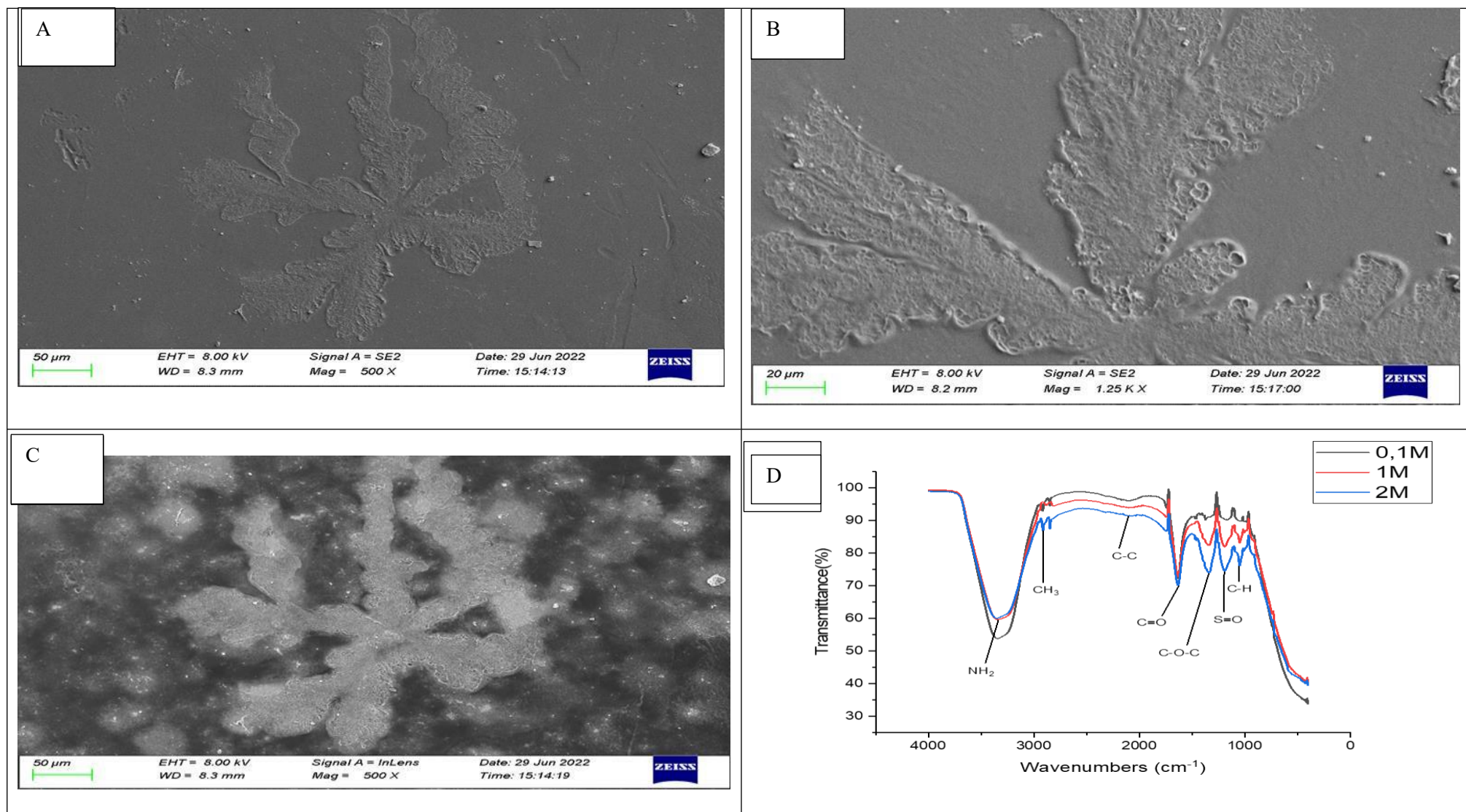


Figure 15. The analysis for pristine PES membrane coated with a concentration of 2M(a-b), © for functionalised PES membrane (d) FTIR spectra of coated PES membranes

5.1.4 The effect of cross-linking agents (Glutaric, Adipic and Pimelic acids) have on the morphology, intersheet spacing and porosity of the PES membrane.

The GO membranes are correlatively elementary to assemble from the aqueous dissipation of the GO. There are a wide variety of methods to prepare the GO membranes which entails the filtration-assisted method, evaporation assisted method as well as the LbL method (Layer-by-Layer) method. In the filtration-assisted method, the membranes can be obtained by either the vacuum or pressure assisted method. The background study conducted pertaining to this research study mainly focused on the synthesis methods for thin film membranes and how well the improved membranes differed when compared to their counterpart traditional membranes. The detailed analysis was strategized regarding the differences in the unmatched characteristics possessed by the modern membranes regarding their unmatched characteristics in being the high durability, well defined morphologies, ability to resist corrosion and chlorine resistance functional groups present within the nanocomposite matrix, their high resistance and membrane stiffness (27). Important to note during the fabrication of the membranes is their structural properties and the reinforcement of the nanomaterials into the polymer matrix. Different functionalised GO nanomaterials were utilised to construct the thin film nanocomposite membrane which would be responsible for separation and adsorption of heavy metallic ions, however, as mentioned by several researchers, to engineer the expected high-quality parameters, the nanocomposite membranes should be fabricated to suit the needs of the wastewater treatment processes (25). One way to tailor such requirements is through the surface grafting or filtration assisted methods in which the nanocomposite membranes are fabricated from inorganic matrix components immersed within the organic phase solutions to configure firm ceramic membrane structures hosted by the conventional polymer PES membranes (25,27). The highlighted advantage and shortcoming regarding the use of this different nanofillers comes in their principal degree of uniqueness which renders their application suitable for enhancing the structural compactness of the membrane. The shortcomings have also been outlined regarding the membrane fabrication using this nanofillers and it has to do with formation of membrane defects which are caused by weak polymer particle adhesion (25). The structural defects formed during the synthesis of nanocomposite membrane have been noted to form voids and agglomerated particles on the host PES polymer membranes leading to poor surface morphologies and inadequate separation performances (43). One of the research objectives was to examine the morphological changes in the host polymer matrix via the addition of functionalised graphene

oxide. The SEM analysis was done to study the effect each crosslinking agent had on the porosity and morphology of the membranes. As can be seen in Figure 16a, the addition of glutaric acid functionalised nanofiller brought changed the surface morphology of the membrane with the formation of cracks compromising the structural integrity of the nanocomposite membrane. The presence of the functionalised graphene oxide was observed however is impeded with the structural integrity of the thin film nanocomposite through creating of multiple porous nanochannels. The incorporation of the functionalised GO increased the porosity of the membranes as it has led to the of macro-voids that have been observed in figure 16b. The formation of macro voids and cracks could be due to the weak polymer particle adhesion forces between the crosslinker solution used, the nanofiller and the functional groups present on the host polymer membrane which were grafted via the mixed acid solution of nitric and sulphuric acid. The images stipulated the construction of those membranes for Glutaric and Adipic acid were recorded in figure 16, and it was observed that the particle adhesion of the nanoparticles on the membranes caused a whole array of defects and ultimately degraded the structural properties of the membranes which wouldn't serve as a good aid for separation processes. The disadvantage of such membranes is that based on their structural defects they can lead to unsatisfactory results during the membrane filtration processes (74). The change in process variables during the separation stage gets largely affected by poor structural integrity of nanofiltration membranes (86,136). It is very imperative to construct well defined nanostructured polymeric membranes with innovated nanofillers. The attached amine functional groups at 2M showed great polymerization and that was utilized for the preparation of covalently grafted graphene oxide infused polyether sulphone nanocomposite membrane. The crosslinker solution was prepared at 2%, whereby the Dimethylaminopropyl-N-ethyl carbodiimide hydrochloride (EDC) was reacted with the amine coated PES membranes for 30 minutes before being dispersed into functionalised GO solution. According to research conducted by Khayet *et al* (129), the free chloride groups of the crosslinker solution reacts with the carboxylic, epoxy and hydroxyl groups of the graphene oxide to form anhydride and ester bonds. The alteration caused by the bondage of GO nanosheet with crosslinker, and amine coated functional groups can be observed on the SEM images depicted in figure 16a to d. The modification of the chain length of the dicarboxylic acid (Glutaric and Adipic) shown greater effect in terms of altering the intersheet spacing of the PES/GO membranes as can be seen in Figure 16b and 16c. However, at the centre of the synthesis method used to fabricate these membranes, it was

detected that there were cracks and wrinkles formed, which according to literature study, they degrade the performance of the resulting thin film nanocomposite membranes in terms of wastewater purification (117). The greater intersheet spacing can be attributed to the effective functionalization process which resulted in the intercalation of greater functional groups into the synthesized graphene oxide. According to Jia & Wang (4), the chemical crosslinking created amongst the GO sheets possess great ability to improve mechanical stability of the membrane and that could be observed in the thin film membrane ability to avoid losing membrane structure. However, due to the poor particle polymer adhesion between the nanofillers and membrane, it was concluded that the properties of the commercial PES membrane and host of the inorganic nanofillers embedded in the EDC solution mixed with the acid solution resulted in the formation of the defects as seen in figure 16. Throughout the years, research work focused on the applications of graphene oxide with regards to improving their chemical and physical properties has led to breakthrough innovation regarding the synthesis methods which entails elemental doping, the intricate functionalization methods of metal nanoparticles and chemical modification of organic molecules with polymers. The above-mentioned processes have been studied in detail with the main aim of improving the function of the carbon material. To fabricate graphene- based covalently bonded nanocomposites which will lead to high separation performance, homogenous dispersion of the nanofillers is very key. One of the factors that would hinder this process is the agglomeration of graphene sheet onto the polymer membrane. This occurs because of uncontrolled assembly of the graphene sheets as well as poor coating of the oleum mixtures during amination reactions. Several research findings revealed that an increase in the GO content will eventually lead to increase in the porosity of the membrane. It has also been noted by (7), that an increase in the graphene oxide content has potential to enhance the selectivity and penetration resistance of the PES grafted membrane. The size of the crosslinking monomers affects the nanochannels (d-spacing), separation performance as well as permeability of the nanocomposite membrane. The functionalised pimelic acid PES membranes formed stable layered structure which showed the ability to resist formation of large cracks and large intersheet spacing. The mechanical properties of the pimelic functionalised membranes were robust when compared to the other two membranes. The challenges of synthesizing and consigning large-area graphene membranes using glutaric and adipic functionalised membranes were outlined in the discussion above, therefore with the pimelic functionalized membranes as shown in figure 17a, the thin film nanocomposite membrane formed for molecular separation met the specifications for an ideal membrane

which can be deployed for molecular separation. The membrane was found to be as thin as possible, with all the chemical constituents utilised to fabricate the membrane being well coordinated. The construction process for a mechanically robust membrane revealed the ability to maximize the permeate flux, preventing it from possible fracture as opposed to two counterpart membranes. The Pimelic functionalized membrane as shown in Figure 17a resembled well-defined pore channels which would guarantee the selectivity process for ion separation (117). The framework utilised to fabricate the pimelic functionalised membrane is shown in figure 17b, also like the one utilised for the other two membranes. However, in comparison of the three membranes, it was found that the reaction mechanism used to synthesize these membranes favoured the dicarboxylic acid possessing the highest number of molecular chains as well as greater intersheet spacing. Such results obtained from this study correlates well with the finding made by Jia & Wang (4), in that the GO membrane composed of increased length of molecular chains generally provides the optimum permeation fluxes. The ideal membrane should be tailored to electrostatic binding, cation- π interaction and metal coordination, therefore the complex reaction mechanism to fabricate the GO thin film matrix membrane has been defined in figure 17b. As outlined in figure 17b, the carboxylate ion O^- from the functionalised GO molecule attacks the Carbon (C^+) ion on the EDC molecule breaking the double bonds of the chain and forming an unstable $C=N$ bond from the proton transfer, and since there is less of the OH groups on the edges of the GO molecule, the amines present then attacks the carboxylic acid functional group to form an highly reactive intermediate, and proceeding that stage the addition and elimination of the molecules occurs to form a stable covalent amide bonded functionalised GO membrane. Several research studies conducted indicates that covalent bonded structure follows a strict and severe reaction process and the molecules introduced are durable. The GO coating process and results obtained for this study was like the one done by Hu & Mi (18).

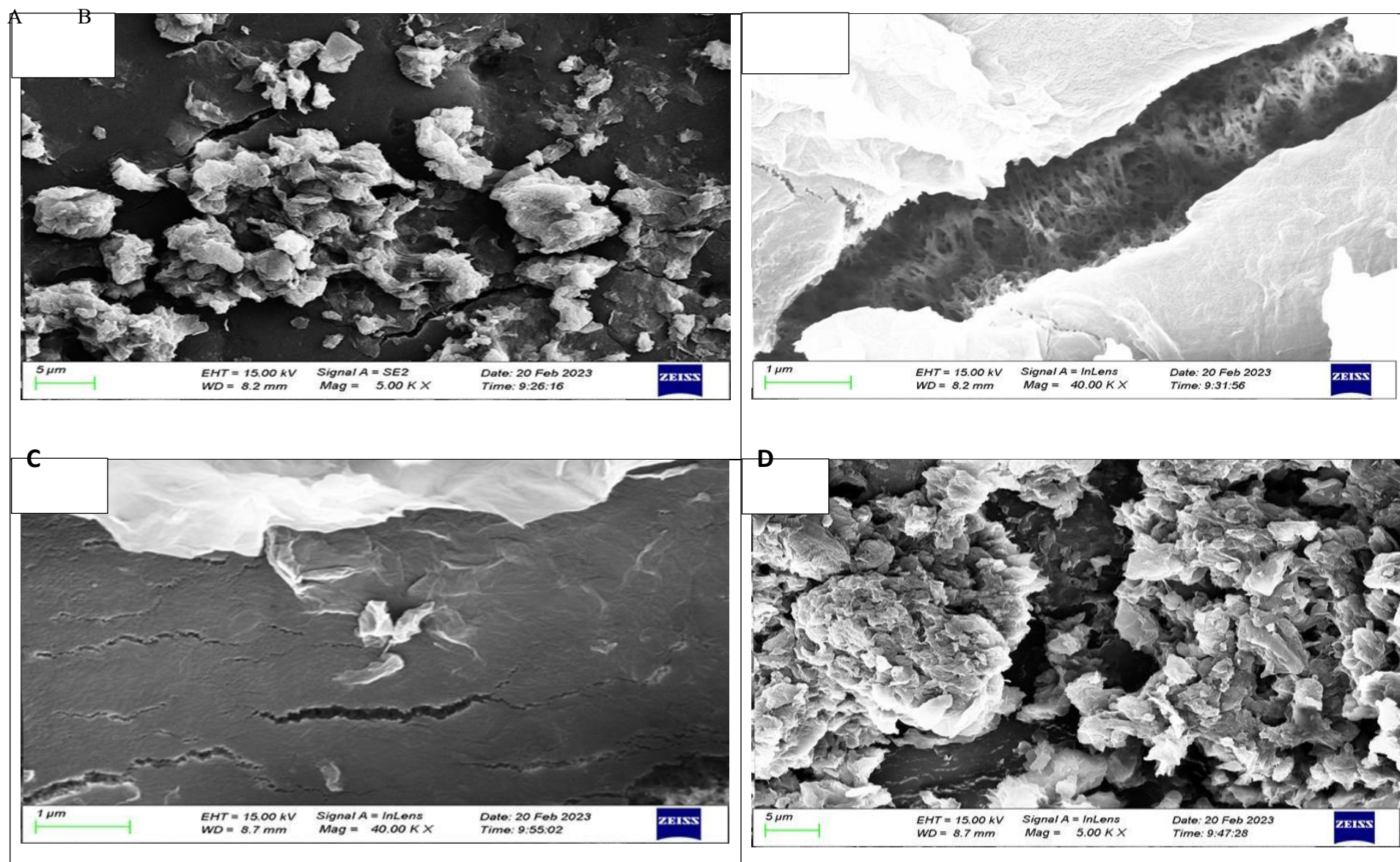


Figure 16 The dicarboxylic acids coated membrane support, (a, b) coated with Glutaric acid, (c, d) coated with Adipic acid.

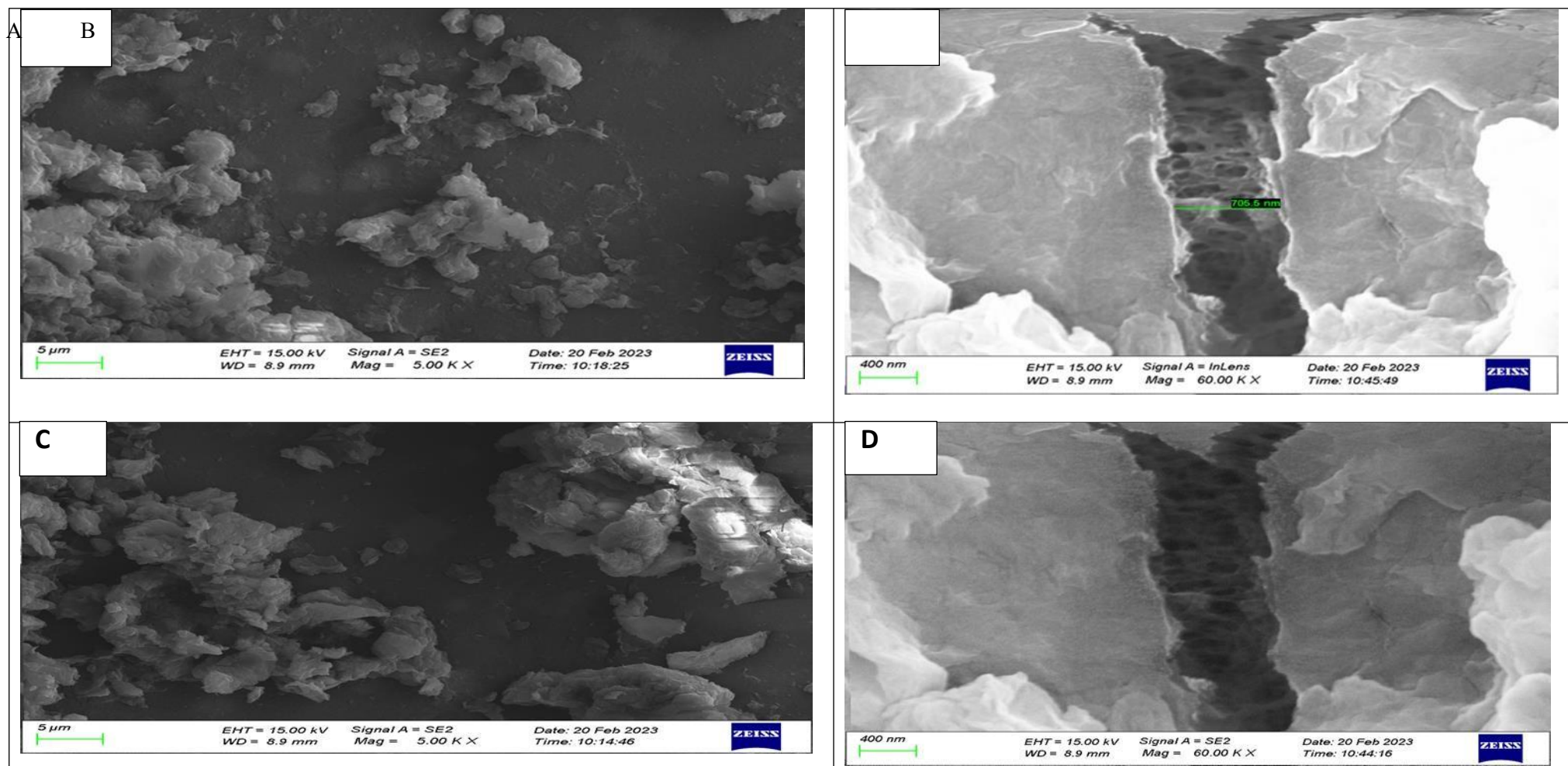


Figure 17. The Pimelic acid functionalization PES membrane support, (a, c) revealing the surface morphology of the attached functionalized GO layers, (b, d) revealing the porosity of the coated membranes as well as the effect crosslinking had on each membrane.

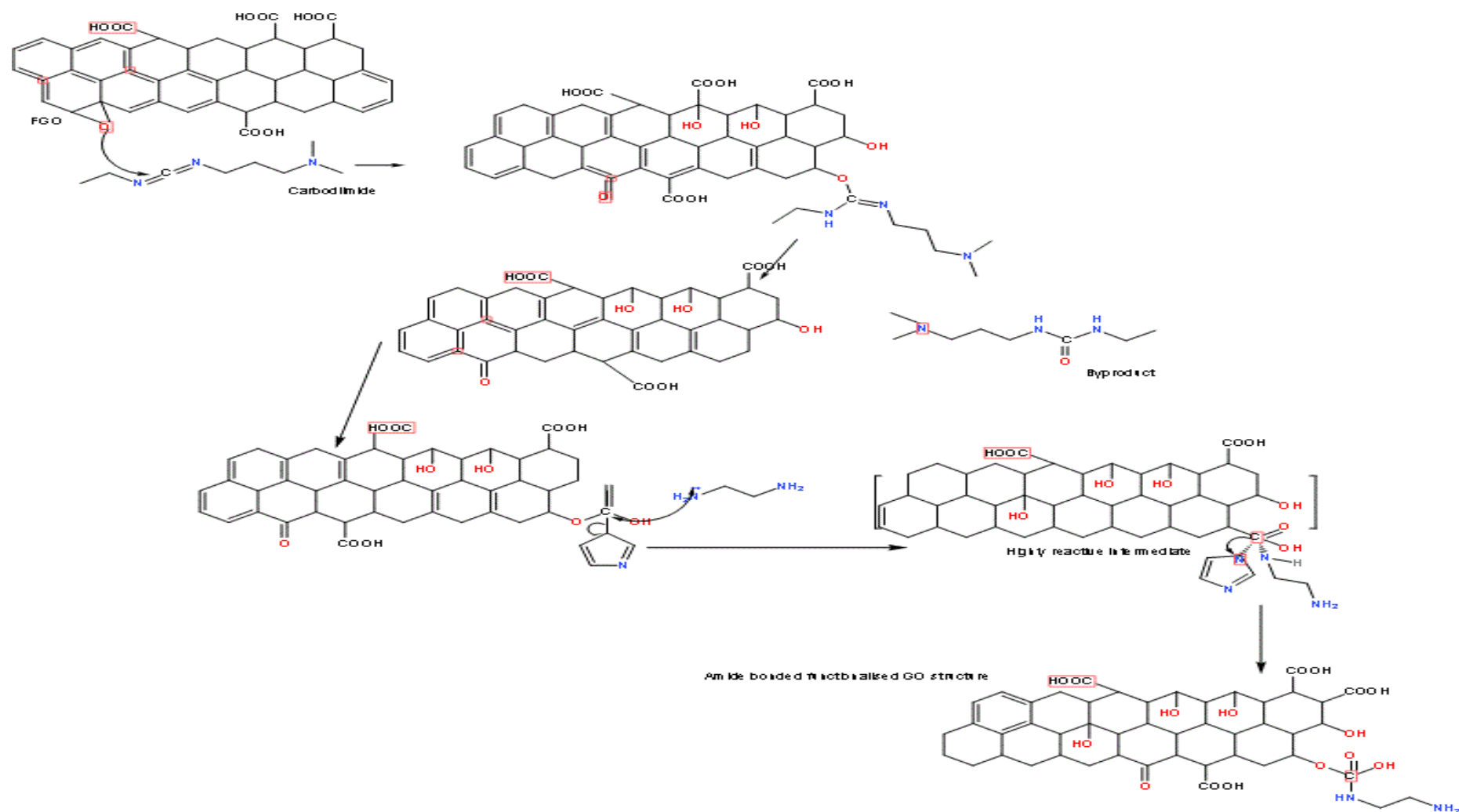


Figure 17b. Diagram representation of reaction mechanism for dicarboxylic acid functionalised GO with N-(3-Dimethylaminopropyl)-N-ethyl carbodiimide hydrochloride.

5.2 Performance evaluation of the commercial PES thin film composite membrane.

5.2.1 Nanofiltration Performance evaluation for commercial PES membrane

The performance of the membrane was estimated by calculating the removal percentage of the heavy metals contained in acid mine drainage wastewater. Research has documented promising performances from GO-nanocomposites membranes in terms of removal of selected pollutants from water. The removal capacity and permeation rates of the commercial PES membrane has been presented in figure 18. From the data represented in figure 18, an increase in the feed concentration has shown a slight decline in the removal of heavy metallic ions. When varying both pressure and operating time, the removal rate reduction because of permeate flow showed similar trend as that observed by Maher *et al* (1) and defined the observation because of solute permeance through the membrane being proportional to the concentration in the feed. The heavy metallic ions present in the synthetic acid mine wastewater and seawater were recorded at low concentrations. At higher metallic ion concentrations using real acid-mine drainage (AMD), the nanofiltration membrane performance index was low and similar trend was observed as function of time and operating pressure. The data depicting the experimental runs for the pure PES membrane was stipulated in table 6 below. In examining the performance index of the commercial PES membrane, the relationship concerning the changes in process variables such as applied pressure, operating time and concentration of the solute on heavy metal removal was analyzed.

5.2.1.1 Process Optimization of the PES membrane using Box-Behnken design.

A total of 14 experimental runs was performed for the commercial PES membrane where it was found that the membrane reached an average of 96% removal rate for low heavy metallic ions from synthetic acid mine drainage wastewater sample. The experimental runs for optimization of heavy metallic ions by PES membrane are outlined in Table 6. The regression models for the metallic removal efficiency and permeate flux are indicated in Table 7. The statistical significance of the regression models was stipulated revealing that the likelihood of margin of errors was low. According to ANOVA, the *f*-value, described as a measure of the variance of data regarding the mean, was examined. In terms of verifying the statistical model of the RS-model, the *f*-value was found to be 127,05, and P-value was <0,0001. The R^2 value was found to be 0.995, being close to unity showing how well the experimental and predicted results correlate. The independent variables interconnections are demonstrated via the 3D surface plots, derived from the quadratic polynomial model. In figure 19 and 20, at each surface plot, two variables were altered, whilst the other variable was maintained at a constant value of zero coded level. The trend analyzed from figure 14, it was found out that the performance of

the membrane was decreased at low operating time when treating high concentration metallic ions, it increased when treating low concentrations within the same operating time of 10 minutes. An increase in the operating time and treating high concentrated metallic ions would imply a decrease in performance of the membrane operating at optimum pressure of 250 KPa, whereas if the system was to operate at optimum time of 30 minutes and treating metallic ions with medium concentrations, the performance of the membrane was at its highest. It was observed that at concentration of 65,22 mg/L, operating time of 30 minutes and operating pressure of 250 KPa the membrane performed at 96,9% removal rate of the manganese metallic ions. The decrease in the solute rejection observed in the commercial PES membrane as depicted in figure 19 and 20 was due to an increase in concentration gradient, which could eventually lead to membrane fouling. The inorganic deposits on the surface of the membrane creates pore blockages which in turn reduces the performance of the thin film composite membrane. The response surface plots showed a decline in metal ion rejection from concentration of 65,22 mg/L (6.522mg/L dilute concentrations) attributing to the phenomenon on of concentration polarization. In figure 20, the two variables analyzed was operating pressure and feed concentration at constant time of 30 minutes, we can deduce that the nanofiltration system could handle low metal concentration at any given pressure. It has been reported that the mechanism of metallic ions rejection is influenced by a variety of factors such as membrane pore size, membrane size, hydrophobicity as well as surface charges. Numerous research studies done has shown that charge repulsion of metallic ions on pure PES membranes depends on the membrane ionic strength, ions capacity as well as membrane charges (23). The more metallic ions present in the wastewater at high concentration, the less the performance of this nanofiltration membrane system. The optimum conditions from using this type of membrane were found to be 30 minutes, pressure of 250 KPa as well as concentration of 6.522 mg/L. At those stipulated conditions the mean permeability of the commercial membrane was found to be 65,74 L/m².hr and removal rate of 96%.

The concentrations of the synthetic AMD feedstock solution used to carry out this experiment has been stipulated in the Appendix under the heading Fe with a series of generated results from the AAS analysis. To calculate the percentage removal values for each metallic ions, there was a system or procedure followed. Since the Box Behnken design generated design expert report explains the input and output concentrations evaluated at different operating process variables, for the illustration of how the percentage removal values were obtained would be clarified by looking into how manganese metallic ion concentration was calculated although it's not shown

in the system of results obtained. The results shown in Table 7 includes concentration inputs and outputs for Iron and Sodium, with the concentration feedstock or input concentration being at 10.414 indicating the higher operating limit, and the sodium being at 2.63 indicating the lower operating limit. The concentration for manganese was measured concurrently with those for iron, hence the results section for these two metallic ions are placed under one folder just being divided amongst the columns. The input concentration for manganese before filtration was 7.323 mg/L as a synthetic AMD solution. The solution was diluted, and experiments were conducted under different operating conditions. The instance where pressure was kept constant at 250 KPa and the operating time was varied between 10-50 minutes the removal rate for manganese metallic ions was calculated using the % rejection equation stated in chapter 3, section 3.4.3. The measurements for both input and output concentration for manganese was analyzed using AAS at University of the Witwatersrand. To compute the removal rate on Microsoft excel, both the initial and final concentrations were inserted into the equation, as follows, $(1 - 0.629 \text{ mg/l} / 7.323 \text{ mg/l}) \times 100 = 91.41\%$, and that percentage removal value was computed on the Design Expert software using two-full factorial Box Behnken design mode. The same principle was applied for other metallic ions in Iron (Fe), sodium (Na) and Magnesium (Mg) to attain the percentage removal rates. The results section in this chapter has elaborated on the membrane system performance regarding the change in the permeate flux and removal rates when altering process variables. So according to the model designed, any other heavy metallic ion besides ones used in the experiment, can be tested using the synthesized membranes, and the outcome would be based on the underlying factors discussed in detail in this chapter as to how the nanocomposite membrane declines or improves its performance.

Table 7 Box Behnken design and experimental responses for synthetic wastewater.

Std	Run	Factor 1 Concentration (mg/L)	Factor 2 Time (min)	Factor 3 Pressure (KPA)	Response1 Permeability (L/m².hr)	Response 2 (Mg, Mn & Fe removal) %
5	1	2.63	30	100	45.91	73.57
1	2	2.63	10	250	67.34	82.5
4	3	10.414	50	250	55.1	17
3	4	2.63	50	250	55.1	84.48
14	5	6.522	30	250	64.28	96.5
7	6	2.63	30	400	88.7	85.32
6	7	10.414	30	100	45.9	17
12	8	6.522	50	400	85.71	97.4
9	9	6.522	10	100	58.16	93
11	10	6.522	10	400	104	85.8
8	11	10.414	30	400	88.7	17.3
10	12	6.522	50	100	30.61	93.8
2	13	10.414	10	250	67.34	17.3
13	14	6.522	30	250	63.26	96.9

Table 8. The analysis of variance (ANOVA) experimental results for heavy metallic ion removal.

Model parts	Source	DF	Mean square	<i>f</i>-value	P-value
	Model	9	1691.05	127.05	0.0001
	Linear	3			
	A- Concentration	1	8273.48	621.95	0.00001
	B-Time	1	24.78	1.86	0.2441
	C-Pressure	1	8.93	0.6706	0.4588
	Interaction	3			
	AB	1	1.30	0.0976	0.7703
	AC	1	32.78	2.46	0.1917
	BC	1	29.16	2.19	0.2129
	Square	3			
	AA	1	6564.15	493.16	0.0001
	BB	1	3.79	0.285	0.6217
	CC	1	30.98	2.33	0.2018
Anova results for PES membrane for removal of metallic ions	R²	0.997	Adjusted R²	0.99	

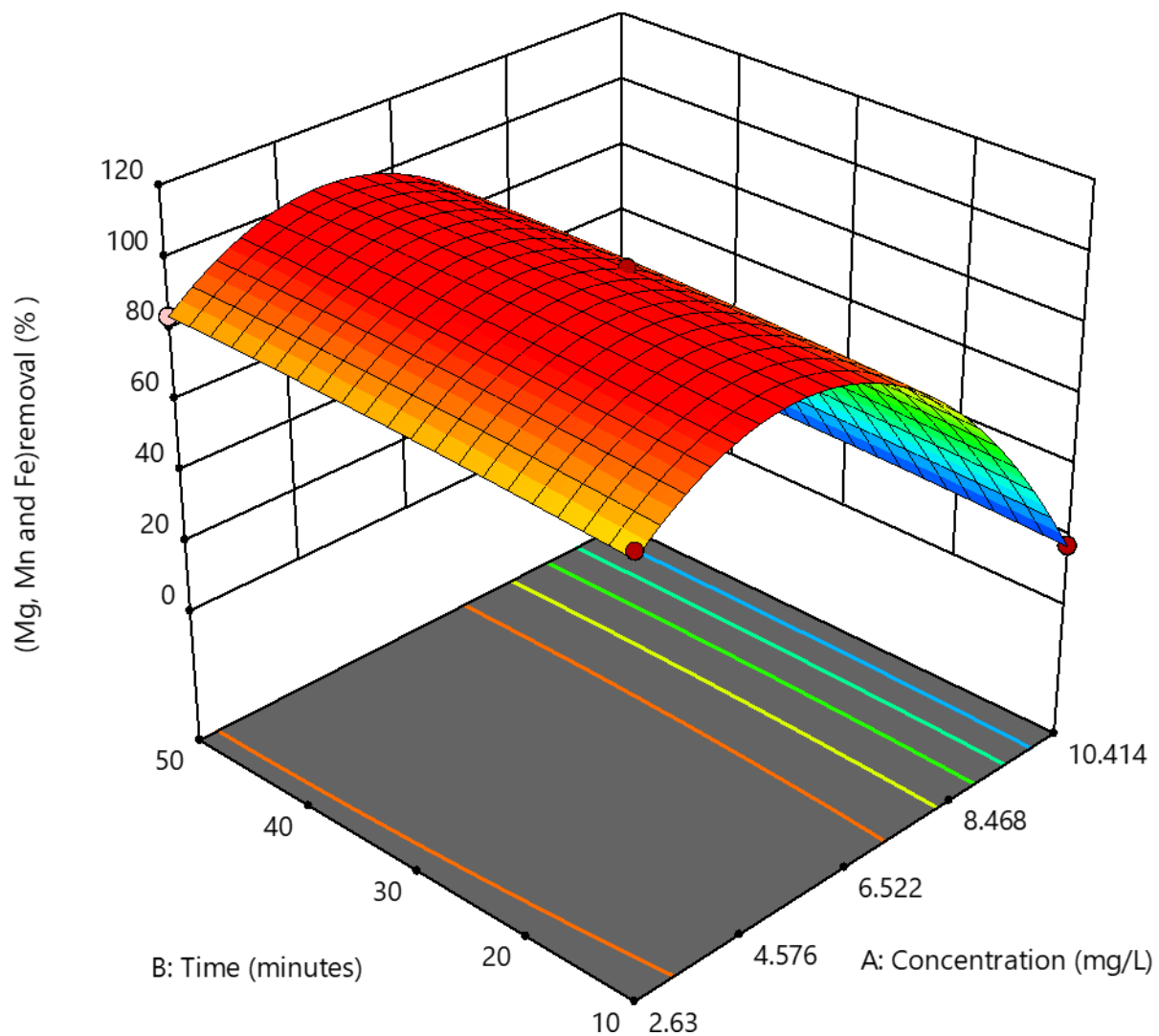


Figure 18. Response surface diagram representation of the predicted NF performance index by RSM for low heavy metallic ions concentration as a function of operating time and input concentration of heavy metals.

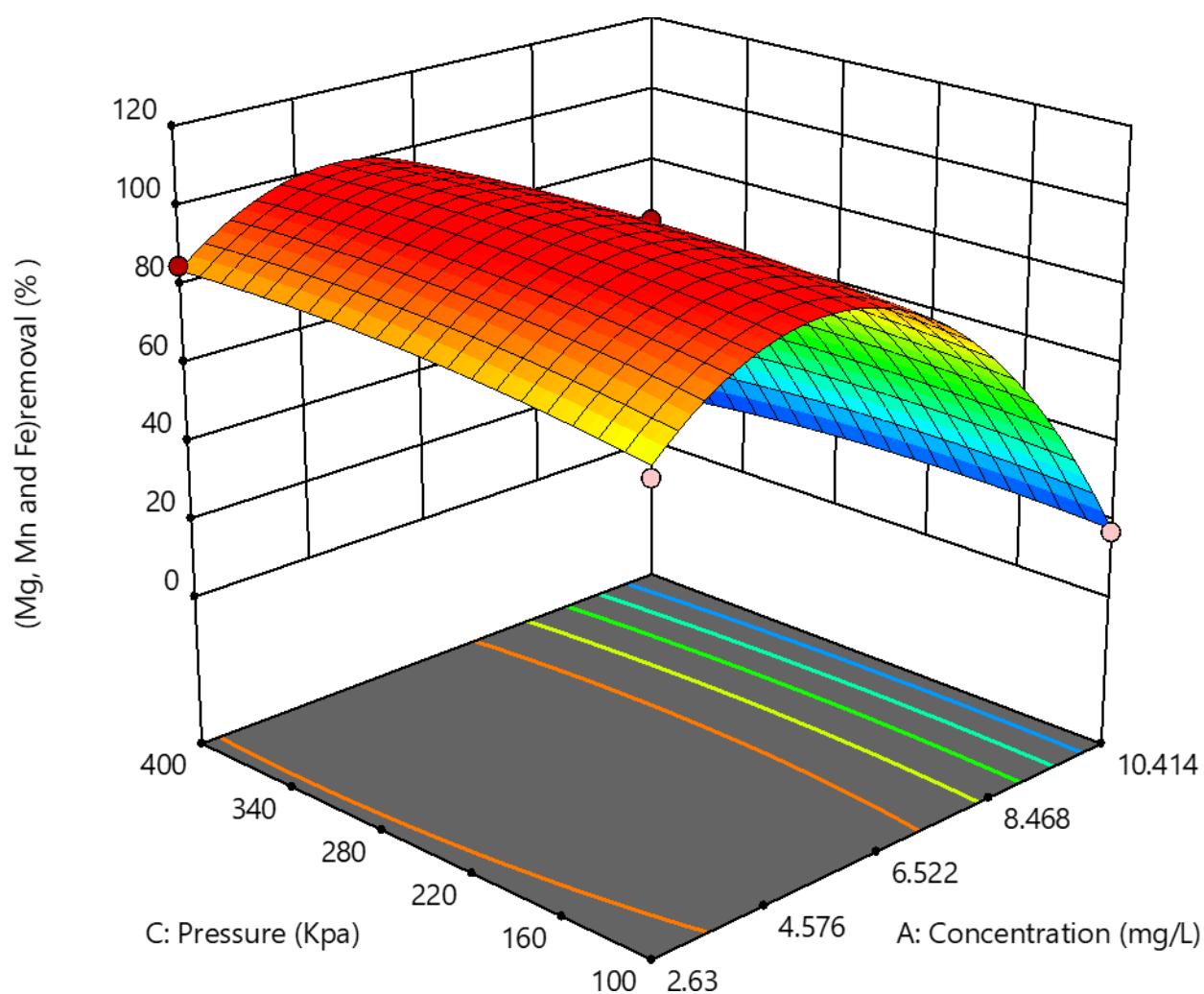


Figure 19. Response surface diagram of the predicted NF performance indicators by RSM for low concentration heavy metallic ions as a function of input operating pressure and concentration of metallic ions.

5.2.1.2 Permeability studies for the filtration capacity of the plain PES membrane.

The Box-Behnken design (BBD) was utilised to analyze the 1st and 2nd response surfaces regarding the assessment of the permeability of the plain PES membrane. Response surface methodology (RSM) and artificial neural networks (ANN) are the utilised mathematical modelling techniques to decode linear and non-linear multivariate regression models (113). The application of RSM in terms of expressing the performance of the thin film composite membrane was examined by researchers such as Idris *et al* (113), with the goal for enhancing membrane permeate flux and heavy metal rejection factor. In this research study, the two-level factorial design was utilised to approximate the relationship between main effects of input factors (independent variables) with their interactions and influence on the output factors (dependent variables). The factors varied in predicting the performance of a commercial nanofiltration membrane was the operating pressure C, the synthetic wastewater feed concentration A and operating time B. All the data and analysis from RSM were presented graphically to obtain a clear perspective of the interactions between the factors and their responses. The response surface graph depicted in Figure 20 revealed a linear function which was based on a simple model which could be adjusted based on the results obtained from the fractionate factorial design, when the output responses (dependent variables) such as permeate flux of the membrane was fitted well into the model. The response surface suggested that increasing both the operating pressures and solute concentration will enhance the nanofiltration performance index of the commercial PES membrane. It can therefore be deduced that the main effect of operating pressure into the nanofiltration system is 4-fold higher than that of the main effect of the solute concentration. However, in examining the interaction effect between the pressure and concentration as stipulated in Figure 20b, the efficiency of the nanofiltration system does not decrease provided that the solute concentrations remain within the parameters assigned to the model. The heavy metal concentration treated by the membrane were Iron (Fe), Manganese (Mn) and Magnesium (Mg). The concentration levels stipulated on the graph were those of dilute concentrations, were Iron (Fe) concentration was 100 mg/L in the solution, with manganese ranging at 76 mg/L as input concentrations. We can thus conclude that the membrane utilised to conduct this research study operates optimally within low metal concentration regions and can withstand high operating pressures. Similar trends were observed by Khayet *et al* (113). The other factor which influenced the permeate flux of the membrane was operating time. Based on the statistical analysis, linear effects of all the studied parameters on permeate flux by pristine PES membrane were significant (p value <0.05). The effects were in such a manner that an increase in operating time, at optimal pressure and

increasing solute concentration caused a decrease in permeate flux. However, the linear effects of operating pressure and concentration was higher than those of operating time. From the graph in Figure 20a, it was found that at system's optimal pressure of 250 Kpa, the permeate flux obtained was 67 L/m².hr, while time remained constant at 10 minutes whilst treating synthetic acid mine wastewater ranging from 20,63 mg/L to 100 mg/L. An increase in operating time from 10 minutes to 50 minutes has caused a decline in the permeate flux to 55,1 L/m².hr. The performance of filtration process has limited variables which can affect how it operates optimally, with operating pressure being one of the driving forces towards the output response (permeate flux), the other factor which affect membrane performance severely is the mobility of heavy metallic ions on the membrane surface (129). It has been noted that the flow feed is in direct relation with the membrane surface velocity, and that affects the shear tension on the composite membrane. The tension force applied onto the membrane surface while in turn affect the permeate variation as well as the rejection factor. From the graph it was observed that at optimal operating time of 30 minutes, the variation in operating pressure from low to high pressure, caused an increase in permeate flux, irrespective of the feed concentration of heavy metal ions present in the solution. Similar observations have been made by Ganesh *et al* (5), where increasing the concentration of the solute having negligible effect on the permeate flow. However, according to the predictive modelling RSM technique, such a membrane system decreased in performance with an increase of input factors. As stipulated in Figure 20 and 21, an increase in operating pressure and time to 400 KPa and 50 minutes respectively, will cause a decrease in both permeate flux and rejection of heavy metallic ions present in wastewater. The phenomenon that causes such variation is known as concentration polarization. This occurs when the solutes accrue on the membrane surface, decreasing the selective capacity and causing a concentration gradient incline. The disadvantage of this phenomenon is the formation of osmotic back pressure which reduces the transmembrane pressure (TMP) of the nanofiltration membrane system. The result of such process variations will lead to membrane fouling due to the occurrence of pore blockages, organic and inorganic precipitation, and cake formation deposits. The membrane fouling problem then becomes a difficult one to solve because of the complexity of the membrane surface structure.

Table 9 The Analysis of Variance (ANOVA) results for the Linear model defining permeate flux of metallic ion using commercial PES nanocomposite membrane.

Model parts	Source	DF	Mean square	<i>f</i>-value	P-value
	Model		1655.76	61.80	0.0001
	Linear	3			
	A - Concentration	1	0.000	4×10^{-7}	0.995
	B- Time	1	618.11	23.07	0.007
	C- Pressure	1	4349.18	162.34	0.00001
Anova results for PES membrane Linear model.	R²	0.95	Adjusted R²	0.94	

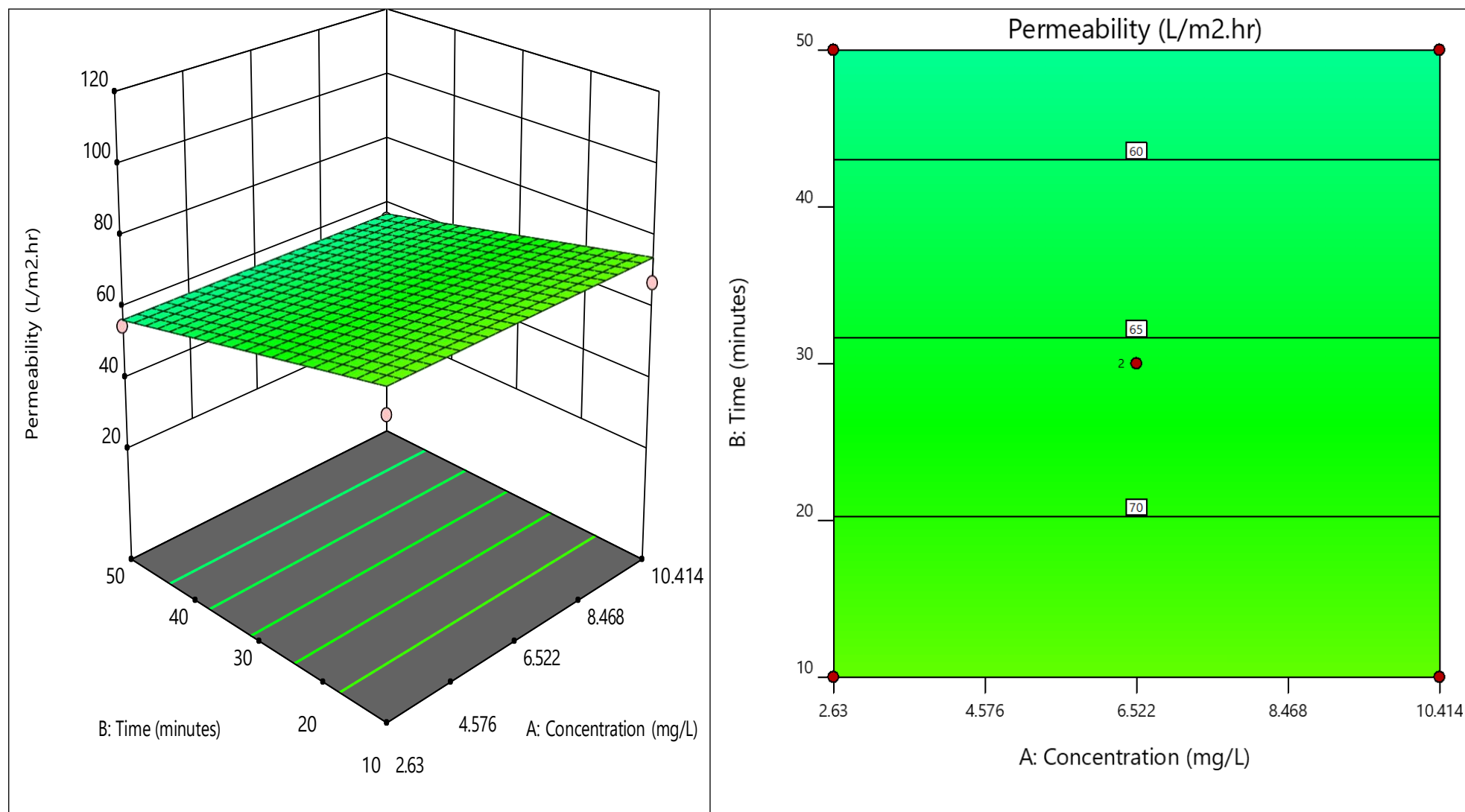


Figure 20 Response surface diagram representation and contour plots for linear and interaction of operating time and concentration for low metal concentrations.

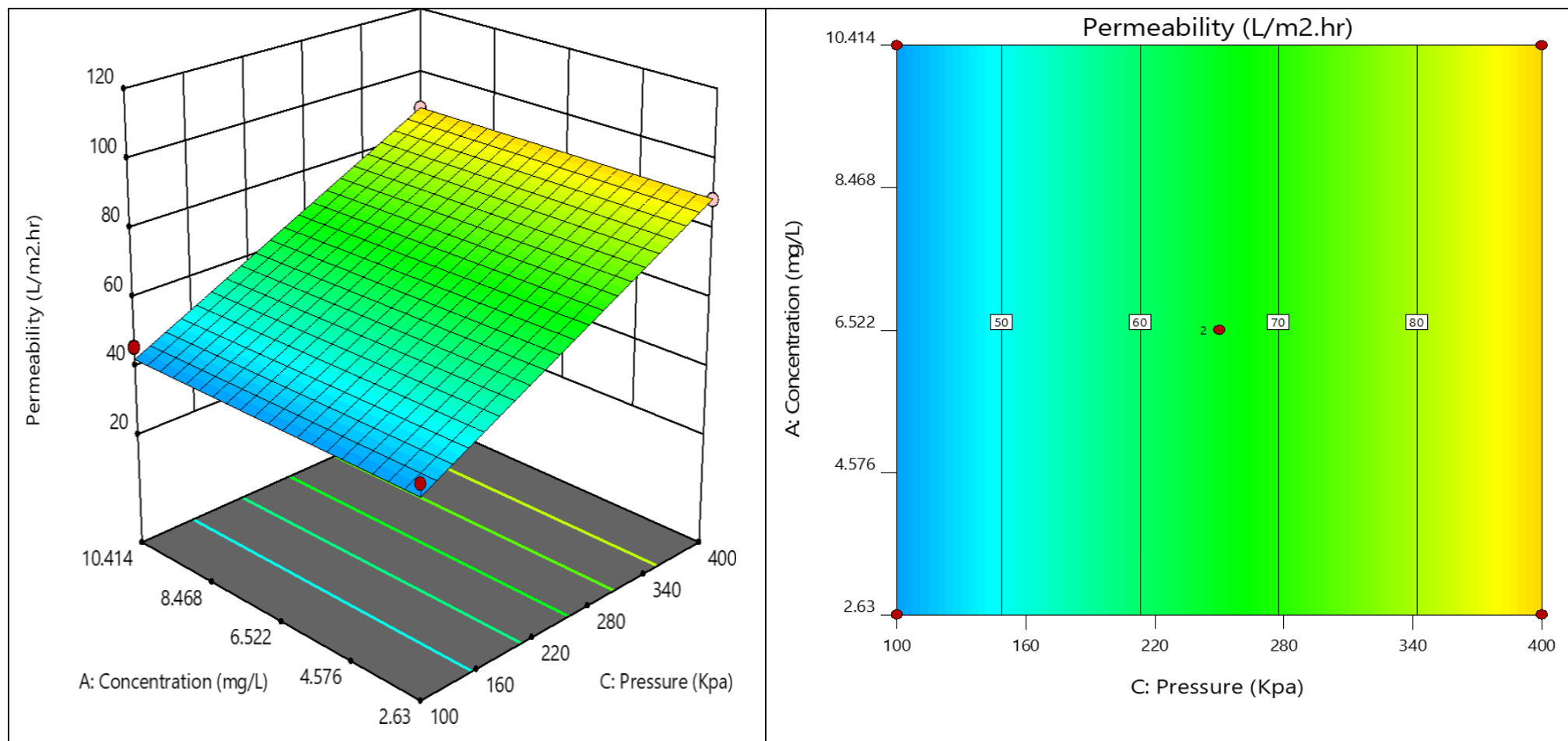


Figure 21 Response surface representation and contour plots for linear + interaction for Operating pressure and concentration of low metallic ion separation NF process.

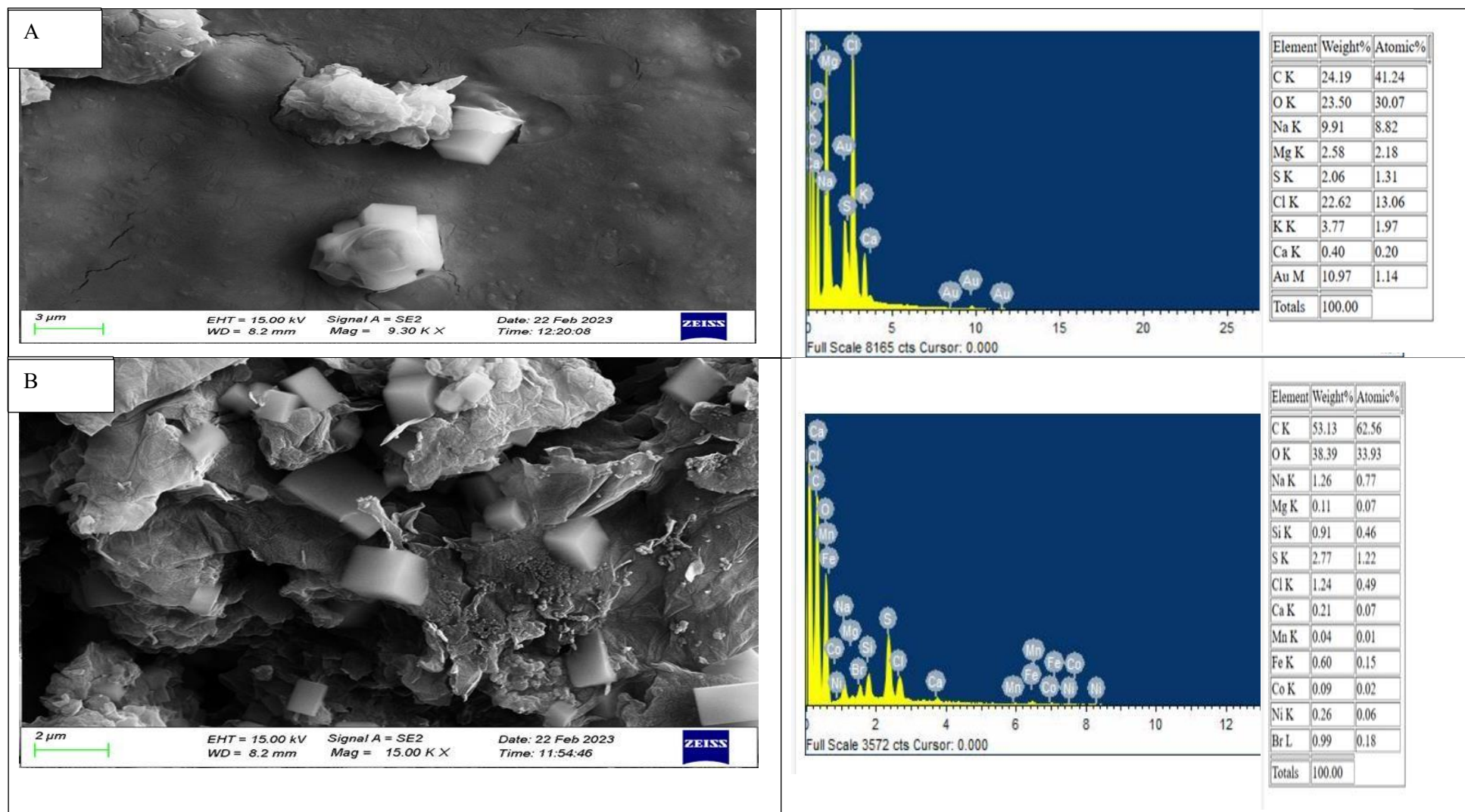


Figure 22. SEM characterization of (a) the Polyethersulphone (PES) membrane attached with synthetic metallic ions, (b) the PES membrane attached to real AMD metallic ionic molecules after dead-end filtration process with their respective EDS indicating elemental compositions for each membrane.

5.3 Nanofiltration performance evaluation for PES-Pimelic acid

GO infused nanocomposite membrane.

Adsorption of heavy metallic ions was assessed at different operating conditions of concentration, operating time as well as pressure. The underlying challenge which nanofiltration membranes were faced with was the trade-off between the permeate flux and heavy metallic ion rejection. This trade-off relationship has always been a bottleneck for most nanofiltration and reverse osmosis membranes. These gave rise the need to fabricate appropriately incorporated GO-infused nanocomposite membranes. This section reviews the optimization study for the removal of Iron (Fe), manganese (Mn) as well as sodium (Na) from acid mine drainage polluted wastewater. Response surface methodology (RSM) was utilised to advance predictive models for the simulation as well as optimizing the nanofiltration process using crosslinked nanocomposite membrane. The input variables were the operating time, concentration of mixed solutions of heavy metals such as Iron (Fe) and Manganese (Mn) and pressure applied to the nanofiltration system. The response surface design has been constructed based on the experimental design. The DOE methodology was applied, and experiments were carried at those given Box Behnken designs. The intention was to study the influence each factor has on the objective function of the study. According to Khayet *et al* (113), design of experiments as well as RSM design surface have been experimentally employed successfully within various areas of membrane separation technology.

5.3.1 The heavy metal rejection study for Pimelic acid functionalised GO/PES nanocomposite membrane.

Despite the separation performance displayed by the rejection rates of the commercial PES membranes, the main challenge of fouling still needs to be resolved to avoid permeation and rejection deficiencies. Under this study, the significance of each model term was evaluated using the p-value. In the case of the experimental runs performed for the purposes of research, the independent variables such as concentration, pressure, the multiple of concentration and pressure and c^2 are significant model terms. Figure 23 displayed the three-dimensional graphs with their respective contour plots representing the effect of three factors influencing the response of heavy metallic ion rejection. It was noticed that the highest factors interaction effects were established between the pressure and metallic ions concentration of the feed solution. The effects were in such a manner that metal removal efficiency was increased with an increase in the operating pressure and metal ion concentration. The linear effects of operating pressure and metallic ion concentration were

much higher than other parameters. The interaction effect of concentration and operating pressure and the quadratic effect of concentration were also significant (p value <0.05). It means that according to the predictive modelling RSM technique applied, any substantial increase in the concentration of the heavy metallic ions beyond the range used in the experimental study will still result in high performance index of the nanofiltration system under the same operating conditions. The interaction effect of time and operating pressure as well as operating time and concentration was not significant ($p > 0.05$). This could be attributed to the fact that the removal efficiency was not substantially influenced by electrostatic repulsion (8). However, the low zeta potential value for the Pimelic GO, stipulated in Figure 11 helps us to conclude that the Donnan exclusion principle did not apply in this study regarding the removal of heavy metallic ions. Hence, we can deduce that the metallic ion rejection for this thin film nanocomposite membrane was not based on charge repulsion. This examination could be substantiated slightly lower permeate flux of Pimelic functionalised membrane when compared to the commercial PES membrane. The Performance index of Pimelic functionalised GO nanocomposite membrane was enhanced with an increase in initial concentrations of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$, MnSO_4 , NaOH and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ present in the synthetic acid mine drainage wastewater solution. The removal efficiency of the metallic ions laden in the wastewater solution could predominantly be attained through ion-adsorption and size exclusion (138). The quantum technological improvements performed applied by several researchers on PES membranes has yielded positive outputs in terms of performance of the membranes. The permeate flux, metallic ion rejection mechanism as well as antifouling properties improvements are the reported technical challenges which the quantum innovations could successfully resolve (23). The functionalised pimelic GO material possesses the carboxylic hydroxyl, phenolic, esters and secondary amines functional groups as shown in Figure 6 for the FTIR spectra of pristine and functionalised GO. Research studies conducted by Qasem *et al* (90), has comprehensively examined that the adsorption efficiency of heavy metal ions removal increases by an increase in the adsorbent dose, initial concentration of the metallic ions, adsorbent surface area as well as contact time between the adsorbent and the adsorbate. According to Figure 23, a linear relationship was recorded between the effects of operating pressure and concentration and could be attributed to high adsorption efficiencies and size exclusion of metallic ions. This is mainly because functionalization of the GO provides specific binding sites which allows for the sorption reactions between the metal cation π -interactions with the negative functional

groups (62). These results are in good agreement with the performance chart for functionalised nano porous graphene averaging at 90% salt rejection in nanofiltration systems which uses graphene-based membranes for molecular separations (117). Similar results were obtained by various other researchers, as reported in Table 5.3 below.

Table 5.3 Nanocomposite membrane permeate flux and rejection rates

Researcher	Membrane synthesized	Heavy metallic ion under study	Permeate flux (L/m ² . hr)	Rejection (% removal rates)
Rezaei <i>et al</i> (23)	PSF/GO	Arsenate	43.05	82%
Ravishankar et al (138)	PSF/GO	Lead	43.62	98%
This study	PES/GO	Iron, Nickel, Cobalt, Manganese, Sodium and Magnesium	43.41	96%

Table 10. The Analysis of Variance (ANOVA) results for heavy metallic ion removal Pimelic functionalised PES nanocomposite membrane.

Model parts	Source	DF	Mean square	F-value	p-value
	Model	9	1074.39	15.12	0.0094
	Linear	3			
	A-Concentration	1	631.90	8.89	0.0406
	B- Time	1	0.0112	0.0002	0.9906
	C- Pressure	1	5637.10	79.34	0.0009
	Interaction	3			
	AB	1	0.0000	0.0000	1.000
	AC	1	815.00	11.47	0.0276
	BC	1	0.0225	0.0003	0.9867
	Square	3			
	A ²	1	39.87	0.5612	0.4954
	B ²	1	38.86	0.5470	0.5006
	C ²	1	2322.44	32.69	0.0046
Anova results for Pimelic GO membrane permeate flux	R ²	0.9714	Adjusted R ²	0.9072	

Table 11. Box Behnken design and experimental responses for removal of heavy metallic ions using pimelic GO membrane.

Std	Run	Factor 1 Concentration (mg/L)	Factor 2 Time (min)	Factor 3 Pressure (KPA)	Response 1 Permeability (L/m².hr)	Response 2 (Fe, Na & Mn removal) %
13	1	18.566	30	250	51.02	96.07
14	2	18.566	30	250	51.02	96.07
3	3	10.414	50	250	30.61	99.91
4	4	26.718	50	250	30.61	99.91
12	5	18.566	50	400	39.79	95.77
2	6	26.718	10	250	45.91	99.91
5	7	10.414	30	100	19.38	7.65
10	8	18.566	50	100	24.48	49.31
6	9	26.718	30	100	30.61	63.98
7	10	10.414	30	400	36.73	95.77
8	11	26.718	30	400	36.73	95
1	12	10.414	10	250	30.61	92.14
11	13	18.566	10	400	39.79	96.07
9	14	18.566	10	100	30.61	49.31

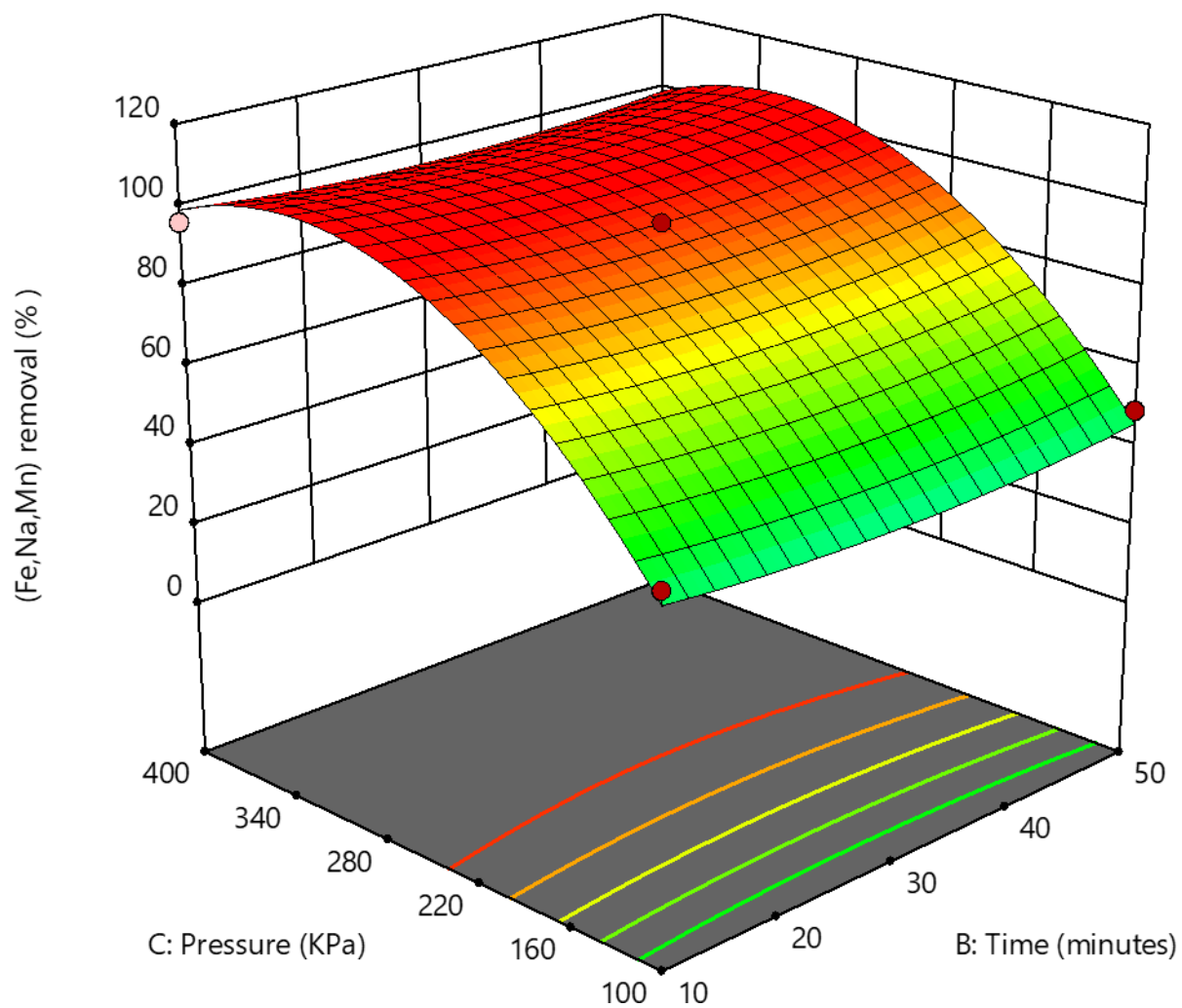


Figure 23. Response surface representation of the predicted NF performance indicator by RSM for high heavy metallic ion concentration as a function of the operating time and input concentration.

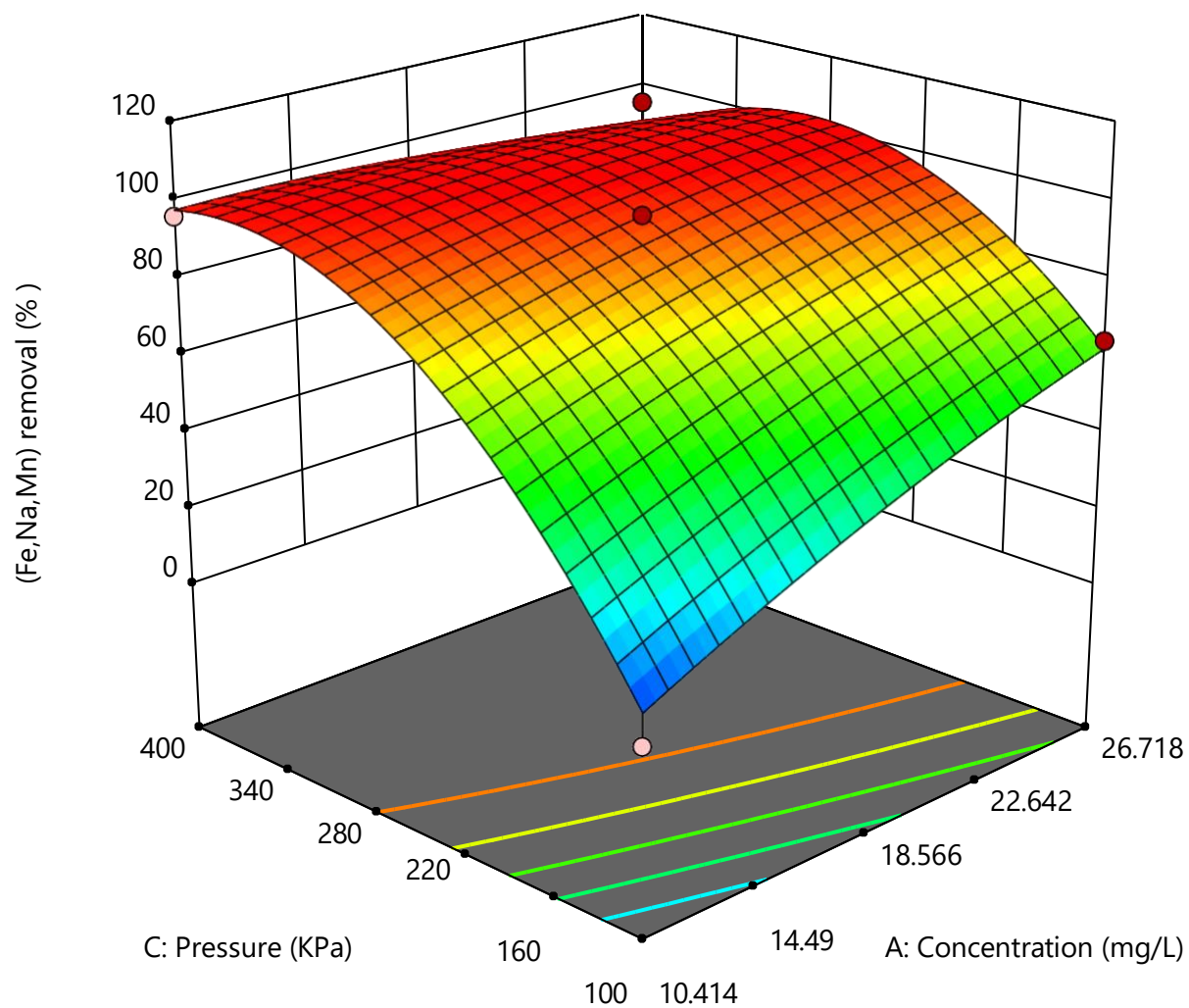


Figure 24. Response surface representation of the predicted NF performance index by RSM for high heavy metallic concentration conditions as a function of Operating pressure and input feed concentration.

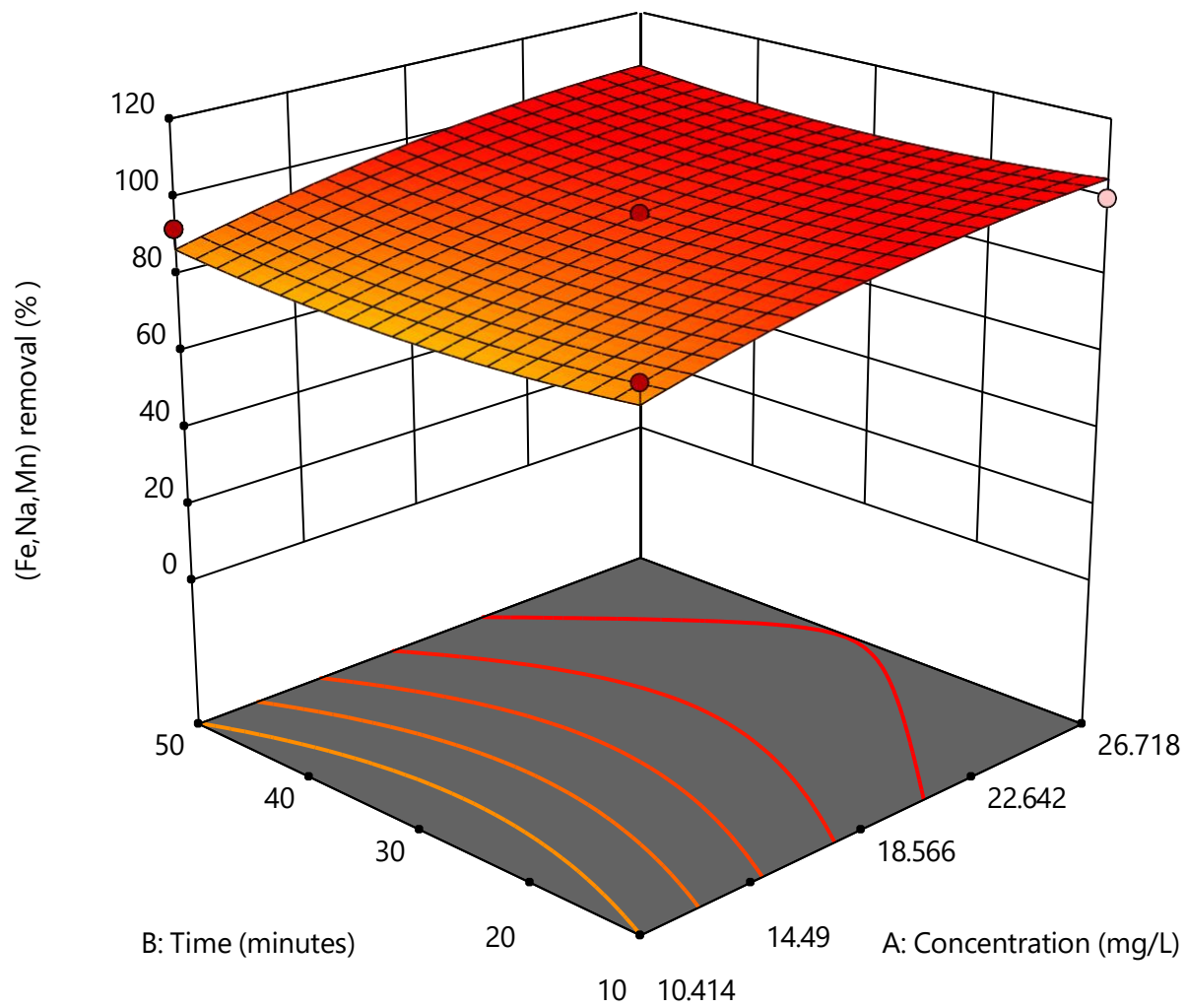


Figure 25. Response surface representation of the predicted NF performance indicators by RSM for high heavy metallic concentration conditions as a function of the operating time and feed concentration.

5.3.2 Permeation modelling for Pimelic acid functionalised nanocomposite membrane.

The performance of Pimelic functionalised GO membrane was evaluated by performing RSM modelling technique to analyze the process and variables which affect its response of interest. This modelling parametric approach was utilised to estimate the relationship between the input and output process variables and recognize the optimal operating conditions for a system being studied or a region of the factor that meets the operating requirements (139). The best fitted regression models for forecasting the permeate flux was determined to be the quadratic polynomial and linear models. Stipulated in Table 8 is the results for the fittings of the quadratic model. The linear and square terms, together with the effects of the prominent variables are all significant in response giving a p-values <0.05. The regression model created for nanocomposite permeate flux yields (Y):

$$Y = 51,02 + 3.32A - 2,68B + 6C - 3,28AB - 2,81AC + 1,53BC - 9,69A^2 - 6,89B^2 - 10,46C^2$$

The analysis of variance (ANOVA) was used to test the statistical significance where the statistical model indicated to be very significant with calculated *f*-value of 39,09 implying that the model is very significant. It means that there is only 0,15% chance that the *f*-value this large could occur due to noise. The optimum conditions for this experiment were found to be an operating time of 30 minutes, operating pressure of 250 Kpa and heavy metal feed concentration of 18,566 mg/L (185,66 mg/L). Most literature studies have noted that the presence of oxygen containing functional groups results in enhancement in hydrophilicity of the synthesized membranes, which in turn result in great permeation fluxes (8,21). The interaction effects were in such a manner that permeability of the thin film nanocomposite membrane decreased by increasing the operating time and at constant operating pressure and concentration. In this research study, at operating time of 10 minutes and constant operating pressure of 100 Kpa and concentration of 185,56 mg/L, the permeability of the membrane decreased from 30.61 L/m².hr to 24 L/m².hr when the operating time was increased to 50 minutes. The decline in the permeate flux could be caused by higher loading of GO in the thin film layer, permeation occurring at non-oxidized regions as well as build-up of cations on the membrane surface. A substantial increase in membrane operating time from 10 minutes to 50 minutes at constant pressure of 400 KPa, with MnSO₄ concentration at 185.56 mg/L, the permeation flux of the membrane remained constant at 39,79 L/m².hr displaying that it is not susceptible to fouling and thus the effect of concentration polarization does not apply to the pimelic GO-infused nanocomposite membrane. One of the aims of conducting this research

study was to enhance the antifouling performance and chlorine resistance of the doped membrane. The experimental results depicted that the nanocomposite membrane flux was 96.07 % whilst the permeability being 51.02 L/m².hr, therefore it can be concluded that the performance of the membrane was excellent. In Figure 26, the response surface which comprised of the minimum, local, maximum and ridge lines was able to depict the region where the most appropriate response took place. It was found that for the covalently crosslinked Pimelic GO membrane, the MnSO₄, FeCl₂ and NaOH the concentrations in the permeate increase with time in a linear manner. This thin film nanocomposite membrane, with increasing metallic feed concentrations (10, 414, 14, 17.50 mg/L), the permeation flux of the solvent increases from 35 to 40 and 45 L/m².hr due to the increased driving force. Similar trend trends from this study regarding the linear and interaction effects between operating time and concentration were found by Jia & Wang (4). From Figure 27, a linear effect between applied pressure and concentration of ions was observed. There was an incremental change in the permeate flux after the solute concentration was increased with increasing the applied pressure. An increase in the feed concentration did not have much effect on the removal of heavy metallic ions, with similar observations found by Maher *et al* (1), however, an increase in applied pressure had drastic effect on removal efficiency. The permeation fluxes increased with an increase in applied pressure, this is because an increase in pressure is directly proportional to an increase in the solute and solvent passages within the membrane matrix. The performance index of the NF system decreased when treating metal concentrations at low pressure of 100Kpa as depicted in Figure 27, resulting in removal rates of 49,31% and 7,65 % respectively with permeation fluxes of 30.61 L/m².hr and 19.38 L/m².hr. This is because at low operating pressure, there is less interaction between transition-metal cations and the negatively charged functional groups present in the GO-Pimelic membrane, thus resulting in slight reduction of the total charge of membrane and the anion repulsion with the membrane surface not decreasing while the passage of the solvent being decreased (1). Nanofiltration is a molecular separation mechanism which can be related to the reverse osmosis and ultrafiltration processes (21). Such processes have been described to possess an overwhelming separation technique regarding solutions of high molecular substances and that of low molecular weight soluble solutes. In these research study, the performance of the thin film nanocomposite membrane was outstanding at higher applied pressure and increase in the solute concentrations of the metallic ions. Numerous research studies have reported that the selective pathway of ions through the nano porous graphene is determined by electrostatic interaction between the pores and ions

(117). Therefore, at high operating pressures, the mobility of the cation's present interactions with water contaminants. Experimental evidence has given clear indication on the in the synthetic and real AMD wastewater was increased, resulting in an increase of electrostatic interaction between the positively charged Iron (Fe^{3+}), Sodium (Na^+), Magnesium (Mg^{2+}), Manganese (Mn^{2+}) and other transition metallic ions with the negatively charged functional groups of hydroxyl, epoxy and carboxylic functional groups located on the basal and sheet edges of the GO mixed matrix membrane. The higher surface area of the functionalised GO nanopores speeds up the ion adsorption reaction between the cations deposited on the membrane surface with the functional groups. The negative charge of the OH^- , chloride and sulphate ions together with the negative charge of the membrane surface result in the increase of Donnan repulsion. All these stipulated rejection mechanisms occurring on the surface of the membrane result in the increase of the performance index of the membrane in terms of high metallic ions removal rate and increased permeate flux. The infusion of GO into the membrane matrix makes it more hydrophilic, therefore the membrane is likely to orchestrate the sorption of water. The porosity of the thin film membrane was displayed via SEM micrograph, as depicted in Figure 18 a and b, the nanochannels were created which allowed for the transport of solvent into the permeate stream of the dead-end filtration method. An increase in applied pressure, results in increased solvent passage due to large intersheet spacing of 782 nm from SEM estimation, as well as d-spacing of 7.82 nm as calculated from Braggs law. The membrane permeate flux was found to be stable in this research study as it ranged between 30.61 L/m².hr to 51.02 L/m².hr due to all those rejection procedures described above, enlarged intersheet spacing between the GO sheets, trans-membrane pressure (TMP) and the order of ion diffusivity as well as the increase in the chain length of the dicarboxylic acids (4,60). It has been reported that the structure of the GO membrane in water strongly influences the permeation rate of the polar solvent available in the contaminated wastewater (96,140). The experimental results presented in the form of the 3D surface plots permits us to predict the permeation properties of GO-infused nanocomposite membranes towards separation of heavy metallic ions. The permeation of water through the stacked GO membrane was not as easy when compared to that of plain PES membrane that was just a function of applied pressure. Although the modelling procedure regarding the true flow rates of the filtered water through the GO membrane is complicated, we can deduct from the experimental permeation rates that the membrane was defect free as the flow rates didn't deviate much with change in combination of factors chosen for the box Behnken design. However, the permeation was not only subjected to the unoxidized regions of the membrane and the presence of other functional groups on the graphene oxide nanosheets

offered greater areas for improved usage of functionalized graphene oxide material regarding water treatment applications as a viable option as the molecular simulations predicted that the contact angle of water molecules towards the stacked GO surface encounters very low friction or flow resistance. The effect of all possible combinations of the independent variables has been assessed in terms of its influence in the response of the nanofiltration system. The linear effects of operating pressure and concentration of the solute was higher than those of operating time and concentration, meaning the increase in pressure increases the cation- π interaction with OH- and -COOH functional groups, whereas the quadratic interaction terms of operating time and concentration was higher than those of applied pressure and concentration.

The layer-by-layer assembly method has been a great procedure in terms of engineering the nanostructure of the thin film nanocomposite membrane (128). The functionalised membrane showed great affinity of the GO laminates and the water molecules because the model was validated and all factors interacting with each other. Ganesh *et al* (5) has also noted that the addition of GO membrane matrix yielded in increased hydrophilic regions, which increase the simplification of sorption of water into the membrane.

Table 12. The Analysis of Variance (ANOVA) results for hydrophilicity of GO Pimelic PES nanocomposite membrane.

Model parts	Source	DF	Mean square	<i>f</i>-value	P-value
	Model	9	124,23	39.09	0.0015
	Linear	3			
	A-Concentration	1	87.98	27.68	0.0062
	B- Time	1	57.44	18.06	0.0132
	C- Pressure	1	287.52	90.47	0.0007
	Interaction	3			
	AB	1	58.52	18.42	0.0127
	AC	1	31.53	9.92	0.0345
	BC	1	9.39	2.96	0.1607
	Square	3			
	AA	1	300.78	94.65	0.0006
	BB	1	151.91	47.80	0.0023
	CC	1	350.28	110.22	0.0005
Anova results for Pimelic GO membrane permeate flux	R-squared	0.9888	Adjusted R ²	0.9635	

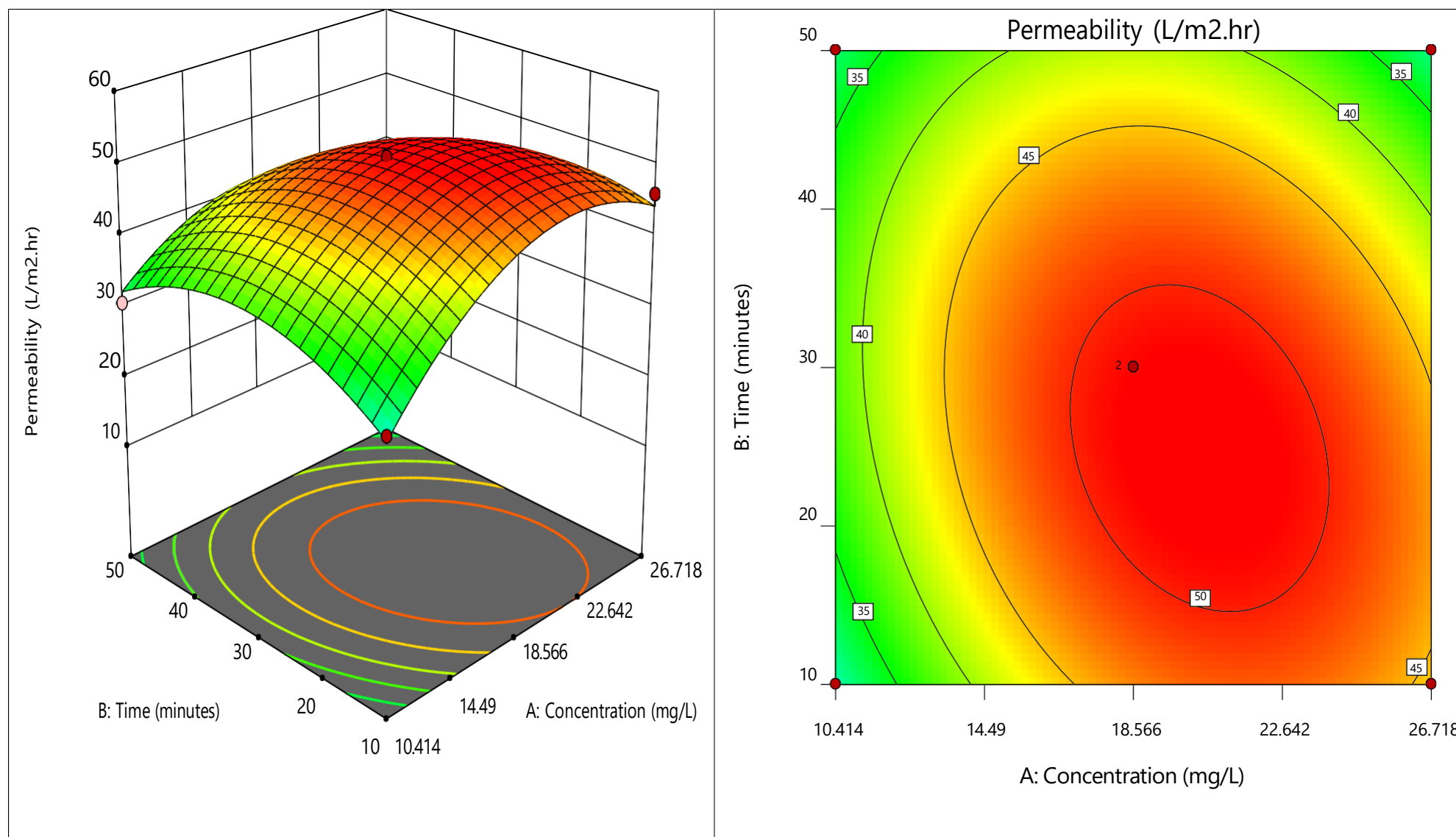


Figure 26 Response surface and contour plots of the predicted NF performance index by RSM for the output permeate flow when varying operating time and feed concentration.

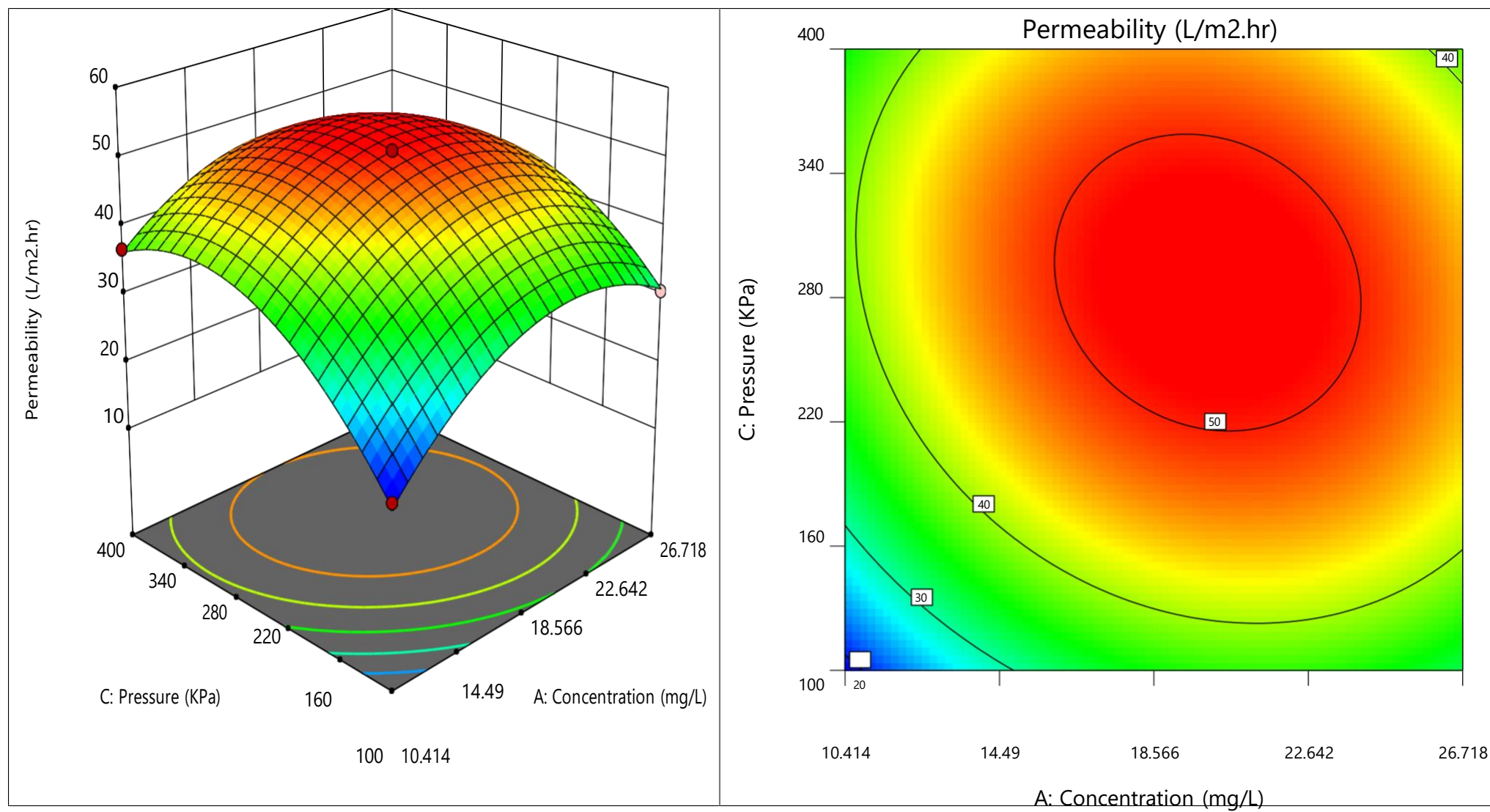


Figure 27 Response surface and contour plots of the predicted NF performance index by RSM for output permeance for Operating pressure and feed concentration.

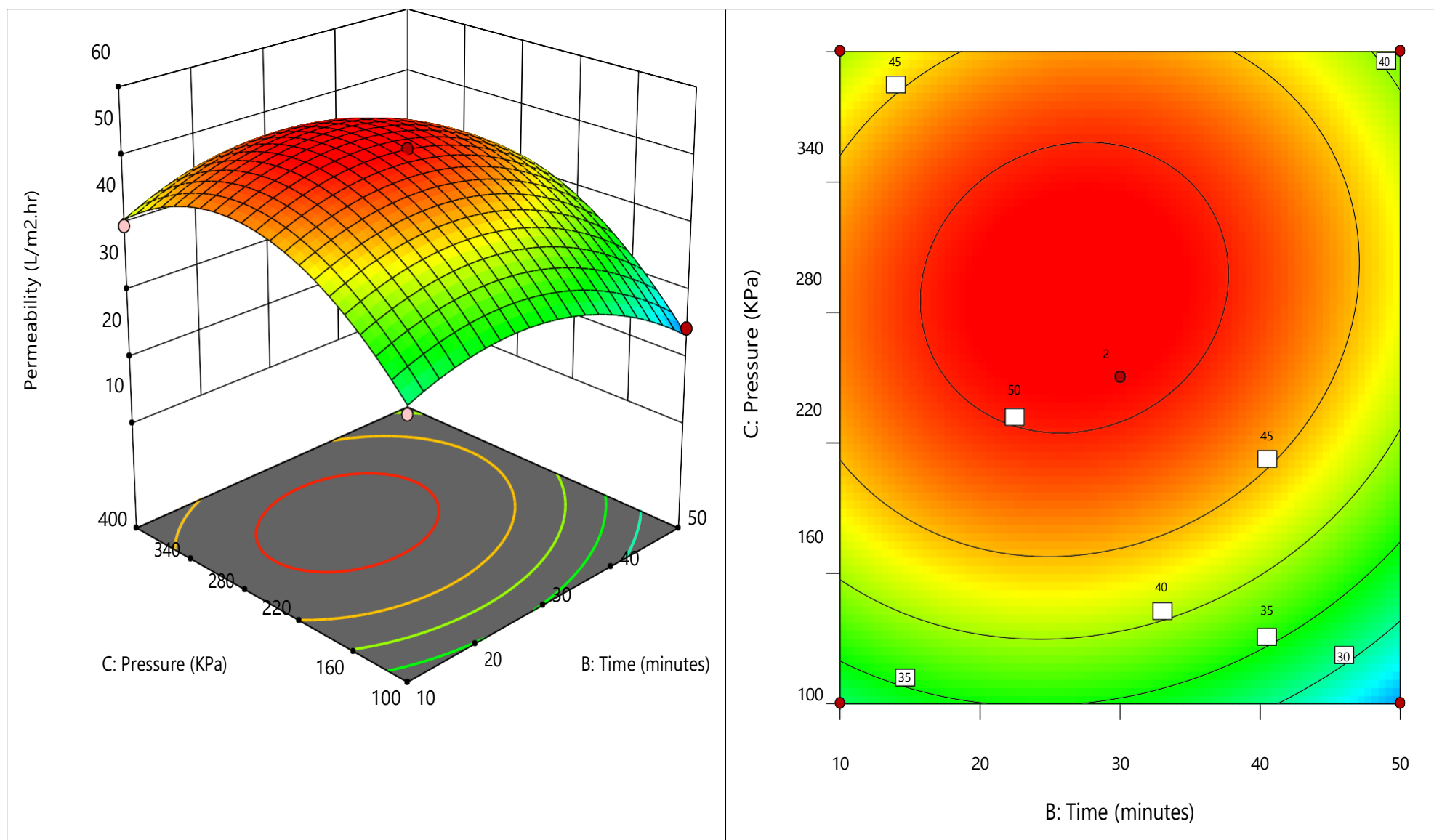


Figure 28 Response surface and contour plots of the predicted NF performance index by RSM for the output permeate while varying operating pressure and time.

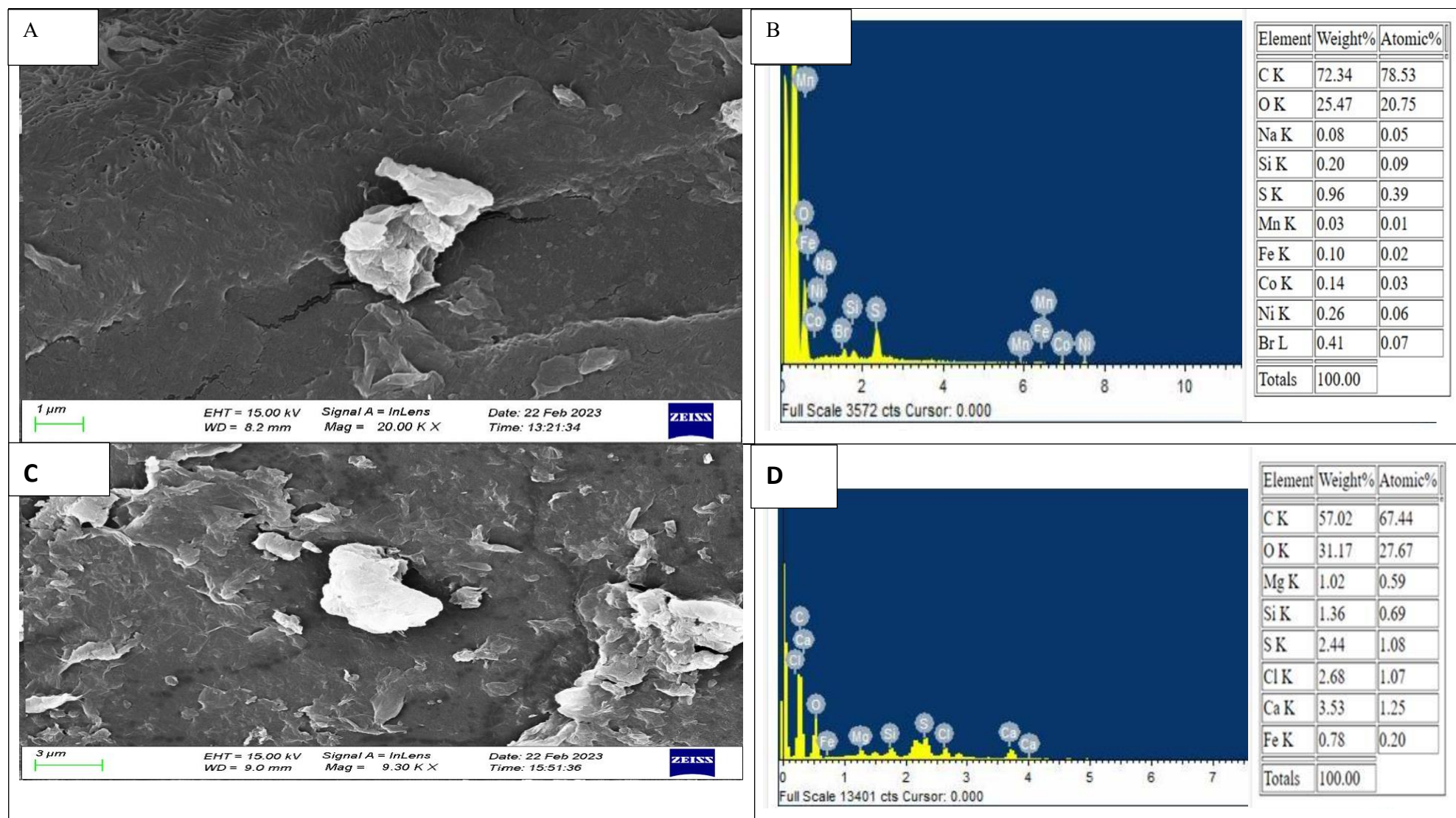


Figure 29. SEM characterization of (a) the Pimelic- GO functionalised PES membrane utilised for separation of Real AMD wastewater, (b) for desalination of seawater.

5.4 The heavy metallic ion Adsorption kinetics and Equilibria mechanism.

The rate of adsorption is pivoted upon the adsorption equilibria and its kinetics in terms of the Freundlich and Langmuir adsorption isotherms for batch studies. The heavy metallic ions were adsorbed onto the adsorbent surface based on the process of ion-exchange and physical-chemical adsorption as the ionic mobility takes great effect in the entire process (16). To study the adsorption performance of the synthesized GO, the degree to which the initial concentration had on adsorption was thoroughly investigated. The process of adsorption has introduced itself as a versatile option, permitting for alteration of heavy metallic ions removal within different reaction conditions with the usage of substantial span of materials like GO as adsorbents. To understand why the process of adsorption is more complex and unpredictable, several researchers such as Zhao and colleagues (141), have studied the adsorption of Cadmium (Cd) and Cobalt (CO(II)) utilizing a few GO nanosheets. Other researchers also interested in examining the adsorption technology have conducted series of experiments to justify the adsorption phenomena, and they reported that GO possessing large surface area as well as different functional groups is amongst the promising adsorbent materials for usage in heavy metallic ions removal, with limitations found in using the material without functionalizing it or adding specific other functional groups rendering the adsorbent as non-feasible. The adsorption capacities were then examined with the use of functionalised GO, and it was found out that a relationship existed between the concentration of the heavy metallic ions and the rate of adsorption kinetics. It was reported that the adsorption of functionalised GO materials increased with an increase in the initial concentration of the heavy metallic ions present in the wastewater solutions, which is deemed favorable towards reaching the objectives of the adsorption continuous improvement technology. The adsorption capacities of different functionalised GO materials differed based upon the functional groups present within each material. To understand the adsorption capacity of GO, the performance of its adsorptive abilities was recorded in Table 12 to 15, whereby the Langmuir and Freundlich isotherms were utilised to examine the adsorption thermodynamics. The adsorption capacities for the GO-Fe, GO-Mn, GO-Ni and GO-Co calculated using the Langmuir model did not correspond to the ones found from the experimental data. The calculated adsorption capacity for GO adsorbing manganese was found to be 2.42 mg/g, whereas the one for experimental (Q_{max}) was found to be 15.6 mg/g, for the GO adsorption of Fe, it was found that the adsorption capacity was 0.795 mg/g, which was very small quantities adsorbed when compared to the experimental value of 3.2 mg/g, whereas there was not much adsorption to be reported from the real AMD

as the data did not fit the Langmuir model. The conclusive observations regarding the process of adsorption were that it occurred on a heterogeneous facet via multi-layer adsorption mechanism. This observation could be supported by the results of R^2 which were at 0.9 and 0.99 for all the adsorption process for heavy metallic ions, both the synthetic and real AMD wastewater as listed in Table 12 – 15. In examining the oxidation of graphite to synthesize GO and how well the GO performed with all the added functional groups, the synthetic and real AMD wastewater was tested. The curves acquired from the plots of C_e or $\ln C_e$ on the x-axis versus C_e/Q_e or $\ln Q_e$ on the y-axis are shown in Figure 30 -33. The observations made from the plots was that the good fit of data applied to the Freundlich isotherm implying that it is multilayer adsorption process which took place in the adsorption of Iron (Fe), manganese (Mn), Nickel (Ni) and Cobalt (Co) using GO as adsorbent surface. This suggests that adsorption using GO membrane took place via electrostatic binding, cation- π interactions and metal coordination as explained in discussing the effect of cross linking, as explained by Huang *et al* (117), regarding the precise separation of nano porous GO membranes. The heavy metallic ions were adsorbed to the GO adsorbent surfaces by the process of physical-chemical adsorption and ion exchange. The mobility of ions and the reaction kinetics were governed by the oppositely charged ions and were more pronounced in dilute solutions, whereby the synthetic wastewater was more adsorbed when compared to the real AMD wastewater. In this research study it was found that the rate of adsorption decreased with an increase in the initial adsorbate concentration as depicted in figure 34. At higher concentrations, the rate of adsorption was low for all four plots of Q_e vs C_e , therefore adhering to the phenomenon explained above, the other reason behind this being that unfunctionalized GO possesses only few adsorptions binding sites to accommodate all the metallic ions which were meant to bind with it during the adsorption process. However, as explained by Agarwal *et al*(16), an increase in the amount of adsorbent would imply the accessibility of more binding sites for adsorption, however the reason using 0.2 g/L of adsorbent was that the process of adsorption gets tricky as with higher dosage of the GO adsorbent in the solution, there is normally a decreasing trend in the rate of adsorption so therefore there has to be an optimum level of dosage to obtain feasible adsorption trend of the metallic ions.

Table 13. The distinction between the Langmuir and Freundlich isotherm constants for GO -Fe.

Langmuir				Freundlich		
Q exp(mg/g)	Q max (mg/g)	b	R ²	K _F	n	R ²
3,2	0,795	30,83	0,99	10,62x10 ⁷	0,54	0,99

Table 14. The distinction between the Langmuir and Freundlich isotherm constant for GO-Mn.

Langmuir				Freundlich		
Qexp(mg/g)	Qmax(mg/g)	b	R ²	K _F	n	R ²
15,6	2,42	0,3	0,9	0,74	2,41	0,99

Table 15. The distinction between the Langmuir and Freundlich isotherm constant for GO-Ni.

Langmuir				Freundlich		
Qmax(mg/g)	Qmax(mg/g)	b	R ²	K _F	n	R ²
2,4	0	0	0,66	2,33x10 ²⁵	0,27	0,93

Table 16. The distinction between the Langmuir and Freundlich isotherm constant for GO-Co.

Langmuir				Freundlich		
Qmax(mg/g)	Qmax(mg/g)	b	R ²	K _F	n	R ²
1,6	0	0	0,53	9,9x10 ⁴⁴	0,16	0,87

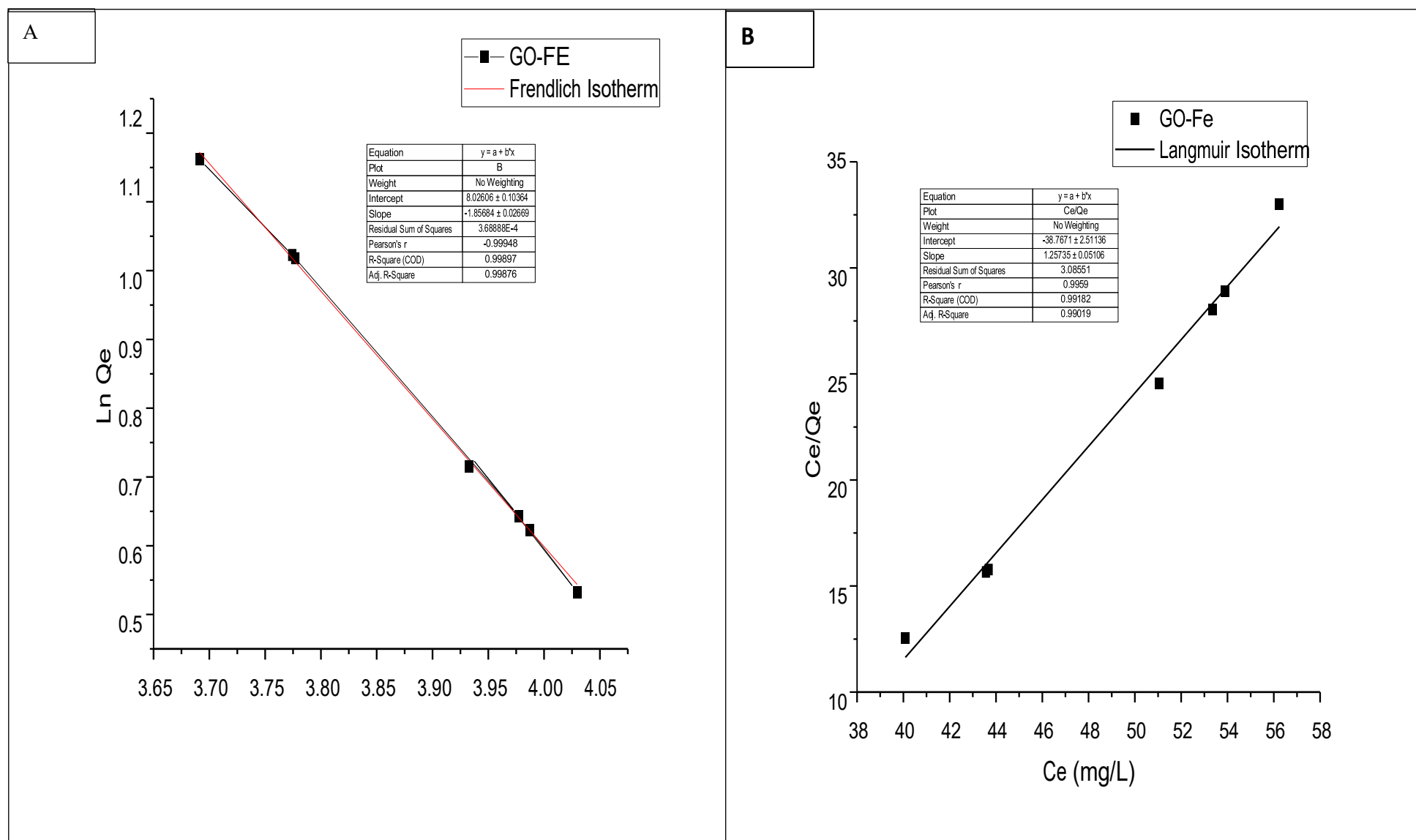
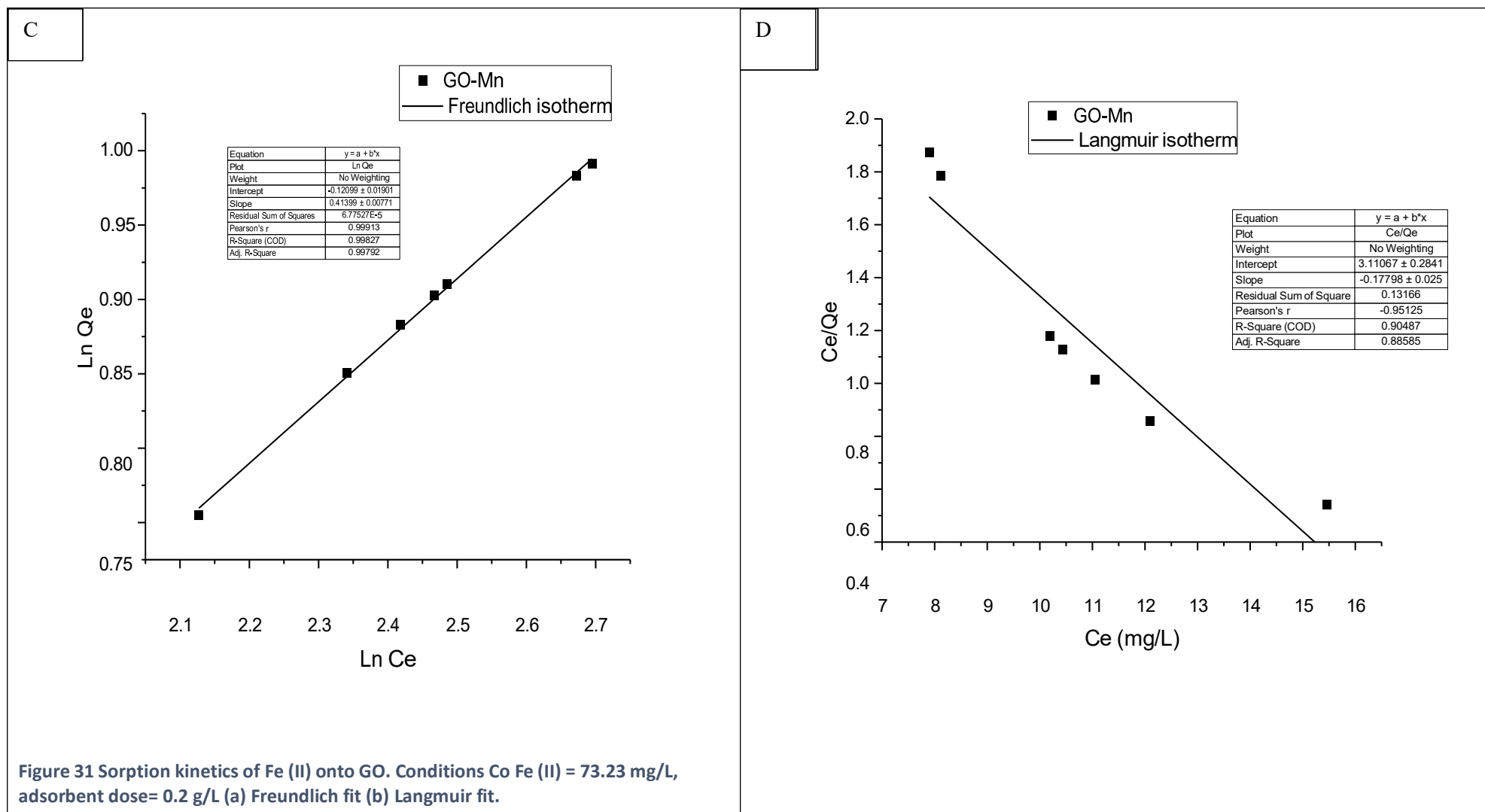


Figure 30 Sorption kinetics of Fe (II) onto GO. Conditions Co Fe (II) = 104.14 mg/L, adsorbent dose= 0.2 g/L (a) Freundlich fit (b) Langmuir fit.



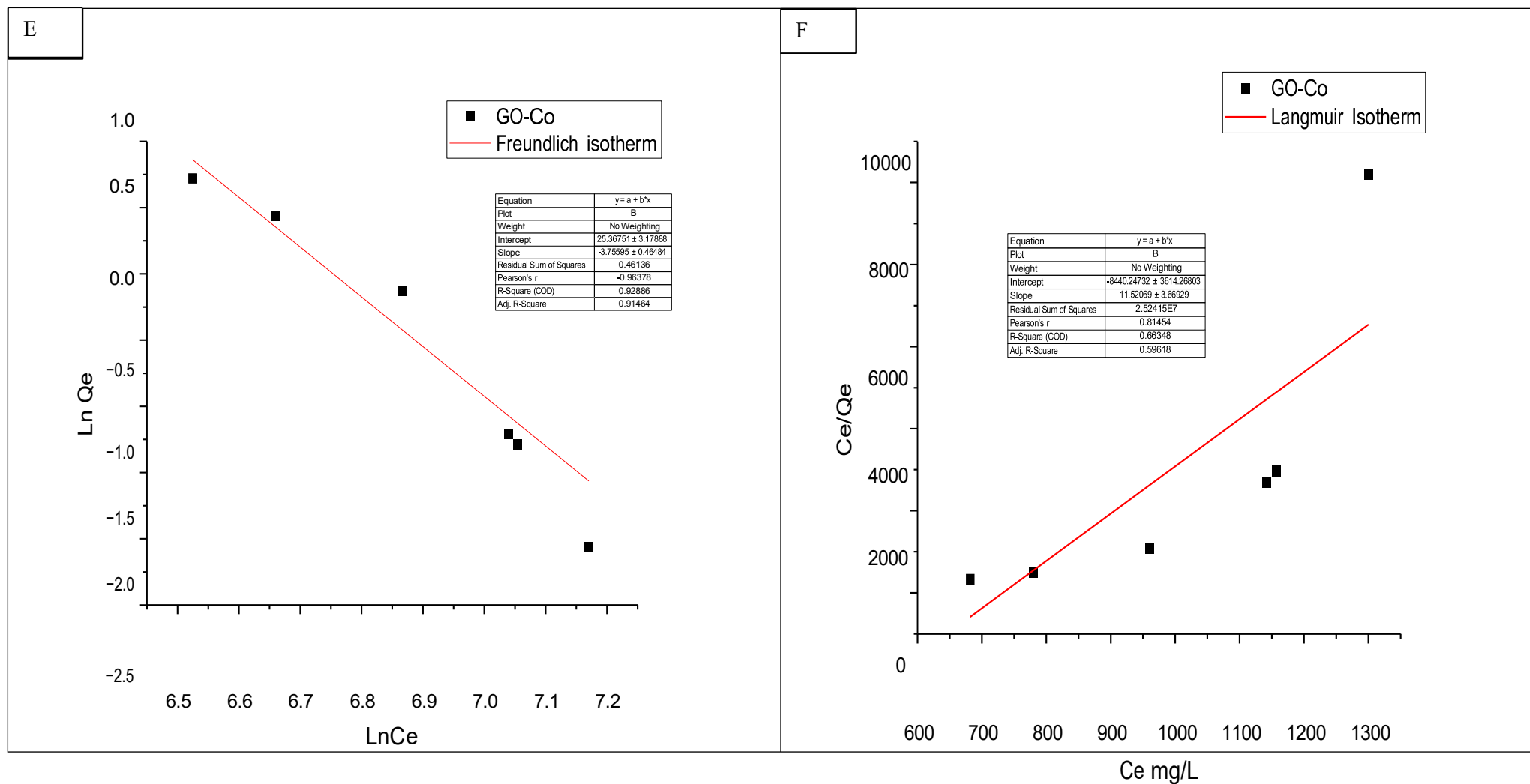


Figure 32 Sorption kinetics of Fe (II) onto GO. Conditions Co Fe (II) = 1383 mg/L, adsorbent dose= 0.2 g/L (a) Freundlich fit (b) Langmuir fit.

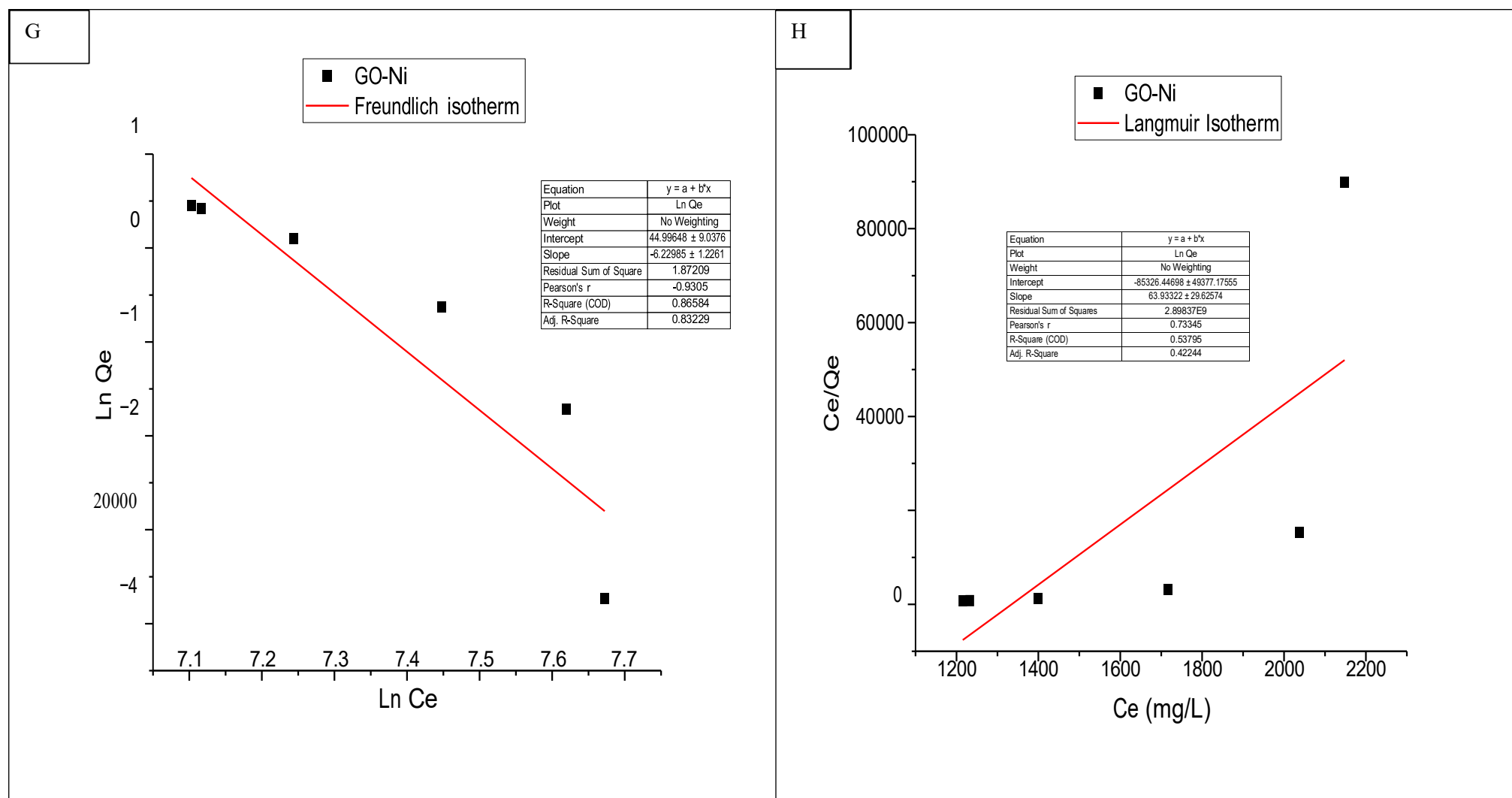


Figure 33 Sorption kinetics of Ni onto GO. Conditions Co Ni = 2173.75 mg/L, adsorbent dose= 0.2 g/L (a) Freundlich fit (b) Langmuir fit.

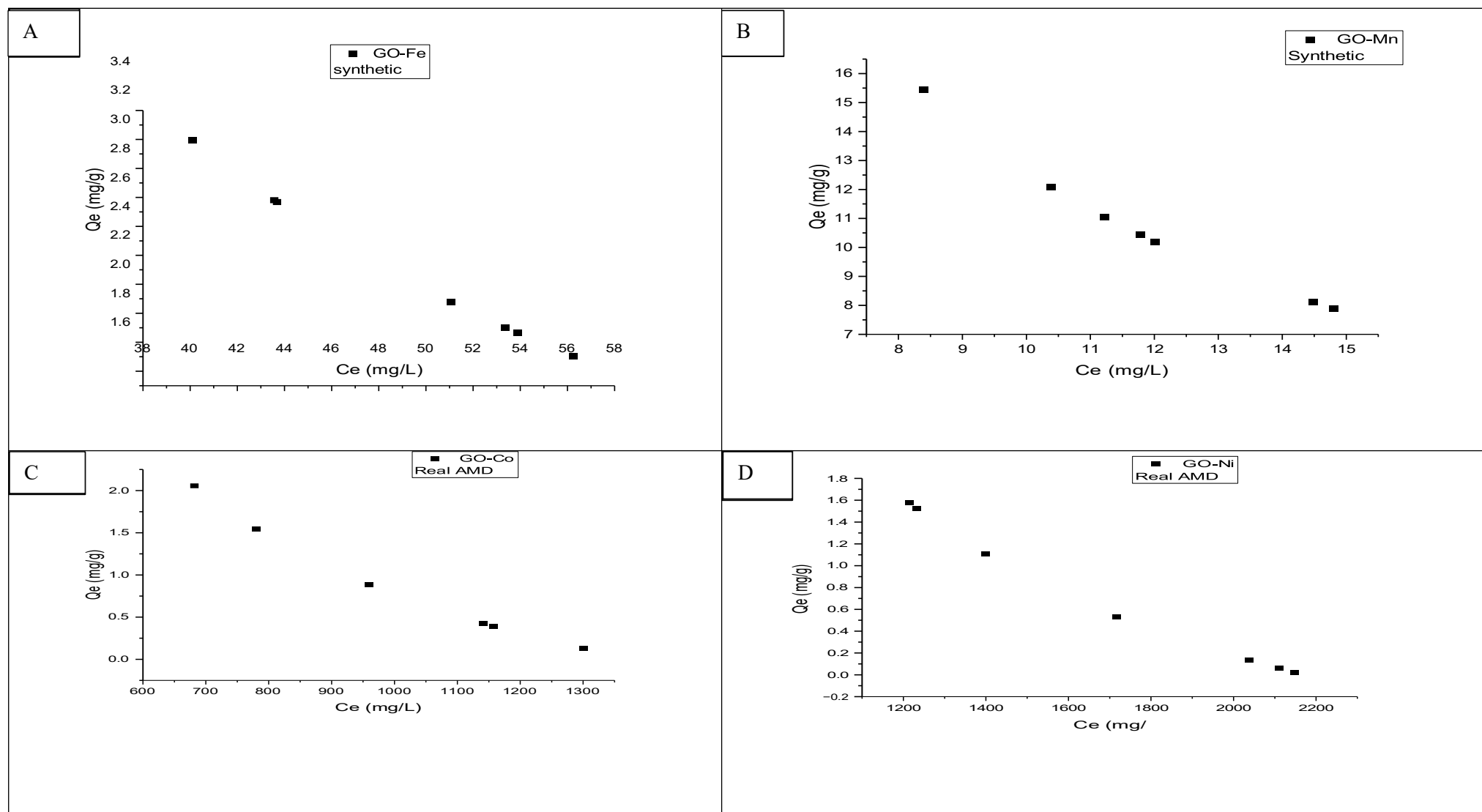


Figure 34 The effect of initial Fe (II) concentration (b) effect of Mn concentration (c, d) effect of initial concentration of Ni &Co on adsorption capacity

6 Conclusion and recommendations.

In this research study, the synthesis of GO via the modified Hummers method was successful. The optimization of the preparation conditions for GO during the functionalization process has proven to be a great difference towards the creation of well layered structure for pimelic functionalised GO-PES membrane due to the improved surface area, as well as improved affinity with water. The Adipic and Glutaric functionalised GO-PES membranes underwent GO attrition during filtration process and hence became a focal point for future improvement in terms of assessing the best assembly techniques when utilizing those two crosslinkers. The layer-by-layer assembly dip-coating method was the effective method for attachment of the pimelic functionalized membrane. The membrane was prepared using the optimal conditions found from the BBD design experiments for the functionalization process. The Pimelic GO- PES membrane resulted in higher rejection rate for heavy metal at very balanced flow of water. The rate of selectivity of the membrane was finely balanced with the rate of water flow through the nanochannels of the stacked GO sheets. The membrane can therefore be used for future wastewater treatment applications due to its high adsorptive capacity of heavy metal ions.

This research study focused on detailed examination of the PES membrane and was utilised as a polymer matrix to develop nanofiltration membrane by the layer-to-layer coating method. The aim was to improve the membrane structural integrity, form chlorine resistant polyamide layer, improve nanocomposite membranes hydrophilicity as well as enhancing its separation performance. The mixed matrix pimelic functionalised PES/GO thin film nanocomposite membrane along with the pristine PES membrane were characterized by scanning electron microscopy, FTIR spectroscopy and X-Ray diffraction. It was found that changing of the synthesis methods for the different types of TFN membranes using different crosslinkers has yielded different types of morphologies. The separation performance is primarily controlled by the proximity of the nanofiller material interrelatedness to the polymer matrix. The formation of cracks and macro voids was observed in Glutaric and Adipic functionalised TFN membranes which meant that those membranes were regarded void to fulfil the filtration process of wastewater. The best performing membrane was found to be the pimelic acid functionalised TFN membrane. The response surface methodology was successfully implemented for the membrane performance prediction. The effects of the operational variables on the removal of heavy metals were established by the contour plots and response surface based on the second order polynomial models. The utilized GO was capable of adsorbing Nickel, Manganese, iron

and Cobalt mainly by the ion-exchange process during the batch adsorption studies where adsorption favored more dilute concentrations of the wastewater feed. The adsorption equilibria and kinetics of the above-mentioned heavy metals will further be studied for future recommendations utilizing the pimelic functionalised GO material to analyze how well the material performs during metal uptake.

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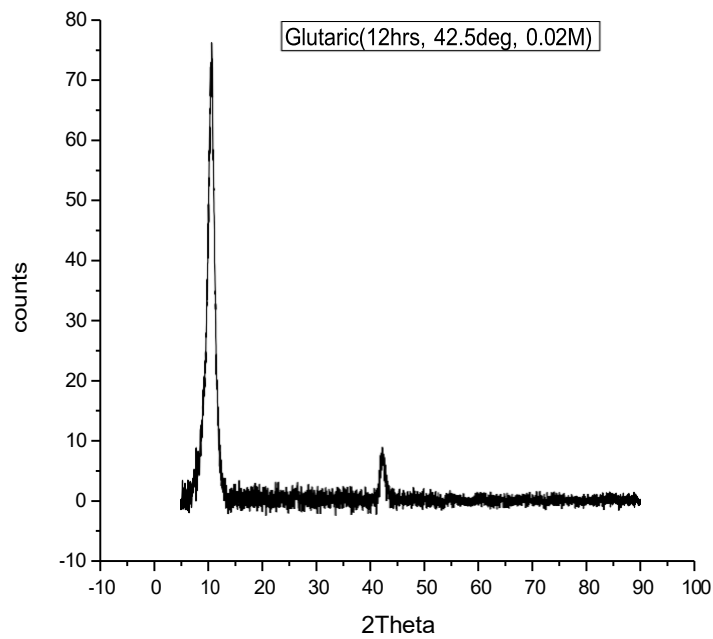
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Appendix

A1. XRD Results of the functionalization process.

1. Glutaric (12hrs, 42.5°C, 0.02M)



Calculation of the spacing between the GO sheets.

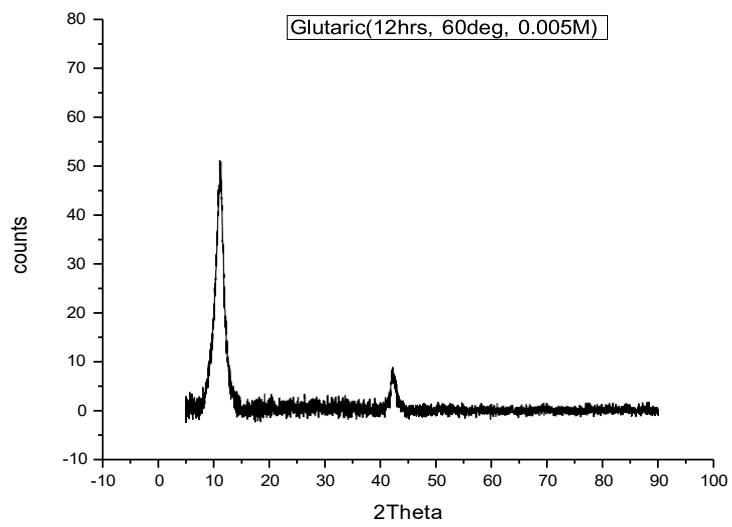
$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 10,26/2 = 5.13$$

$$d = \frac{1.54060}{2\sin(5.13)} = 8,61 \text{ nm}$$

2. Glutaric (12hrs, 60°C, 0.005M)



Calculation of the spacing between the GO sheets.

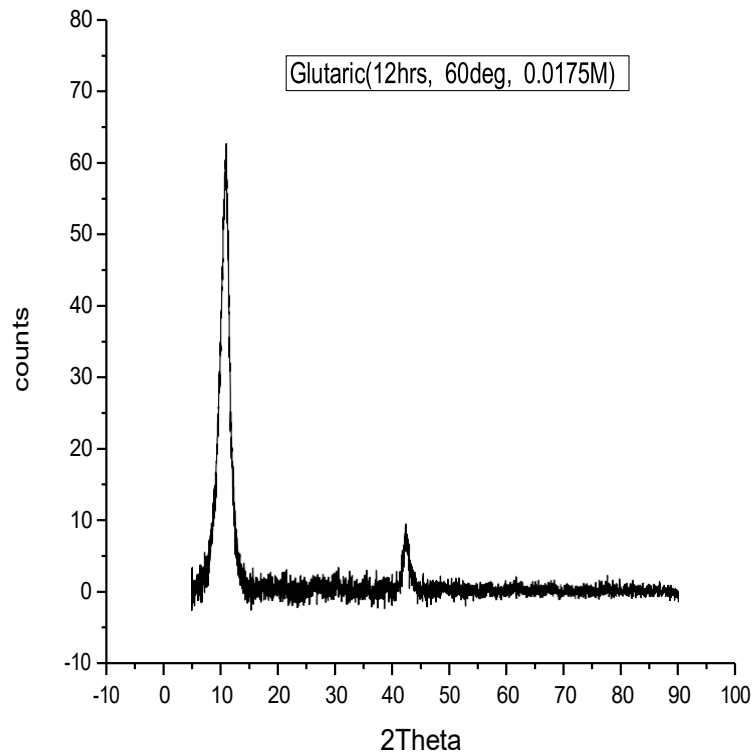
$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 9.96/2 = 4.98$$

$$d = \frac{1.54060}{2\sin(4.98)} = 8.74 \text{ nm}$$

3. Glutaric (12hrs, 60°C, 0.0175M)



Calculation of the spacing between the GO sheets.

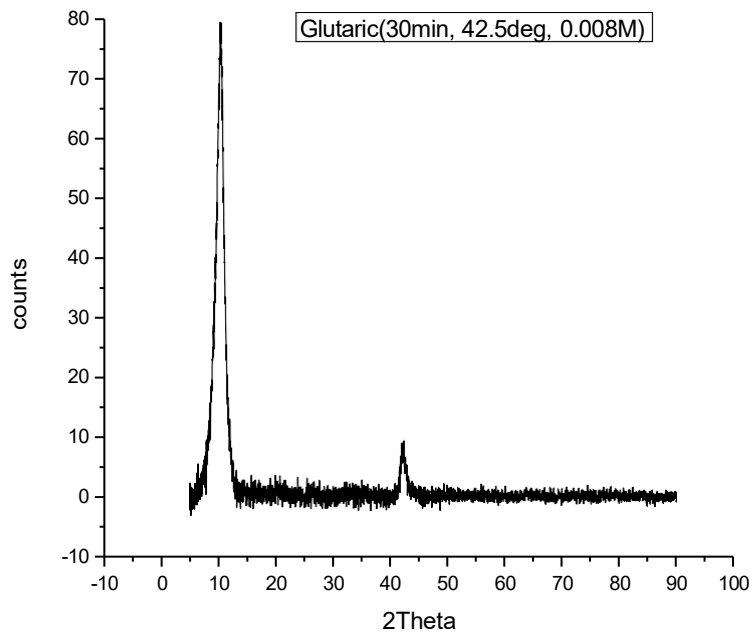
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 10,1/2 = 5.05$$

$$d = \frac{1.54060}{2 \sin(5.05)} = 8,75 \text{ nm}$$

4. Glutaric (30 min, 42.5°C, 0.008M)



Calculation of the spacing between the GO sheets.

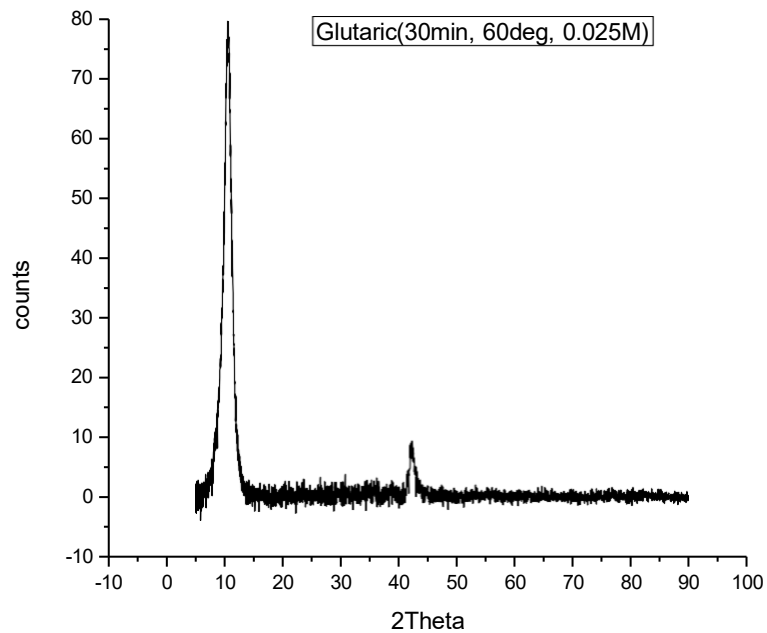
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 10,96/2 = 5,48$$

$$d = \frac{1.54060}{2 \sin (5.48)} = 8,07 \text{ nm}$$

5. Glutaric (30min, 60°C, 0.025M)



Calculation of the spacing between the GO sheets.

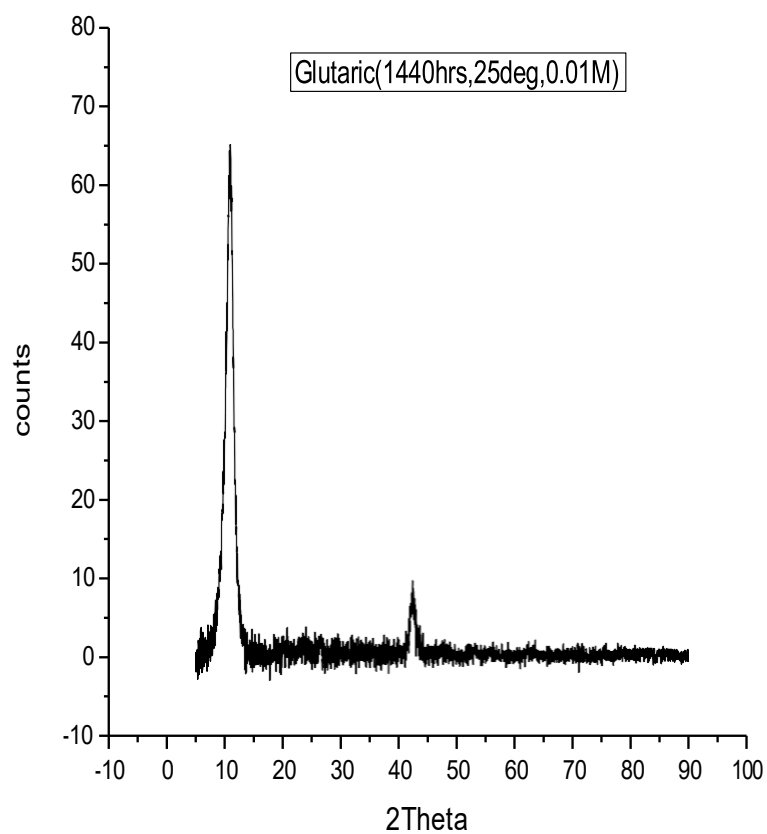
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 10,8/2 = 5,4$$

$$d = \frac{1.54060}{2 \sin (5,4)} = 8,19 \text{ nm}$$

6. Glutaric (12hrs, 25°C, 0.01M)



Calculation of the spacing between the GO sheets.

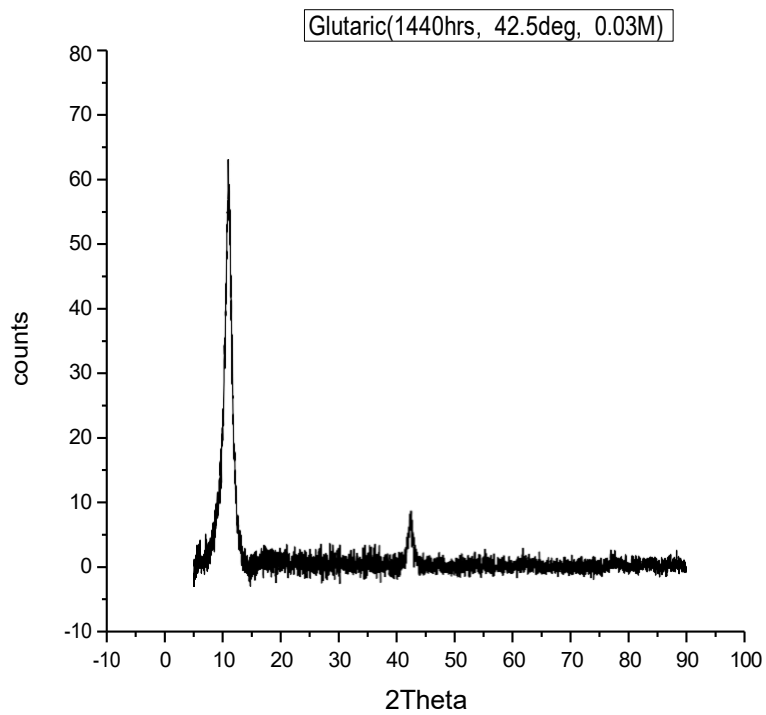
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\theta = 11,5/2 = 5.65$$

$$d = \frac{1.54060}{2 \sin (5.65)} = 7.82 \text{ nm}$$

7. Glutaric (**12hrs**, 42.5°C, 0.03M)



Calculation of the spacing between the GO sheets.

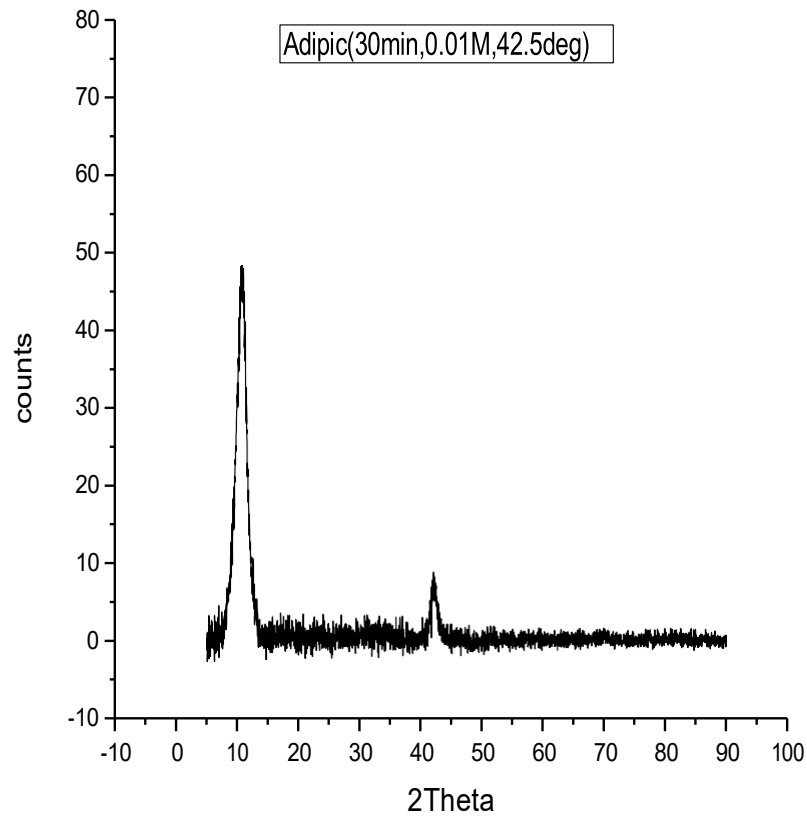
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\theta = 11,8/2 = 5,9$$

$$d = \frac{1.54060}{2 \sin (5.9)} = 7.49 \text{ nm}$$

8. Adipic (30min, 42.5°C, 0,01M)



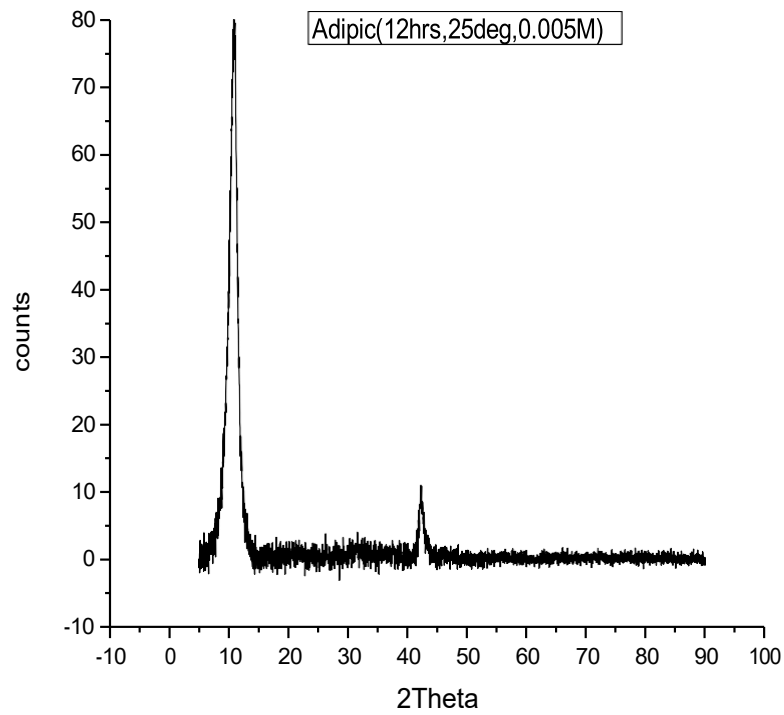
Calculation of the spacing between the GO sheets.

$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\theta = 10/2 = 5 \quad d = \frac{1.54060}{2\sin(5)} = 8,84 \text{ nm}$$

9. Adipic (12hrs, 25°C, 0.005M)



Calculation of the spacing between the GO sheets.

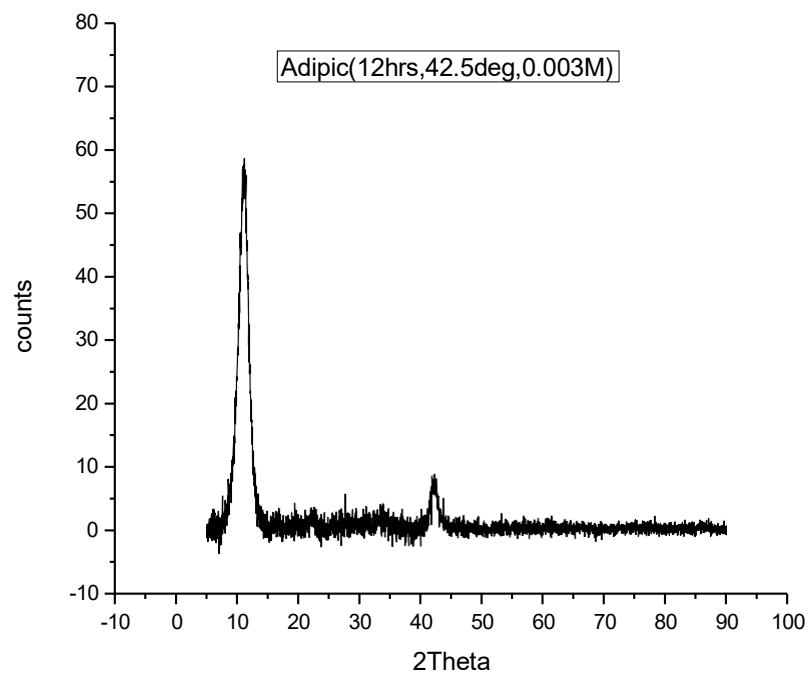
$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 9.98/2 = 4.99$$

$$d = \frac{1.54060}{2\sin(4.99)} = 8.86 \text{ nm}$$

10. Adipic (12hrs, 42.5°C, 0.003M)



Calculation of the spacing between the GO sheets.

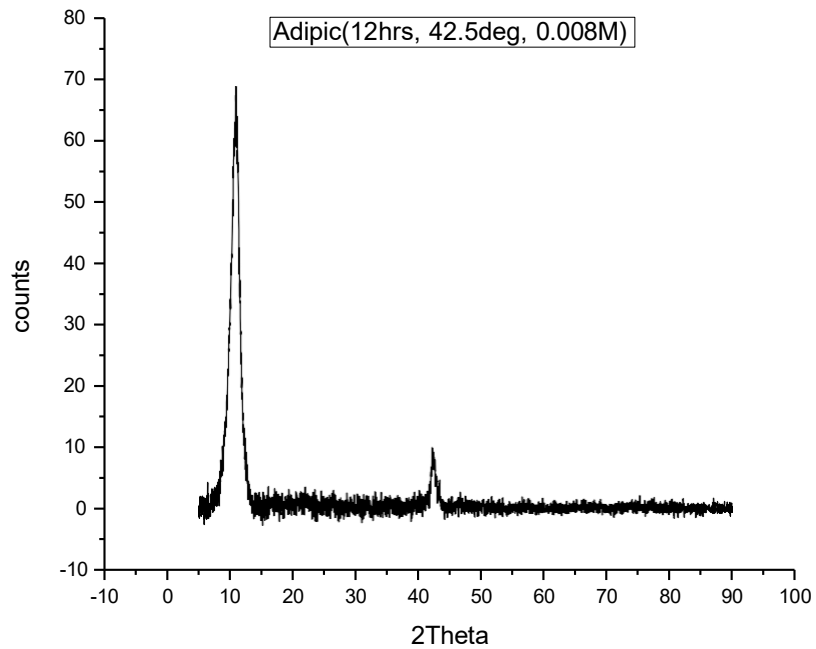
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\theta = 10.55/2 = 5.275$$

$$d = \frac{1.54060}{2 \sin(5.275)} = 8.38 \text{ nm}$$

11. Adipic (12hrs, 42.5°C, 0.008M)



Calculation of the spacing between the GO sheets.

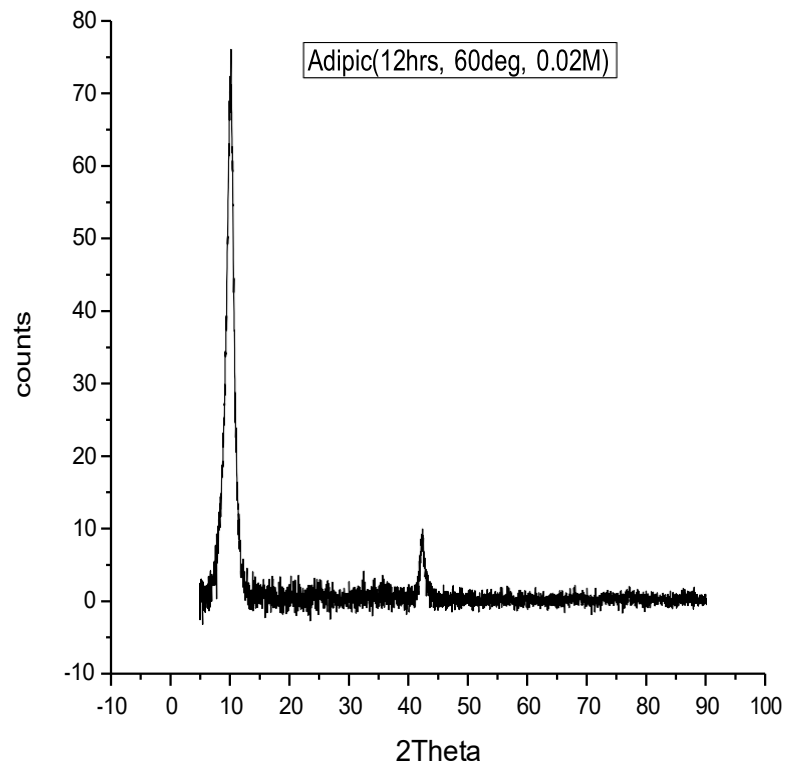
$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 11,5/2 = 5,75$$

$$d = \frac{1.54060}{2\sin(5.75)} = 7.69 \text{ nm}$$

12. Adipic (12hrs, 60 °C, 0.02M)



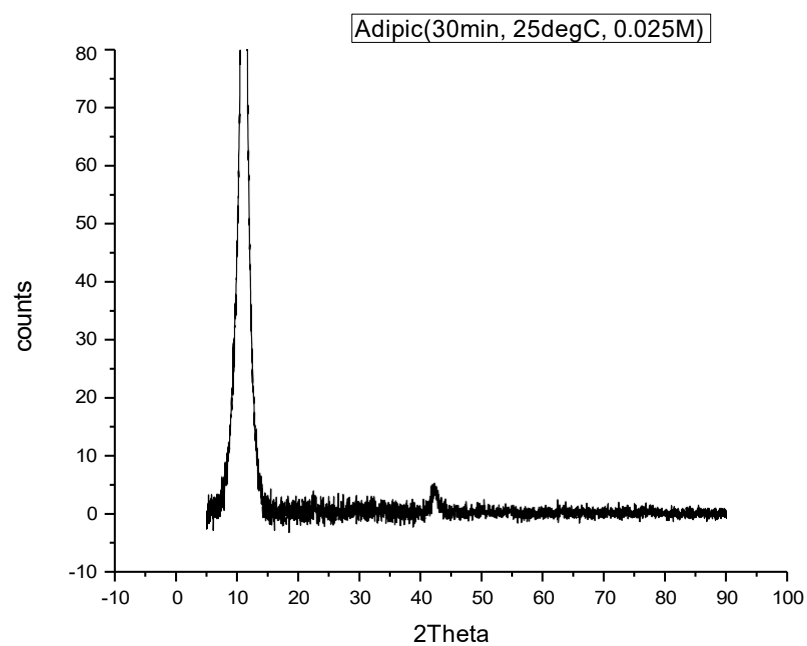
Calculation of the spacing between the GO sheets.

$$\lambda = 2d\sin(\theta)$$

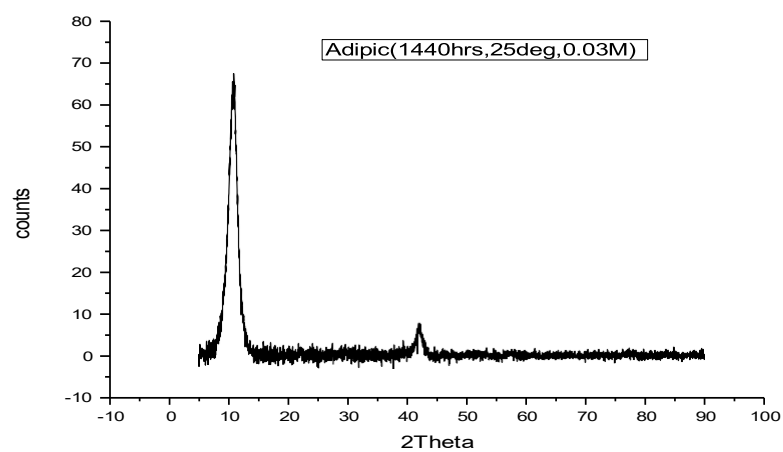
$$\Lambda = 1.54060 \text{ nm}$$

$$\theta = 11,1/2 = 5.55 \quad d = \frac{1.54060}{2\sin(5.55)} = 7.96 \text{ nm}$$

13. Adipic (30min, 25°C, 0.025M)



14. Adipic (12 hrs, 25°C, 0.03M)



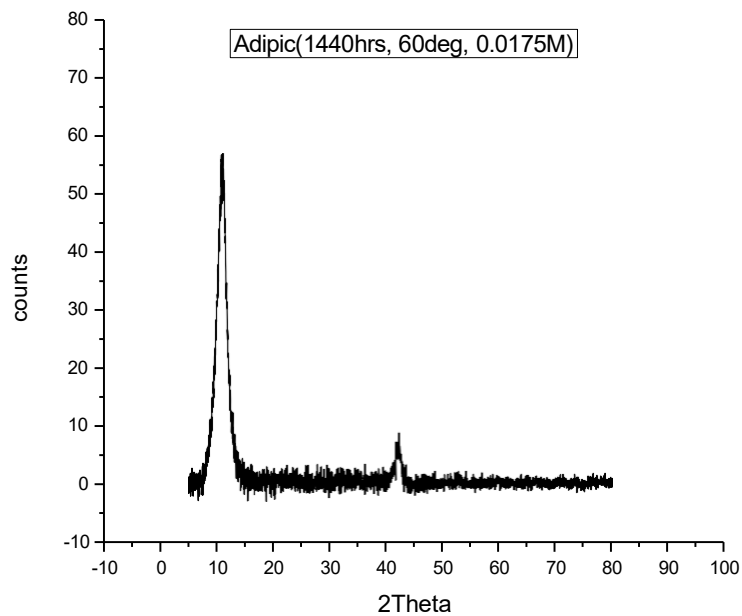
Calculation of the spacing between the GO sheets.

$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 11,4/2 = 5.7 \quad d = \frac{1.54060}{2\sin(5.7)} = 7,75 \text{ nm}$$

15. Adipic (12hrs, 60°C, 0.0175M)



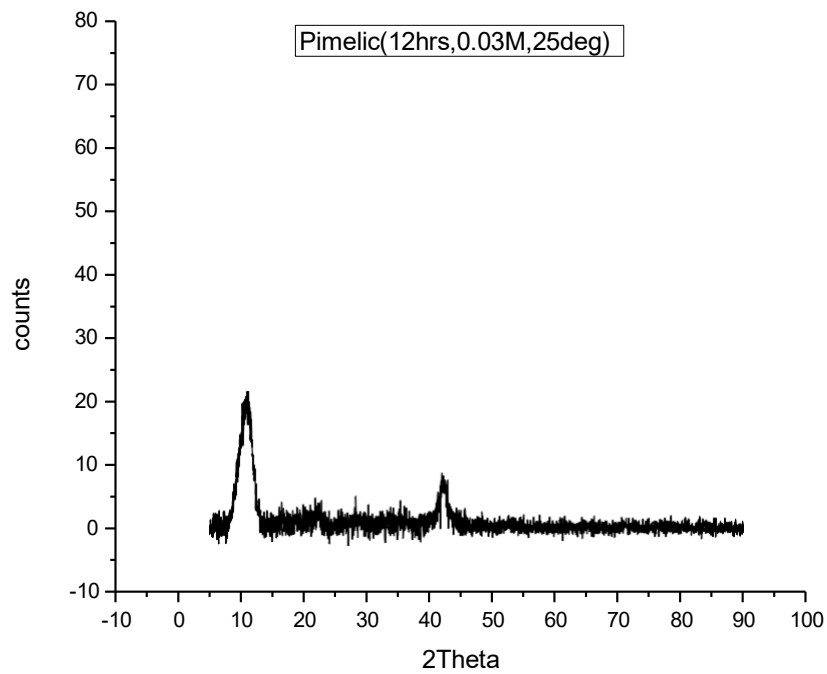
Calculation of the spacing between the GO sheets.

$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 10,4/2 = 5.2 \quad d = \frac{1.54060}{2\sin(5,2)} = 8,49 \text{ nm}$$

16. Pimelic (12 hrs, 25°C, 0,03M)



Calculation of the spacing between the GO sheets.

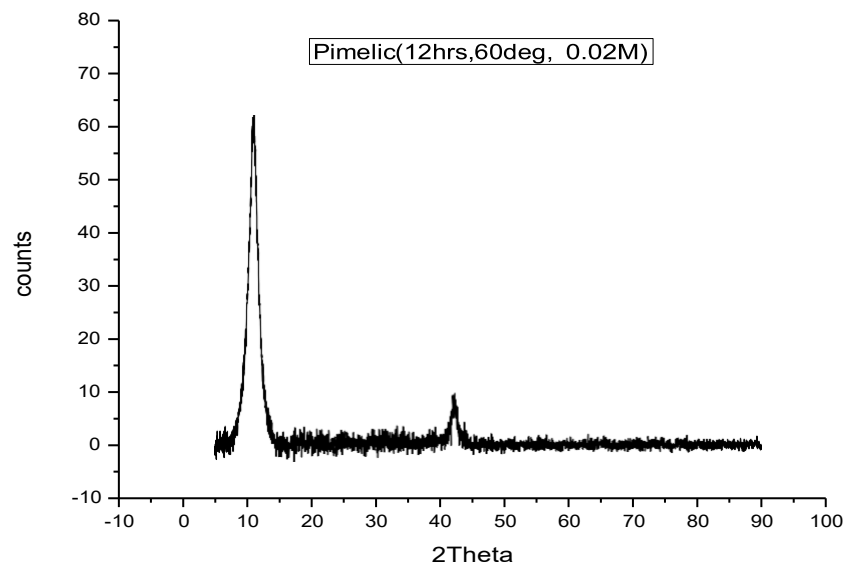
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 11,8 / 2 = 5,9$$

$$d = \frac{1.54060}{2 \sin (5,9)} = 7,49 \text{ nm}$$

17. Pimelic (12hrs, 60°C, 0,02M)



Calculation of the spacing between the GO sheets.

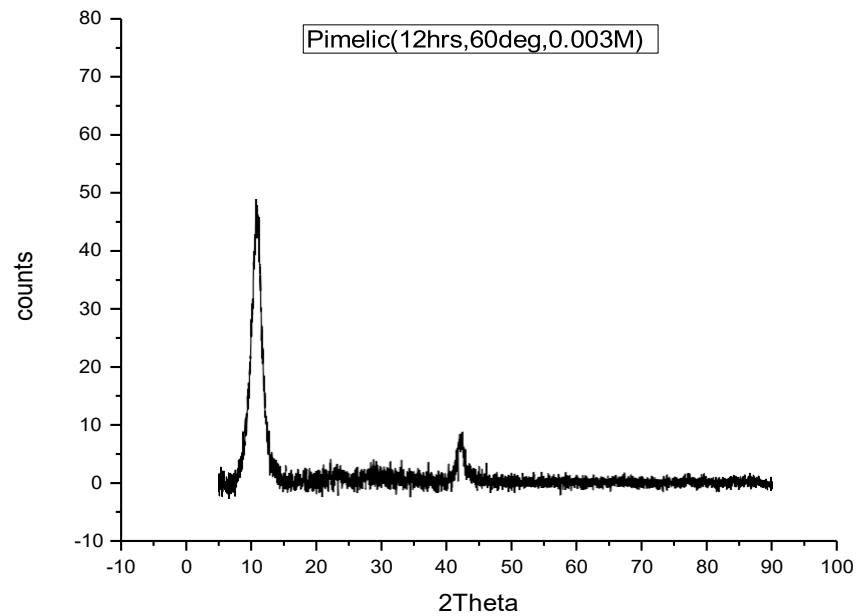
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\theta = 11,8 / 2 = 5,9$$

$$d = \frac{1.54060}{2 \sin (5,9)} = 7,49 \text{ nm}$$

18. Pimelic (12 hrs, 60°C, 0,003M)



Calculation of the spacing between the GO sheets.

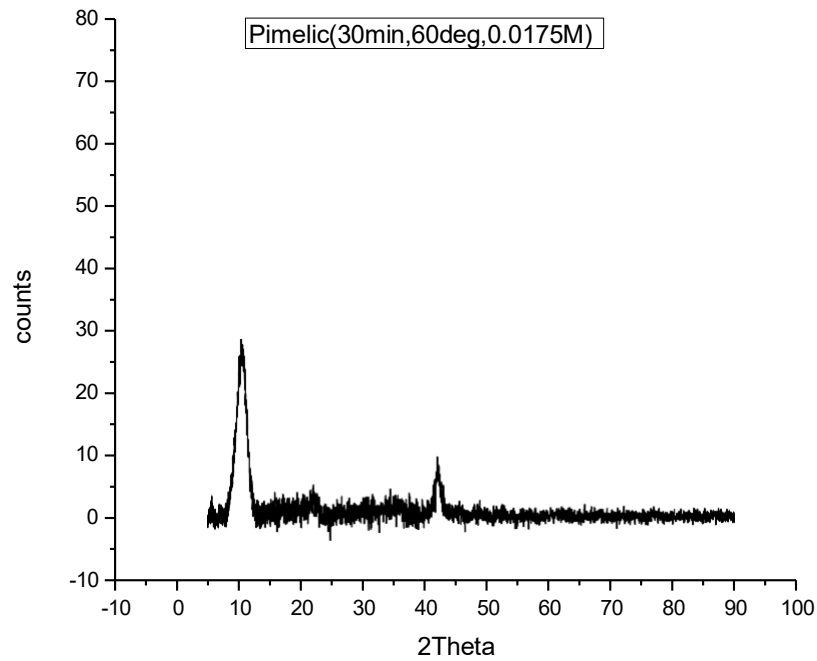
$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 11,6/2 = 5.8$$

$$d = \frac{1.54060}{2\sin(5,8)} = 7,62 \text{ nm}$$

19. Pimelic (30 min, 60°C, 0,0175M)



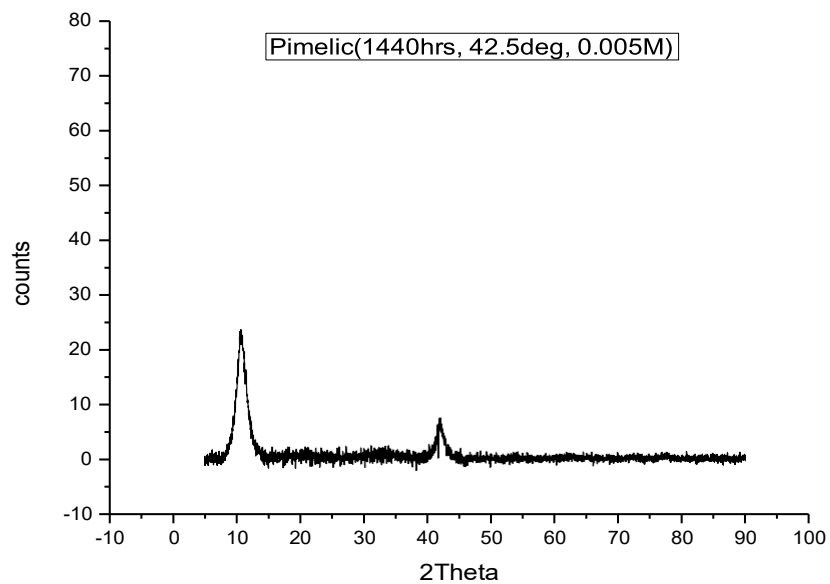
Calculation of the spacing between the GO sheets.

$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\theta = 11,3 / 2 = 5,65 \quad d = \frac{1.54060}{2\sin(5,65)} = 7,82 \text{ nm}$$

20. Pimelic (12, 42,5°C, 0,005M)



Calculation of the spacing between the GO sheets.

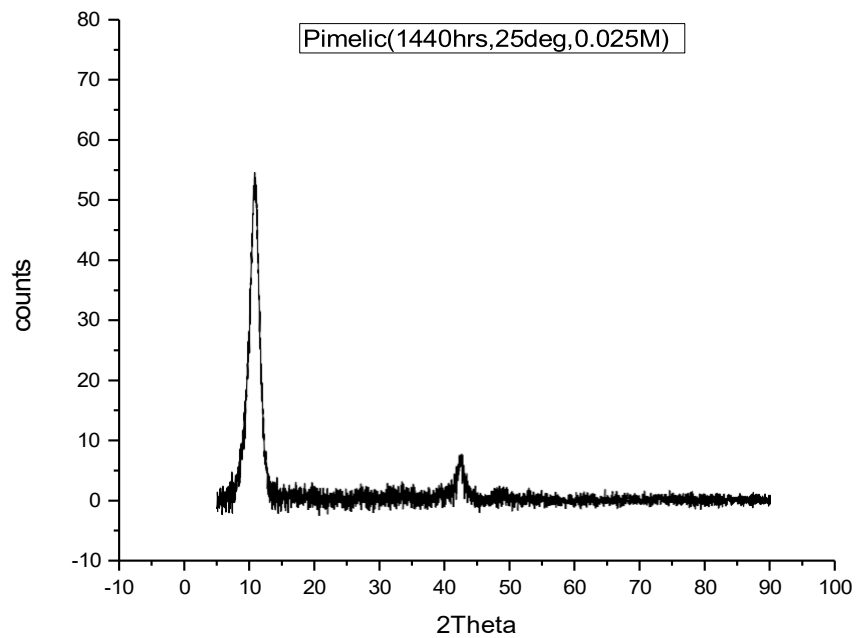
$$\lambda = 2d\sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 12,2 / 2 = 6,1$$

$$d = \frac{1.54060}{2\sin(6,1)} = 7,25 \text{ nm}$$

21. Pimelic (12, 25°C, 0,025M)



Calculation of the spacing between the GO sheets.

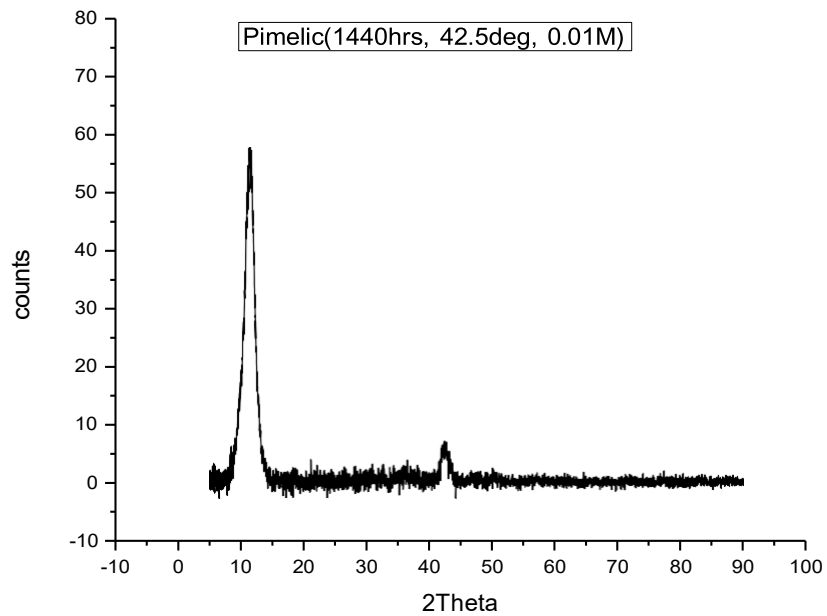
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\Theta = 12,8/2 = 6,4$$

$$d = \frac{1.54060}{2 \sin(6,4)} = 6,91 \text{ nm}$$

22. Pimelic (12, 42,5°C, 0,01M)



Calculation of the spacing between the GO sheets.

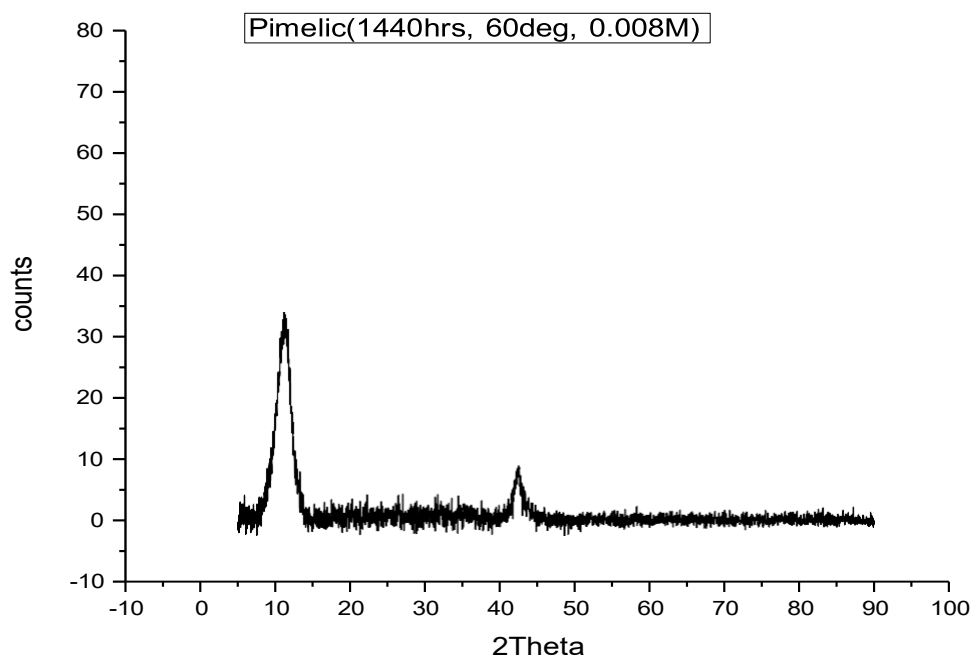
$$\lambda = 2d \sin(\theta)$$

$$\Lambda = 1.54060 \text{ nm}$$

$$\theta = 13,1/2 = 6,55$$

$$d = \frac{1.54060}{2 \sin(6,55)} = 6,75 \text{ nm}$$

23. Pimelic (12hrs, 60 °C, 0,008M)



Calculation of the spacing between the GO sheets.

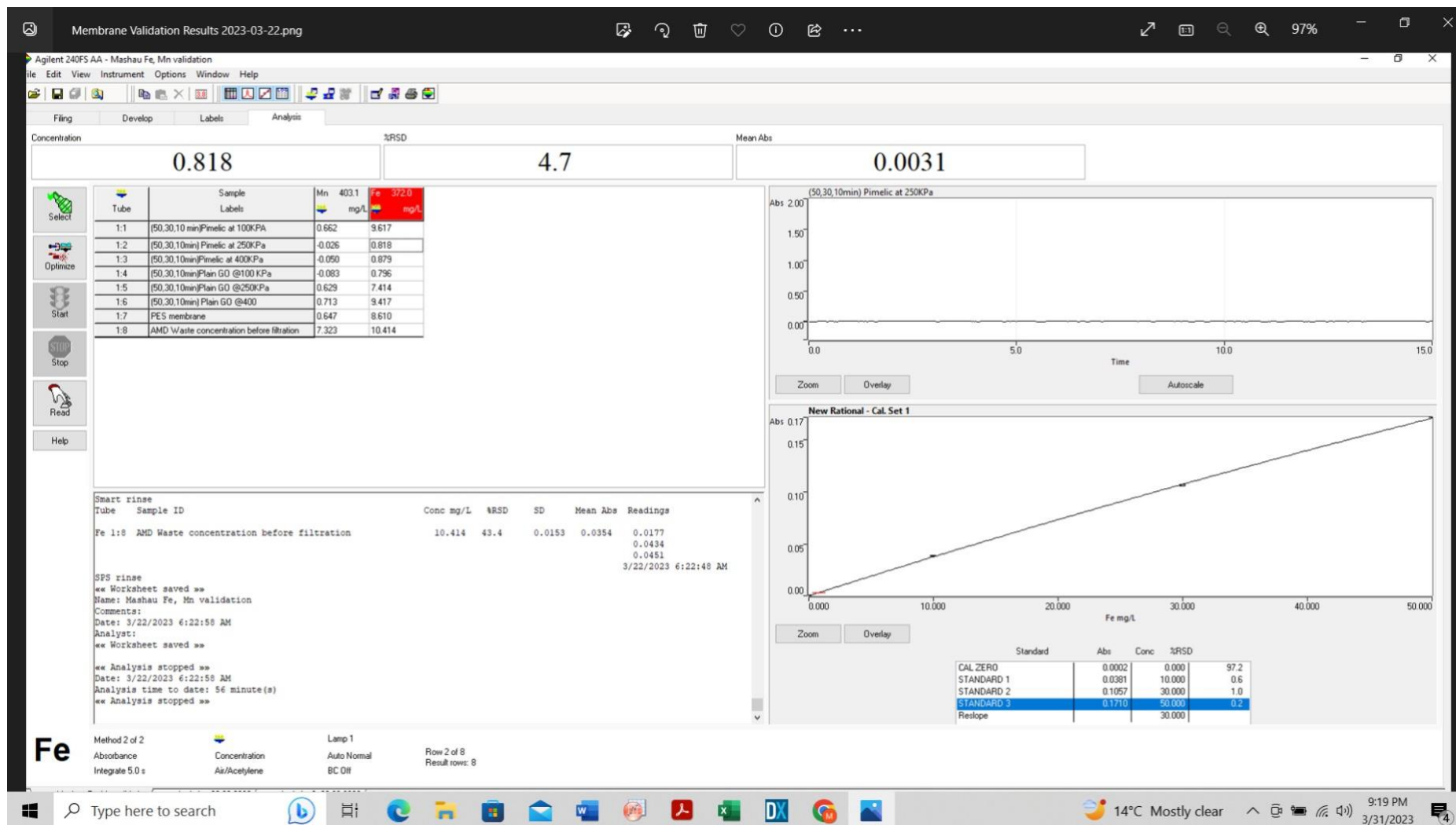
$$\lambda = 2d\sin(\theta)$$

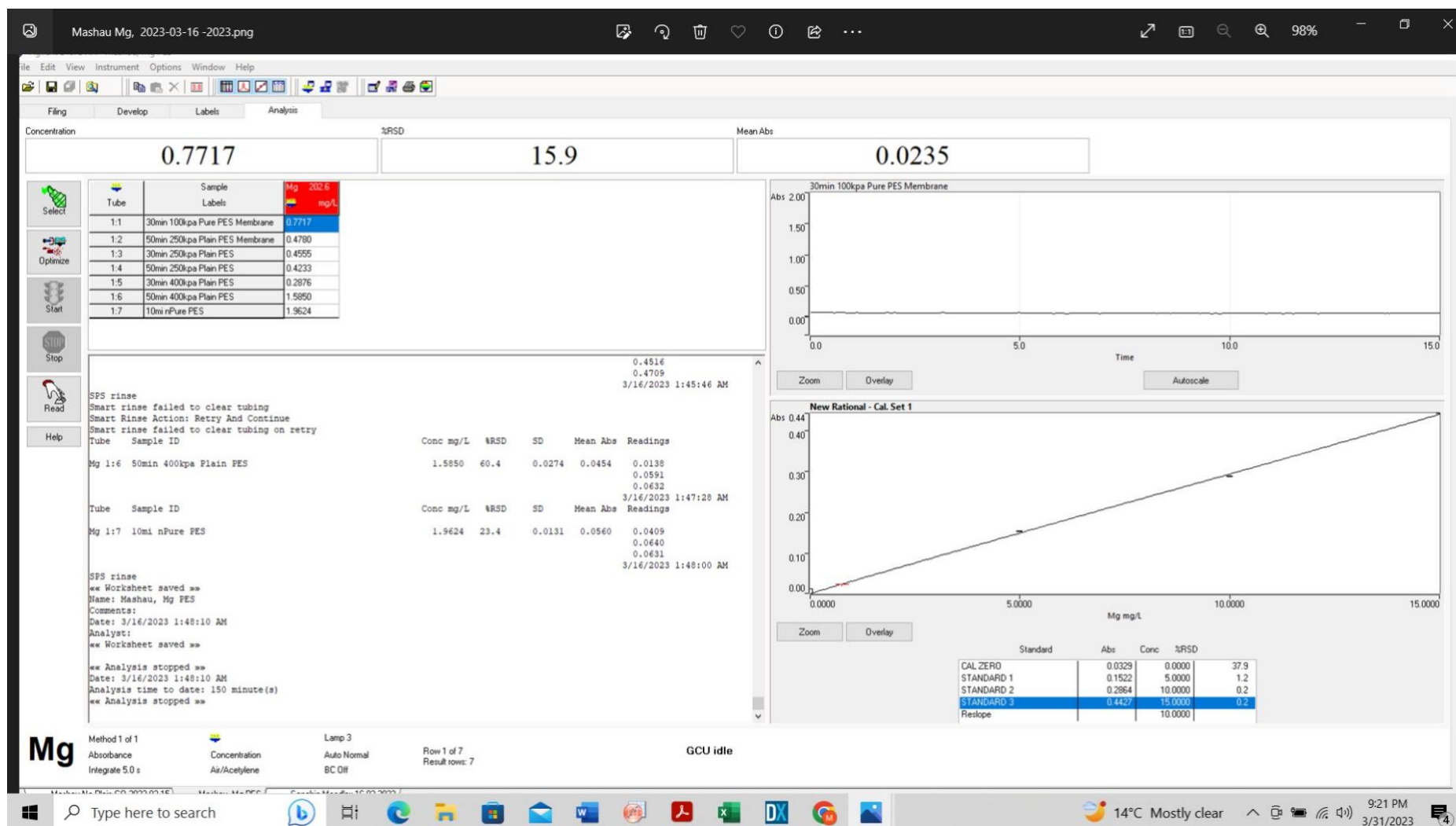
$$\Lambda = 1.54060 \text{ nm}$$

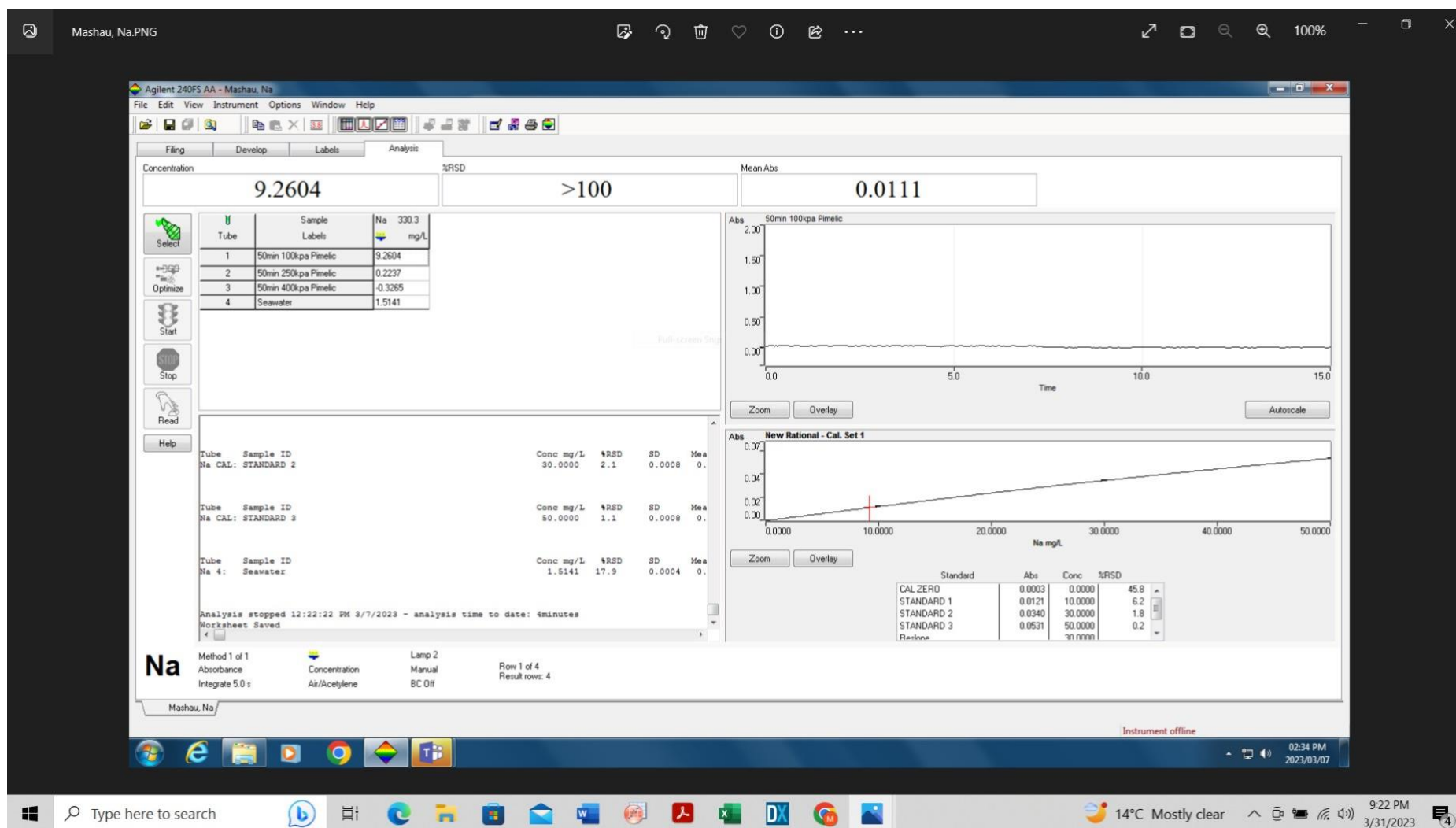
$$\Theta = 12,1/2 = 6,05$$

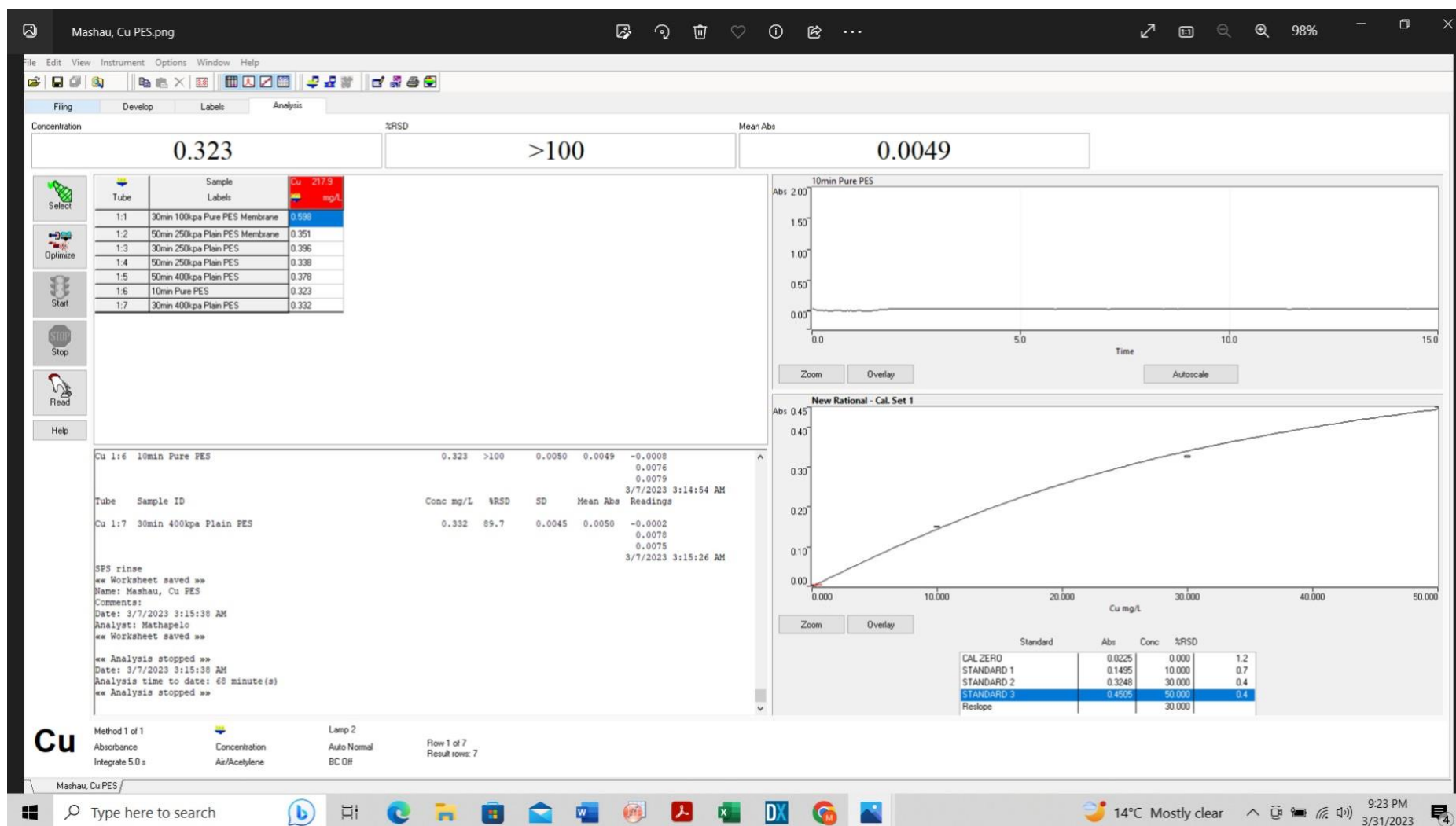
$$d = \frac{1.54060}{2\sin(6,05)} = 7,31 \text{ nm}$$

Appendix B: Set of Experimental results utilised to perform calculations.
The feedstock synthetic AMD concentrations for 1. Manganese and Iron, 2-
Magnesium and the third spreadsheet was for sodium









Pimelic Functionalised membrane after heavy metallic ion filtration process.

