

SYNTHESIS AND EVALUATION OF CYSTEINE AND PHOSPHATE- FUNCTIONALISED GRAPHENE OXIDE BASED THIN-FILM COMPOSITE MEMBRANES FOR ACID MINE DRAINAGE TREATMENT



Dineo Sonia Nhlane

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science

University of the Witwatersrand

Johannesburg

September 2020

DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted for the degree of Master of Science to the University of the Witwatersrand, Johannesburg, South Africa. It has not been submitted before for any degree or examination to any other University.



.....

.....

Miss Dineo Sonia Nhlane

School of Chemistry, University of the Witwatersrand, Johannesburg.

DEDICATION

This dissertation is dedicated to the following:

I would like to give thanks to my parents, Zacharia and Sabina Nhlane, I appreciate your support, love, dedication and the will to make sure that I succeed in my career endeavors. Without your support structure and encouragement, I wouldn't be where I am right now. Through sleepless nights and dark days, you were always there. I appreciate the love.

To my cousin, Michael Hlabathe, you were always there when I needed an academic ear. Always advising me when I was lost and confused about my work. Always pushing me to be greater in what I do.

To my cousin and brothers, thank you for the love and support. It helped me through some difficult times. Just know you were with me in spirit every step of the way.

To my friends, Mimi, Masego, Tebogo, Lydia and Godfrey, without those sleepless nights studying together and always challenging each other this dissertation wouldn't have been possible.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor Dr Anita Etale for the wisdom, guidance, a shoulder to cry on and for willing to work with me through my difficult times. I know it wasn't easy, but I am forever grateful. You pulled me out of a situation I didn't think I would pass. I am also thankful for the financial support and skills you have taught me about life and research.

I would also like to thank Dr Heidi Richards for being there for consultations and advice on my research work. Also, to Profs Luke Chimuka and Ewa Cukrowska for leading the Environmental Analytical Chemistry (EACH) research group with ease and always encouraging us to do the best we can every time.

To the EACH group members for their support and input during presentations, that has helped shape the direction of my research and improve my presentation skills. Especially to Miss Phumlile Kunene your suggestions and input towards my research were very fruitful, your analytical mind is what I admire the most.

To Kagiso at UNISA, thank you for helping me with analysis and for staying up late making sure that I get my results on time. I am grateful also for the time you took to teach me how the instruments operate.

I am grateful for the chance to do volunteer work for WHIZZBANG by encouraging learners to pursue science in school. The exposure I received helped me to change at least one pupil's mind about the benefits of pursuing science. And also, to the ChemSoc group for giving me a chance to learn how to lead and tutor undergraduate chemistry students. The time spent with them helped me realize that I was making an input towards their learning.

I was fortunate to supervise three students during their assistantship program and honours. I had a clear meaning about my research while I was supervising and thank them for assisting in that.

I would also like to thank the Volkswagen foundation and the National Research foundation for funding my master's degree.

ABSTRACT

Acid mine drainage (AMD) exerts significant negative environmental effects by contaminating fresh water sources and potentially affecting human health. Thin film nanocomposite (TFN) membranes provide an opportunity for treatment of metal-ion-contaminated water due to their enhanced adsorption capacity for heavy metal ions, increased water permeation and anti-fouling properties. The aim of this study was to assess the applicability of GO containing membranes for removal of Hg(II) and U(VI) ions from AMD-contaminated waters.

GO nanosheets were prepared via modified Hummer's method. Thiol-functionalised GO nanosheets were then prepared by reaction of GO with *L*-cysteine and evaluated for removal of Hg(II) ions. Phosphate functionalised GO (GO-PO₄) for removal of U(VI) ions were prepared via the Arbuzov reaction. Plain GO nanosheets and their functionalised derivatives were characterised for structure, elemental composition and functionalisation by TEM, XRD, FTIR and CHNS and the removal efficiencies of Hg(II) and U(VI) were determined in batch experiments. TFN membranes were fabricated by in-situ interfacial polymerization and characterised for elemental composition, surface morphology, interlayer spacing and water permeability using SEM-EDX, CHNS, AFM, FTIR and Contact angle. Hg(II) and U(VI) removal efficiencies were quantified using a dead-end filtration system.

GO nanosheets in TEM ranged in size from 1 μm to 200 nm and X-ray diffraction revealed that while phosphate functionalisation increased GO inter-sheet spacing from 0.48 to 1.24 nm, thiolation using *L*-cysteine decreased inter-sheet spacing to 0.38 nm. Further, thiolation using *L*-cysteine reduced GO, resulting in thiol-functionalised reduced graphene oxide (rGO-SH). Optimal removal of Hg(II) by rGO-SH nanosheets was 0.0436 mg g⁻¹ (~95% efficiency) and U(VI) removal by GO-PO₄ nanosheets was 0.062 mg g⁻¹ (~100% efficiency), the capacities were achieved at pH 4.

In TFN membranes, the presence of functionalised GO nanosheets in the polyamide (PA) layer resulted in a decrease in membrane surface roughness and contact angle, and an increase in water flux and fouling resistance. Water flux increased from 38.6 L m⁻² h⁻¹ in membranes with unfunctionalized GO, to 50.9 L m⁻² h⁻¹ and 51.8 L m⁻² h⁻¹ in membranes containing rGO-SH and GO-PO₄, respectively. In comparison to membranes with unfunctionalized GO, membranes with rGO-SH and GO-PO₄ displayed higher Hg(II) and U(VI) rejection (~100%) compared to those with unfunctionalized GO (~90%). Similar results were seen when membranes were tested on field samples of mine-drainage contaminated water (pH 2.78). The

presence of GO in TFN membranes increased rejection of U(VI) by up to 100% and these membranes were also found to be suitable for rejection of other ions present in AMD including As, Cu, Pb, Cr, etc. indicating that the membrane is not selective towards the ions in study.

While GO nanosheets are a good adsorbent for cationic pollutants, the results of studies reported here show that functionalisation increases contaminant removal considerably. Further, when used in membranes for practical application, cysteine and phosphate functionalisation of GO also increases the flux and fouling resistance of membranes. Together, these results suggest that functionalisation of GO nanosheets by cysteine and phosphate are simple and green approaches that can improve the performance of membranes used for treatment of AMD-contaminated water.

TABLE OF CONTENTS

DECLARATION.....	ii
DEDICATION.....	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
TABLE OF CONTENTS	vii
List of Figures.....	xii
List of Tables	xiv
Abbreviations	xv
Structure of dissertation.....	xvi
1 Introduction	1
1.1 Background and motivation.....	1
1.2 Aims	2
1.3 Objectives.....	3
1.4 Research Questions	3
2 Literature review	5
2.1 The history of gold mining in the Witwatersrand Basin	5
2.2 Chemistry of AMD formation.....	5
2.3 Ecological and human health impacts of AMD	6
A. Human health	6
2.4 Large scale techniques for treatment of AMD-contaminated waters	7
A. Chemical Precipitation	8
B. Ion Exchange	9
C. Adsorption.....	11
2.5 Adsorption techniques using nanoparticles for AMD remediation.....	13
A. Metal-containing nanoparticles	13
B. Zeolites.....	14

C. Carbonaceous nanomaterials	14
2.6 Membrane technology.....	15
A. Microfiltration and ultrafiltration membrane process.....	16
A. Nanofiltration membrane process	19
B. Reverse and Forward osmosis membranes.....	23
C. Nanocomposite membranes.....	26
2.10 Conventional nanocomposite membranes.....	26
2.6.4.2 Surface located nanocomposite membranes	27
2.6.4.3 Thin film composite with nanocomposite substrate	27
2.6.4.4 Thin film nanocomposite membranes.....	28
2.11 Thin film nanocomposite (TFN) membranes with graphene oxide.....	32
2.12 Instruments used in the characterization of nanocomposite membranes.....	34
A. Scanning Electron Microscopy	34
B. Energy Dispersive X-ray.....	36
C. Transmission Electron Microscopy	37
D. Atomic Force Microscopy.....	38
E. Inductively coupled plasma mass spectrometry (ICP-MS)	39
3 Materials and Methods	42
3.1 Materials	42
A. Glassware	42
B. Chemicals.....	42
3.2 Synthesis and characterisation of graphene oxide and derivatives	42
A. Synthesis of graphene oxide	42
B. Synthesis of L-cysteine-functionalised GO (rGO-SH).....	43
C. Synthesis of phosphate-functionalised GO (GO-PO ₄)	43
D. Characterisation of GO and functionalised derivatives	43
3.3 Adsorption of Hg and U ions using GO nanosheets and its derivatives.....	43

3.4	Application of GO nanosheets and functionalised derivatives on actual AMD-contaminated water.....	44
3.5	Synthesis of membranes	45
A.	Synthesis of support polymer	45
B.	Synthesis of polyamide layer containing graphene oxide nanosheets and the functionalised derivatives.....	45
3.7	Membrane performance experiments	46
A.	Leaching and Pure water flux	46
B.	Membrane hydrophilicity	47
C.	Membrane fouling resistance	47
3.8	Removal of Hg(II) and U(VI) ions by TFN membranes.....	47
4	Adsorption of Hg(II) and U(VI) by graphene oxide and functionalised derivatives.....	50
4.1	Cysteine-functionalised graphene oxide (rGO-SH)	50
A.	TEM characterisation of nanosheets.....	50
B.	XRD analysis.....	50
C.	FTIR analysis.....	51
D.	Elemental analysis of nanosheets.....	52
4.2	Hg adsorption studies between graphene oxide and Cysteine-functionalised graphene oxide (rGO-SH)	53
A.	Effect of adsorbent concentration.....	53
B.	Effect of contact time	53
C.	Effect of pH	55
D.	Effect of initial concentration.....	57
4.3	Phosphate functionalised graphene oxide.....	59
A.	XRD analysis.....	59
B.	FTIR	59
C.	TEM.....	60

4.4	U(VI) adsorption studies.....	61
A.	Effect of contact time	61
B.	Effect of pH	62
C.	Effect of initial concentration.....	64
4.5	Application studies	66
4.6	Comparison on performance between the rGO-SH and GO-PO ₄ nanosheets compared to GO	67
5	Removal of Hg(II) and U(VI) using membranes containing graphene oxide and its functionalised derivatives.....	69
5.1	Cysteine functionalized graphene oxide thin film nanocomposite membrane (rGO-SH TFN).....	69
5.1.1	Characterisation.....	69
5.2	Thin film nanocomposite membranes with GO and GO-PO ₄	75
5.2.1	Characterisation.....	75
5.3	Membrane performance	80
A.	Permeate Flux.....	80
B.	Membrane fouling	81
5.4	Removal of Hg(II) by TFN membranes with GO and rGO-SH	83
5.5	Removal of U(VI) by TFN membranes with GO and GO-PO ₄	86
5.6	Application studies	88
5.7	Comparison on performance between the rGO-SH and GO-PO ₄ thin film nanocomposite membranes	90
6	Conclusions and Future work	93
6.1	The effect of nanosheets functionalization on removal efficiency.....	93
6.2	The effect of GO nanosheets on metal uptake by TFN membranes.....	94
A.	Membrane performance	94
B.	Application of membranes to field samples	95
6.3	Conclusions	95

7	References	97
8	Appendices	111
8.1	Copyright licenses for figures.....	111
8.2	Calibration curves for GO and functionalised GO leaching.....	114
8.2	Leaching studies	114

List of Figures

Figure 2.1: The principle of membrane separation. Reproduced with permission from (Liu and Xu, 2016a). Copyright 2020, Elsevier Science Ltd	15
Figure 2.2: Pressure driven membrane processes and the particles rejected from waste water treatment. Reproduced with permission from (Liao et al., 2018). Copyright 2020, Elsevier Science Ltd.	16
Figure 2.3: Fabrication of thin film nanocomposite membrane through interfacial polymerisation. Reproduced with permission from (Yin and Deng, 2015). Copyright 2020, Elsevier science Ltd.	26
Figure 2.4: Structure of graphene oxide showing its different reactive groups (Wilkinson, 2016)	32
Figure 2.5: The basic components of SEM (Leng, 2008).....	35
Figure 3.1: Schematic diagram of the dead end filtration system (Koyuncu and Wiesner, 2007)	48
Figure 4.1: TEM images of (a) GO, (b) rGO-SH.....	50
Figure 4.2: XRD pattern of A) GO and B) rGO-SH nanosheets	51
Figure 4.3: FTIR spectrum of A) GO and B) Cysteine functionalised GO nanosheets....	52
Figure 4.4: The effect of varying dosage amount of GO, rGO-SH and GO-PO ₄ on removal	53
Figure 4.5: The effect of contact time on removal of Hg(II) by GO and rGO-SH	54
Figure 4.6: Species distribution of Hg(II) across pH 1-10.....	55
Figure 4.7: Effect of change in pH on adsorption of Hg(II) ions onto GO and rGO-SH .	56
Figure 4.8: Effect of Hg(II) concentrations on removal.	57
Figure 4.9: XRD pattern of GO (A) and GO-PO ₄ (B) nanosheets.....	59
Figure 4.10: FTIR spectra of GO and GO-PO ₄	60
Figure 4.11: Reaction scheme for the synthesis and phosphorylation of GO.....	60
Figure 4.12: Effect of contact time on the adsorption of U(VI) ions onto GO and GO-PO ₄	61
Figure 4.13: Effect of pH on adsorption of U (IV) ions onto GO and GO-PO ₄	63
Figure 4.14: Species distribution of U(VI) through pH 1-10 at experimental concentration of 100 µg L ⁻¹	63

Figure 4.15: Removal efficiency of U(VI) onto GO and GO-PO ₄ with change in initial concentration.....	64
Figure 4.16: Graphene oxide and functionalised derivatives on treatment of real AMD-contaminated water	66
Figure 5.1: SEM-EDX of TFC (A), GO (B) and cysteine functionalised GO (C) TFN membranes	70
Figure 5.2: FTIR spectra of rGO-SH TFN (A), GO TFN (B), TFC (C) membranes	72
Figure 5.3: AFM image of TFC (A), GO TFN (B) and rGO-SH TFN (C) membranes showing the ridge and valley morphology	73
Figure 5.4: SEM-EDX of TFC (A), GO (B) and phosphate functionalised GO (C) TFN membranes	76
Figure 5.5: FTIR spectra of GO-PO ₄ TFN (A), GO TFN (B), TFC (C) membranes	77
Figure 5.6: AFM image of TFC (A), GO TFN (B) and GO-PO ₄ TFN (C) membranes showing the ridge and valley morphology	78
Figure 5.7: Permeate flux of TFC, GO TFN membrane and its functionalised derivatives	81
Figure 5.8: Fouling tests for TFC, GO TFN membranes and its functionalised derivatives	82
Figure 5.9: Effect of contact time on the adsorption of Hg(II) ions onto TFC, GO and rGO-SH functionalized TFN membrane	83
Figure 5.10: Change in pH on removal efficiency of Hg(II) ions onto TFC, GO and rGO-SH functionalized thin film nanocomposite membrane.....	84
Figure 5.11: Removal efficiency of Hg(II) by TFC, GO and rGO-SH TFN membranes against concentration effect of Hg(II) ions.	85
Figure 5.12: Effect of contact time on the removal of U(VI) ions by GO and GO-PO ₄ functionalized TFN membranes.....	86
Figure 5.13: Effect of change in pH on removal of U (IV) ions by GO and GO-PO ₄ functionalized thin film nanocomposite membranes	87
Figure 5.14: Removal efficiency of U(VI) onto GO and GO-PO ₄ functionalized TFN membranes with change in initial concentration	88
Figure 5.15: Removal of metal ions from AMD-contaminated water samples by functionalized graphene oxide thin film composite membranes.	90

List of Tables

Table 2.1: Heavy metals and their effects on human health with their permissible limits (Simate and Ndlovu, 2014), (Department of Water affairs and forestry, 1996).	7
Table 2.2: Types of polymer-enhanced ultrafiltration membranes and their application in the adsorption of metal ions	18
Table 2.3: Selected nanofiltration studies showing different membranes used, target metals and removal efficiencies.	22
Table 2.4: A summary of studies using RO membranes for removal of different target metals from aqueous solution	25
Table 2.5: Summary of studies involving the use of thin film nanocomposite membranes for removal of metal ions	31
Table 2.6: Differences between SEM and TEM	38
Table 4.1: Elemental composition of GO and rGO-SH	52
Table 4.2: Kinetic parameters of Hg(II) sorption at 298 K.....	54
Table 4.3: Langmuir and Freundlich adsorption isotherm constants for Hg(II) sorption .	58
Table 4.4: The fit of kinetics models to data for adsorption of U(VI) by GO and GO-PO ₄	62
Table 4.5: The fit of isotherm models to adsorption data	65
Table 5.1: CHNS results for the membrane with and without graphene oxide	71
Table 5.2: Surface roughness and water contact angle for the TFC, GO TFN and rGO-SH TFN membrane types.....	74
Table 5.3: Surface roughness and water contact angle for the TFC, GO TFN and GO-PO ₄ TFN membrane types.....	79

Abbreviations

AFM	Atomic Force Microscopy
AMD	Acid Mine Drainage
CHNS	Carbon Hydrogen Nitrogen Sulphur
EDX	Energy Dispersive X-ray
FTIR	Fourier-transform infrared spectroscopy
GO	Graphene Oxide
GO-PO ₄	Phosphate functionalised graphene oxide
Hg	Mercury
ICP-MS/ -	Inductively coupled plasma mass spectroscopy/ optical emission
OES	spectroscopy
PSF	Polysulfone
rGO-SH	Cysteine-functionalised graphene oxide
RPM	Rotation per Minute
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TFC	Thin Film Composite
TFN	Thin Film Nanocomposite
U	Uranium
XRD	X-Ray Diffraction

Structure of dissertation

This dissertation was written in the form of research articles for conference proceedings and were published. The articles form part of the results section (chapter 4).

The dissertation consists of the following chapters:

Chapter 1- Introduction

This chapter includes the background and motivation of conducting studies based on the adsorption of elements onto nanoparticles and TFN membranes in the vicinity of mining operations. The aim of the study and underlying objectives are clearly stated out, and research questions are posed.

Chapter 2-Literature review

The literature review relevant to this study is presented in this chapter. The generation of AMD, health risks and mitigation measures used such as sorption processes and their advantages and disadvantages. The history of membrane technology, membrane technology processes and their use in heavy metal ion removal, and the use of nanomaterials to improve membrane performance.

Chapter 3- Materials and methods

In this chapter, the materials with their purity are reported alongside the methods used for synthesis of the nanosheets, functionalization and use in batch adsorption studies. Synthesis of TFN membranes along with functionalization is reported and their use in removal of targeted metal ions and in application studies.

Chapter 4- Adsorption of Hg(II) and U(VI) by graphene oxide and functionalised derivatives

In this chapter, the results were published in two open access research articles. The section focuses on the characterization of the synthesized GO nanosheets and its functionalized derivatives, the effect of adsorbent amount, contact time, pH and initial concentration on Hg(II) and U(VI) removal. The isotherm and kinetic models are also included in this chapter. The use of nanosheets in real AMD-contaminated water is also evaluated.

Chapter 5- Removal of Hg(II) and U(VI) using TFN membranes containing graphene oxide and its functionalised derivatives

This chapter presents characterization results of the TFN membranes, removal of Hg(II) and U(VI) by TFN membranes synthesized with functionalized and unfunctionalized GO in the PA

layer and membrane performance. The membranes' removal efficiencies of Hg(II) and U(VI) were determined by investigating the effect of pH, concentration and contact time. Applications studies are also reported based on field samples of AMD-contaminated water.

Chapter 6-General conclusions

This chapter describes the overall conclusions from the study.

References

References from this study are included in this section.

Appendices

Supplementary information is included in this section

CHAPTER 1

INTRODUCTION

This chapter includes the general background and motivation, problem statement, aims and objectives and research questions.

1 Introduction

1.1 Background and motivation

Water contamination by various industrial and mining activities is a concern globally. This includes Johannesburg, South Africa, where previous mining activity has resulted in ground and surface water that is contaminated by elements including Cd, Hg, U, Zn, Pb, Ni, As and Se. Such contaminated water has detrimental effects for the environment, aquatic organisms and human beings (Abhang et al., 2013). Significant contamination of water resources through the formation of acid mine drainage (AMD) has been reported due to gold mining in the Witwatersrand Basin, Johannesburg (Naicker et al., 2003).

South Africa is a country that receives an annual rainfall of 465 mm and evaporation and transpiration exceed precipitation by about 65 % (Mccarthy et al., 2011). Due to population growth and the water scarcity problems, several policies implemented by the South African Department of water Affairs (DWA) ensure water security. In addition to these policies, research is also advancing to develop techniques and methods for treatment of AMD-contaminated water. However, these have mainly been on a large scale (Simate and Ndlovu, 2014). Technologies aimed at small-scale/point-of-use treatment are also necessary.

Membrane technology is gaining momentum in the field of water research as the number of articles published a year keeps on increasing. Membranes have been used for seawater desalination (Emadzadeh et al., 2014; He et al., 2015; Li et al., 2017; Shibuya et al., 2017; Wu et al., 2013a; Yin et al., 2016), removal of organic matter (Rajaeian et al., 2013), disinfection (Park et al., 2016), and removal of metal ions (Dialynas and Diamadopoulos, 2009; Mohsen-Nia et al., 2007; Ozaki et al., 2002; Zhu et al., 2014). Polymer membranes are the most common membranes manufactured and these polymers include polysulfone (Tang et al., 2015), polyethersulfone (Abdi et al., 2018), polyacrylonitrile (Jia et al., 2019), cellulose acetate (Huang and Feng, 2019), polyvinylidene fluoride (Zheng et al., 2016). The manufactured membranes indicated signs of fouling and reduced removal efficiency, therefore, to solve the issue nanomaterials were introduced. The inclusion of nanomaterials (materials with at least one dimension in the 1-100 nm range) in membranes has attracted interest due to the advantages they confer on membranes, particularly with respect to reduction of membrane fouling, enhance membrane flux and improve selectivity of targeted contaminants (Yin and Deng, 2015).

Polymer membranes with nanomaterials in their matrix are called nanocomposite membranes. Polymer-matrix nanocomposite membranes are a form of advanced membranes with nanomaterials dispersed in the polymer matrix. Based on the location of nanomaterials and the structure of membrane, polymer matrix membranes are classified into four groups:

- 1) *Conventional nanocomposite membranes*: These are membranes with nanoparticles dispersed in the polymer solution prior to the phase inversion. They can be prepared in either hollow fibre or flat sheet configurations (Xia et al., 2015)
- 2) *Surface located nanocomposite membranes*: These are membranes where the support polymer is coated with nanoparticles on the surface. They can be fabricated through self-assembly, coating/deposition, adsorption-reduction or layer-by-layer assembly methods (Jia et al., 2019; Wen et al., 2017).
- 3) *Thin film composite with nanocomposite substrate*: These have nanoparticles embedded in the polymer substrate for mechanical support e.g. to prevent collapse of the porous structure thus increasing water permeability (Son et al., 2016; Zhao et al., 2017).
- 4) *Thin film nanocomposite (TFN) membranes*: These have nanoparticles as an ultra-thin layer atop a support substrate.

Despite the efficiency of TFNs in water treatment, there are limited studies on their use for AMD-contaminated water (Choi et al., 2019; Kim and Deng, 2011; Yin et al., 2012). Therefore, the use of graphene oxide nanoparticles in modification of thin film composite membranes will bridge the gap of membrane fouling whilst maintaining the selectivity for targeted metal ions. In addition, the ability to functionalise GO nanosheets and embed in thin film layer for selectivity towards Hg and U, and the stability of the graphene oxide particles in membrane matrix have not been studied previously. The motivation for this work was therefore to investigate the removal of these ions under AMD conditions.

1.2 Aims

The aim of this study was to investigate the removal of Hg and U ions from contaminated water, using (i) graphene oxide nanosheets and its derivatives and (ii) thin film nanocomposite membranes with graphene oxide and its derivatives.

1.3 Objectives

The aims were achieved by addressing the following objectives:

- To synthesize and characterize thiol and phosphate functionalised graphene oxide nanoparticles and apply them in the removal of Hg and U;
- To fabricate and characterise thin film nanocomposite membranes containing functionalised and unfunctionalized graphene oxide, and assess their efficiency in the removal of Hg and U ions;
- To investigate the possible leaching of the GO sheets from the prepared thin film nanocomposite membrane.

1.4 Research Questions

The study tends to answer the two key questions:

1. What is the effect of functionalization of GO nano-sheet and TFN membranes on the adsorption of Hg and U?
2. Are embedded GO nanosheets stable in the matrix of the thin film nanocomposite membranes?

This dissertation reports on the techniques applied in the fabrication and characterisation of functionalised GO particles and TFN membranes, and the contaminant removal efficiencies of these materials under various conditions.

CHAPTER 2

LITERATURE REVIEW

This chapter presents a concise overview of the literature relating to adsorption of heavy metals using nanomaterials and membrane technology.

2 Literature review

2.1 The history of gold mining in the Witwatersrand Basin

Gold mining commenced in the Johannesburg area in 1886. Although the sedimentary rocks of the Witwatersrand Super group contained gold in layers of composite rock, not all contained gold. As such only in certain localised areas was gold present in economically recoverable concentrations. These areas were called the goldfields. Within any individual goldfield, only a few of the composite layers have been mined (Simate and Ndlovu, 2014).

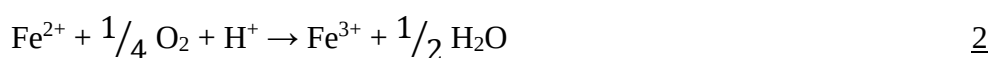
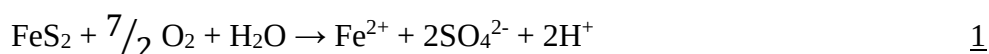
The process of mining involves extracting the gold-containing composite layer and transporting it to the surface where it is crushed, and the gold is extracted. Some composite is left unmined to provide support for the workers underground and because gold concentrations may be insufficient to justify extraction. After extraction of the gold, the residual crushed rock is deposited in slimes or tailings dumps. The rock composites contained about 3 % pyrite, which ended up on the dumps. Rainwater falling on the dumps oxidised the pyrite, forming sulphuric acid which percolated through the dump, dissolving heavy metals along the way, and emerging from the base of the dump to join the local groundwater as a pollution plume. The process was how acid mine drainage (AMD) was formed. There were cases in which the polluted water emerged on the surface in the streams draining the areas around the dumps. Streams draining the tailings dumps were, therefore, typically acidic and have high sulphate and heavy metal concentrations (Naicker et al., 2003).

When the gold mines on the Witwatersrand basin closed, water began to accumulate in the underground voids and eventually discharged to neighbouring mines. To contain this situation, the water was pumped out into local streams and rivers after treatment with calcium carbonate to neutralise it (Philippus, 2006). The discharged water was clear with neutral pH but had remarkably high sulphate content. In other parts of the Basin, the discharged water was not treated and had a pH of between 2 and 3, along with heavy metal ions like Zn, Ni, Cd, Pb, Cu, U, Hg, etc. (Mccarthy et al., 2011).

2.2 Chemistry of AMD formation

AMD is formed via a cascade of reactions when pyrite (FeS), and to a small extent pyrrhotite, arsenopyrite and chalcopyrite encounter oxygenated water. The pyrite

undergoes oxidation in a two-stage process, the first of which produces sulphuric acid and ferrous iron (Eq. 1) and the second of which produces ferric iron and water (Eq. 2). The ferric iron, which is soluble below pH 3.5 acts as an additional oxidiser for pyrite (Equation 3) producing even more sulphuric acid. The reactions are dependent on several factors such as temperature, pH, Eh, pyrite grain size, and, most importantly microorganisms. Microorganisms like *Leptospirillum ferro-oxidans* and *Thiobacillus ferro-oxidans* catalyse reaction 2 below the pH of 3.5 (Gazea et al., 1996). Above pH 3.5, ferric iron precipitates as Fe(OH)₃ (Equation 4)



Pyrite is a common minor constituent in many mineral deposits and is associated with coal, in which it is the main source of sulphur and the gold deposits. During normal weathering of these deposits, acid is produced but at a very slow rate, so slow that natural neutralisation processes occur readily to remove the acidity (Mccarthy et al., 2011). However, mineral extraction extensively fragments the rock mass and dramatically increasing the surface area of reactions, the rate of acid production is greatly increased, and the neutralising effect of calcite and dolomite are overwhelmed, resulting in the release of acidic water into ground and surface water. This acidic water increases the solubility of ores that occur alongside pyrite hence the presence of other ions such as Zn, Hg, Se, Ni, Co, Cd, Mn, Ag and Au in AMD. (Mccarthy et al., 2011).

2.3 Ecological and human health impacts of AMD

AMD contains high concentrations of acid and dissolved metals which are toxic to some aquatic organisms and ecosystems.

A. Human health

The dangers that AMD imposes on human health are indirect. The risks posed by heavy metal pollutants can be conceptualised firstly in the ability of the metals to persist in natural ecosystems for long periods of time and secondly in their ability to bio accumulate in the food chain. The bio accumulation aspect is what exposes humans to the effects of AMD. For example, the heavy metals accumulated in animal organs or vegetables can

be accumulated in human organs e.g. brain, kidneys and/or liver following consumption of these foods over time. Some of these metals could then disrupt metabolic functions by inhibiting the absorption of vital nutrients for intended function. The table below shows summary of some heavy metals with their impact on human health (Simate and Ndlovu, 2014)

Table 2.1: Heavy metals and their effects on human health with their permissible limits (Simate and Ndlovu, 2014), (Department of Water affairs and forestry, 1996).

Heavy metal	Effect	Permissible level (mg L ⁻¹)
Arsenic	Bronchitis, skin lesions, pulmonary diseases	0.02
Cadmium	Renal dysfunction, lung disease, bone defects (osteomalacia), gastrointestinal disorder, pneumonitis	0.06
Lead	Mental retardation in children, developmental delay, fatal infant encephalopathy, sensor neural deafness, acute or chronic damage to the nervous system, epilepticus	0.10
Manganese	Loss of coordination and balance, bronchitis	0.26
Mercury	Protoplasm poisoning, spontaneous abortion, minor physiological changes, tremors, gingivitis, acrodynia	0.01
Zinc	Seizures, jaundice, frequent infections due to suppressed immune system	15.0
Chromium	Fatigue, irritability, asthma, shortness of breath	0.05
Copper	Anaemia, liver and kidney damage, stomach and intestinal irritation	0.10
Uranium	Kidney and liver failure due to accumulation and mostly available as α -emitters, U ²³⁸ and ²³⁴	0.02

2.4 Large scale techniques for treatment of AMD-contaminated waters

The environmental effects of AMD have been more prominent over the years and a lot of research has been done to develop remediation techniques. The remediation techniques developed over the years have been migration control techniques which are directed towards treating the drainage formed and drainage-contaminated waters and are divided into four categories: Precipitation, ion-exchange, adsorption and membrane technology.

A. Chemical Precipitation

Chemical precipitation technique is the most applied method for AMD treatment, and it involves addition of alkaline reagents to increase pH and precipitate dissolved metals as hydroxides, in other words neutralizing the acidic pH of AMD. The chemicals mainly used for precipitation in AMD treatment are limestone, sodium hydroxide, ammonia, calcium hydroxide, etc (Akciil and Koldas, 2006). The precipitation process occurs when AMD effluent is introduced to a dry or slurry form of the neutralising agent in a mixing chamber, generally limestone. The low concentrations of ferrous iron are treated to a pH of 6 then put into a settling chamber while higher concentrations of pH 8-10 are put into an aeration tank for oxidation of ferrous into ferric, where the latter is easier to precipitate. The water then flows to the settling chamber and the heavy metal ions are precipitated out of solution (Akciil and Koldas, 2006; Pozo-Antonio et al., 2014).

Many studies have been done for treating acid mine drainage by chemical precipitation technique; the studies were both on small- and large-scale treatment. A sequential precipitation process was used to remove Fe, Mn, Cu, Al and Zn from AMD. The process first involved oxidation of ferrous iron to ferric iron using hydrogen which decreased the pH and then the ferric iron was precipitated out by adding sodium hydroxide. The precipitate was filtered, and the filtrate solution pH was adjusted to a higher value which precipitated out the heavy metals. After filtration of the precipitate, the filtrate solution was returned to the mixing chamber and the whole process was repeated while the pH value increased. The recovery of the metals was as follows: Fe, Cu, Al, Zn and Mn respectively with an increase in pH and reported to be 99 % (Macingova and Luptakova, 2012). In a study by Sampaio et al., 2009, Cu was continuously and selectively precipitated from water containing Cu and Zn using Na_2S in a continuously stirred tank reactor. The precipitation process yielded Cu concentrations below $0.3 \mu\text{g L}^{-1}$ (100 % recovery) from a feed solution containing 600 mg L^{-1} of Cu and Zn. The achieved 100 % recovery was due to the pH and strength of sulphide concentration being selective towards Cu.

The disadvantages of this treatment are that it produces large amounts of secondary waste in form of sludge which is difficult to treat, selective extraction is very difficult, precipitation of heavy metal ions is pH-dependent and if the lining of the streambed is coated with the neutralizing agent, the effectiveness of the agent decreases rapidly due to

coating by iron, calcium sulphate and biological growth, etc. (Akcil and Koldas, 2006; Kuyucak, 2002; Pozo-Antonio et al., 2014; Simate and Ndlovu, 2014). To overcome the disadvantages, selective metal precipitating agents have been developed that can chelate metal ions such as dipropyl di-thiophosphate or CH collectors, because the formed metal compounds have exceptionally low solubility and there is less production of metallic residue in comparison to production of sludge. Examples of the studies include removal of Pb, Cd, Cu and Hg by chelation with dipropyl di-thiophosphate. The study showed that 99.9 % of the metal ions were removed by the chelator, the treatment is pH independent and the chelator complex is stable, thus reducing the risk of polluting the environment (Ying and Fang, 2006).

Another study was on chelating precipitants termed the CH collectors. The precipitating agents are solid materials that bind heavy metals to their surface. They contain groups with hydrogen atoms easily replaceable such as carboxyl (-COOH), hydroxyl (-OH), thiol (-SH) or sulphonic (-SO₃H) groups along with functional groups of basic character, such as amino (-NH₂), (-NH-) or carbonyl where the analyte metal coordinates to form a four, five- or six-member ring. The unique property about the method is that ion channels are formed inside the material, where metal ions are collected from the solution. The method is advantageous because no additional steps are required, such as a separate precipitation step or adjustment to the pH of the solution for collection of heavy metal ions. The new method allowed for recovery of metals in exceptionally low concentrations, for example, the complete removal of uranium from samples collected in a Finnish mine. The study reported pre-treatment of the water samples to not be a requirement even though it contained high concentrations of other metals. The efficiency of the method was also tested on scandium with 98% recovery (Turhanen et al., 2015). The excessive cost of these metal precipitating reagents inhibits their use on an industrial and/or pilot scale, hence other methods that are cheaper and easier to handle have been explored such as ion exchange and adsorption.

B. Ion Exchange

Ion exchange is defined as an exchange of ions between a substrate and surrounding medium that the overall electroneutrality is maintained. The method is simple because it can be reversible, can be used to efficiently remove even trace amounts of heavy metal ions and be used in large volumes of effluents (Drahansky et al., 2016; Simate and

Ndlovu, 2014). Ion exchangers can either be inorganic or organic, where inorganic exchangers involve cation or anion exchangers and the toxic ions in solution will exchange with ions that are benign and abundant in the environment from the substrate; for example Ni ions in wastewater can be removed with a carboxylic cation exchanger in sodium form where Ni is taken up and sodium is released into the surrounding medium. Examples of inorganic exchangers include: zeolites, metal sulphides, etc. (Bashir et al., 2018). Organic exchangers are polymer-based exchangers that can either remove ions in wastewater without replacing them or replacing with non-toxic ones. They are mostly resins, which are completely insoluble mostly in aqueous and organic solutions, can resist physical degradation, stable at high temperatures and can be used over a wide pH range. The resin ion exchangers can be classified based on the functional groups of exchanging ions, such as strongly acidic exchangers e.g., sulphonate ($-\text{SO}_3\text{H}$), weakly acidic e.g., carboxylate ($-\text{COOH}$), strongly basic e.g., quaternary ammonium ($-\text{N}^+\text{R}_3$) and weakly basic e.g., tertiary ($-\text{N}^+\text{R}_2\text{H}$) and secondary ($-\text{N}^+\text{RH}_2$) amines should be mentioned. The strong acidic cation exchangers dissociate over a wide pH range and thus reach their maximum adsorption capacity. Meanwhile, weak acidic cation exchangers containing, for example, carboxylic functional groups reach the maximum adsorption capacity at $\text{pH} > 7.0$. There are amphoteric exchangers also called zwitterionic ion exchangers, that can exchange either cations or anions depending on the pH of the medium solution (Dąbrowski et al., 2004).

There are several studies done on ion exchangers in industrial wastewater to remove heavy metal ions: Budak, 2013, studied the removal of synthetic strong acid cation-exchanger resin called Amberlite 252 and Amberjet 1200 for removal of Cu(II) and Zn(II) in rinse water from the electroplating industries. The study showed that the Amberjet 1200 resin has a higher removal efficiency for Cu and Zn at 100% compared to the Amberlite 252 resin and the reason is because Amberjet 1200 is more strongly acidic with the sulphonic groups, SO_3H and can be used for recovery of Cu and Zn from electroplating industry rinse water waste (Budak, 2013). A natural ion exchanger that has been studied in detail involves zeolite and bentonite and many researchers have used zeolite to remove heavy metal ions in wastewater. For example; Pb from wastewater was removed using zeolite clinoptilolite and bentonite as exchangers at initial pH 4. The study reported a 100 % removal of Pb by bentonite and 55 % by clinoptilolite. It was observed that removal of Pb increased with increase in pH from 1-4. The high removal efficiencies

was due to the minerals being in powder form compared to granular because of increased surface area (Inglezakis et al., 2007). Wingenfelder et al., used natural zeolite to remove Fe, Cd, Pb and Zn from mine waters. Pb was the one removed efficiently at acidic and neutral solutions while Zn and Cd uptake decreased at low pH and high Fe concentration. When Ca concentrations in solution increased due to the exchange, elimination of Zn and Cd became poorer while removal of Pb remained the same. The zeolite was stable in acidic solutions (Wingenfelder et al., 2005). Zeolite was found to be a dual user as either an ion exchanger or an adsorbent depending on the conditions of heavy metal removal. While a wide number of techniques have been investigated and/or used for heavy metal removal including the two mentioned, adsorption has evolved as the most preferred method.

C. Adsorption

Adsorption is a surface phenomenon that involves mass transfer process in which the dissolved toxins in the liquid interact with a solid surface either via chemical or physical interaction. The advantages of using adsorption processes for heavy metal removal are that they provide flexibility in design and operation, can make small- or large-scale treatment plants, have the ability to produce high quality treated effluent because the process is highly efficient and because the process is sometimes reversible the adsorbents can be regenerated by suitable desorption processes i.e. the adsorption process thus becomes cost effective (Bashir et al., 2018). The adsorbent materials studied provide adequate surface area for adsorption, highly reactive and include a wide range of materials from biological adsorbents such as fungi or algae to agricultural wastes and industrial by-products. These materials include activated carbon, clay minerals, industrial wastes, microbial biomass, polymeric materials, etc. (Kütahyalı and Eral, 2004; M.K. Sureshkumar et al., 2010; Wu et al., 2001).

The most successful adsorption processes provide non-biased results, where the effects of various physical parameters are investigated to determine the optimum experimental conditions to have the maximum adsorption efficiency of an adsorbent. The parameters investigated are effect pH of the solution, concentration of heavy metal of interest, amount of adsorbent used per cycle, contact time between adsorbent and adsorbate, temperature of solution and effect of co-existing and competing ions in solution. The experimental data collected is used to describe and determine the best fit model for the

adsorption process. The models are used to determine the kinetics of adsorption to whether the mechanism of interaction is chemical or physical. The most used models are the pseudo first or second order kinetics which are further confirmed by isotherm models such as Langmuir and Freundlich isotherms (Dada et al., 2012; Largitte and Pasquier, 2016; Wu et al., 2001).

Studies have been done on the different adsorbents and effect of the physical parameters mentioned above. Activated carbon or charcoal is a highly porous carbon material that is synthesised by a combination of heat and pressure then followed by carbonization to increase porosity and surface area of the material for adsorption (Ghaedi et al., 2014). Several studies have been conducted with activated carbon or charcoal for adsorption of heavy metal ions from wastewater. Mellah et al. (2006), removed U(VI) using activated carbon and the optimum conditions for adsorption capacity of 28.30 mg g⁻¹ U (IV) were pH of 3 with 240 minutes of contact time and 100 mg L⁻¹ of initial uranium concentration. The pseudo-second order kinetic model and Freundlich isotherm model best described the mechanism of adsorption to be a chemical interaction. Activated carbons have been used to remove arsenic species, Mohan et al., used activated carbons from coconut husk to remove As (III) and As (V) from wastewater. The adsorption capacity was found to be 29.9 and 30.48 mg g⁻¹ for As (III) and As (V) respectively at optimum experimental conditions of pH 6.4 and 7.5 at 80 mg L⁻¹ initial concentration of arsenic species (Mohan and Pittman, 2007).

Biological biomass and polymer materials are also used such as Kowanga and colleagues, using *Moringa oleifera* seed powder for removal of Cu (II) and Pb (II) from pharmaceutical effluents. The results showed that the optimum pH for biosorption of Cu (II) was 6.5 while that of Pb (II) was 5.5. Contact time for Cu (II) was observed to occur after 30 min while that of Pb (II) occurred after 40 min. initial concentration at 100 mg L⁻¹ for Cu (II) and 50 mg L⁻¹ for Pb (II) with removal percentage of 52.8 % and 58.3 % for Cu (II) and Pb (II) respectively (Kowanga et al., 2016). Thiolated cross-linked polyethylenimine was used for selective removal of mercury. The synthesized polymer exhibited high selectivity towards Hg(II) with 97 % removal efficiency at pH 3 and contact time of 70 minutes at 40 mg L⁻¹ initial concentration of Hg(II). The removal was efficient even in the presence of competing ions such as Se, Zn, Ni, etc. (Saad and Cukrowska, 2013).

The adsorption process was improved by functionalizing the adsorbent materials with functional groups that are selective towards certain heavy metal ions and improve the

surface area and porosity properties of the material. For example, Saad et al., functionalized polyethylenimine with thiol-based functional groups to make it insoluble and selective towards mercury adsorption (Saad and Cukrowska, 2013), rice husk modified with phosphoric acid for adsorption of Zn (II) (Dada et al., 2012), activated carbon functionalized with iron to remove As (III) and As (V) (Mohan and Pittman, 2007).

The disadvantages of adsorption are the decreased rate in adsorption due to intraparticle diffusion and available capacity. At low concentrations there are difficulties in heavy metal removal and some powder adsorbents are insoluble and also some adsorbents are expensive such as commercial coal-based activated carbon (Bashir et al., 2018; Savage and Diallo, 2005; Simate and Ndlovu, 2014). The discovery of nanomaterials as adsorbents helped circumvent the drawbacks by solving the high intraparticle diffusion resistance (Hu et al., 2006) and generate low-cost adsorbents.

2.5 Adsorption techniques using nanoparticles for AMD remediation

Nanomaterials used as adsorbents for water treatment are porous, so they provide large surface areas compared to bulk particles, have small diffusion resistance and highly reactive. Nanomaterials are easily modified by addition of functional groups to increase selectivity i.e. affinity towards specific metal ions (Bashir et al., 2018; Simate and Ndlovu, 2014). There are three main classes of nanoscale materials that are being studied as functional materials for AMD treatment: 1) metal-containing nanoparticles, 2) carbonaceous nanomaterials and 3) zeolites. For each class, examples of how the nanoparticles were used as adsorbents for removal of heavy metals are described.

A. Metal-containing nanoparticles

Metal- or metal oxide based nanoparticles are nanoparticles made metals like Fe_2O_3 , MnO_2 , TiO_2 , ZnO , etc. have high number of active sites, large surface area and increased magnetic properties because they can remove heavy metals from solution via magnetic field and the adsorbent can be recycled. Hu et al. (2006) performed adsorption studies on selective removal of Cr (VI), Cu (II) and Ni (II) from wastewater using nanoscale maghemite ($\gamma\text{-Fe}_3\text{O}_2$) synthesised using a sol-gel method. The adsorption efficiency was found to be pH dependent, where Cr, Cu and Ni had optimum removal efficiency at pH 2.5, 6.5 and 8.5 respectively. It was also found in the regeneration and re-adsorption studies that the maghemite nanoparticles can be reused. A more recent study on

maghemite nanoparticles was on removal of Cu (II), Mn (II) and U(VI) ions from acid mine drainage. The removal efficiencies were found to be maximum at pH 9 where it was 86%, 62% and 77% for Cu, Mn and U respectively. The capacity of the nanomaterial was tested on ground and surface water and up to 54 % was the removal efficiency for the heavy metals and that showed the maghemite nanoparticles are efficient in remediation of AMD-contaminated waters (Etale et al., 2016).

B. Zeolites

Zeolites are effective, ion-exchange sorbents. The sorbents can be modified to be anion-exchangers or cation-exchangers for heavy metal ions such as (Nekhunguni, Tavengwa and Tutu, 2017a, 2017b) modifying zeolite with ferric oxide for removal of As (V) and U(VI), where maximum removal efficiency was > 99% and 60.8% for As and U respectively at pH 2.23. (Inglezakis et al., 2007) removed Pb (II) up 55% with clinoptilolite and bentonite at pH 4.0.

C. Carbonaceous nanomaterials

For carbonaceous nanomaterials, the most well studied adsorbents are carbon nanotubes which were first developed in 1991 (Iijima, 1991). Metal ions adsorbed onto CNTs appear to be via electrostatic, sorption-precipitation and chemical interaction with the functional groups. Carbon nanotubes are easily modified depending on mode and type of adsorption like being oxidised by HNO₃, NaClO and KMnO₄ to improve adsorption efficiency (Fu and Wang, 2011a). Li et al. (2010) had maximum removal of 69.9% for Cu (II) with CNTs modified with calcium alginate at pH 2.1 and 98% removal of Cr (VI) at 100 µg L⁻¹ concentration was obtained with functionalised multiwalled-CNTs at pH 2.05 by (Pillay et al., 2009). The removal of heavy metals from AMD using the technologies mentioned above has several disadvantages which include pH dependence meaning mostly the optimum efficient removal of a mixture of heavy metals cannot be achieved at a single pH level and/or contamination of the remediated waters by nanoparticles creating another water pollution problem. Therefore, these led to exploration of other methods that are not dependent on pH of the aqueous media and immobilisation of the nanoparticles and that include membrane technology (Kefeni et al., 2017; Simate and Ndlovu, 2014).

2.6 Membrane technology

Membrane technology has shown great promise for heavy metal removal because it is highly efficient, reduces effluent discharge, easy to operate and saves space (Abdullah et al., 2019). However, some membrane technology processes require additional energy for operation and sometimes the membrane is not selective enough to reject specific contaminants and that eventually might lead to fouling of the membrane (Fu and Wang, 2011; Kefeni et al., 2017).

The principle of membrane separation involves two mechanisms; size exclusion and ion adsorption as illustrated in Figure 2.1 below. In size exclusion, heavy metal ions are removed from wastewater due to the radius of the metal i.e. they cannot pass through the membrane because of small pore size relative to the radius of the metal. Ion adsorption involves an interaction between the metal ion and the functional groups on the membrane. It can be physical, where there is electrostatic binding between the charged metal ion and functional group or chemical where a bond is formed by coordination to the metal ion or electron donation from an electron-rich functional group to the cationic metal (Liu and Xu, 2016a).

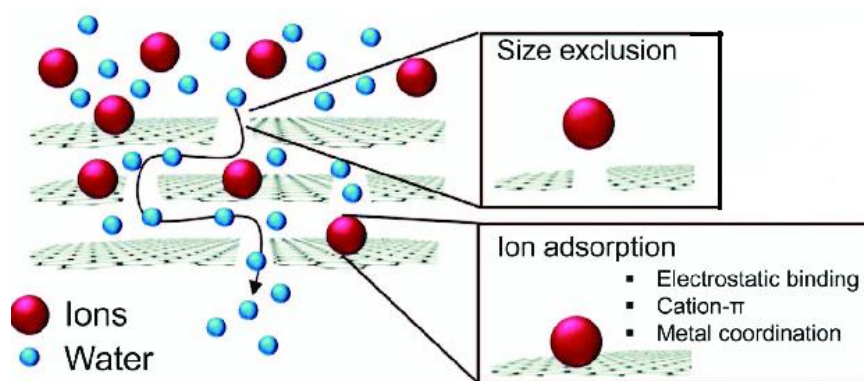


Figure 2.1: The principle of membrane separation. Reproduced with permission from (Liu and Xu, 2016a). Copyright 2020, Elsevier Science Ltd

The types of membranes used for separation are categorised into four classes based on their mode of performance: Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse osmosis (RO). Figure 2.2 below shows the characteristics of each membrane type.

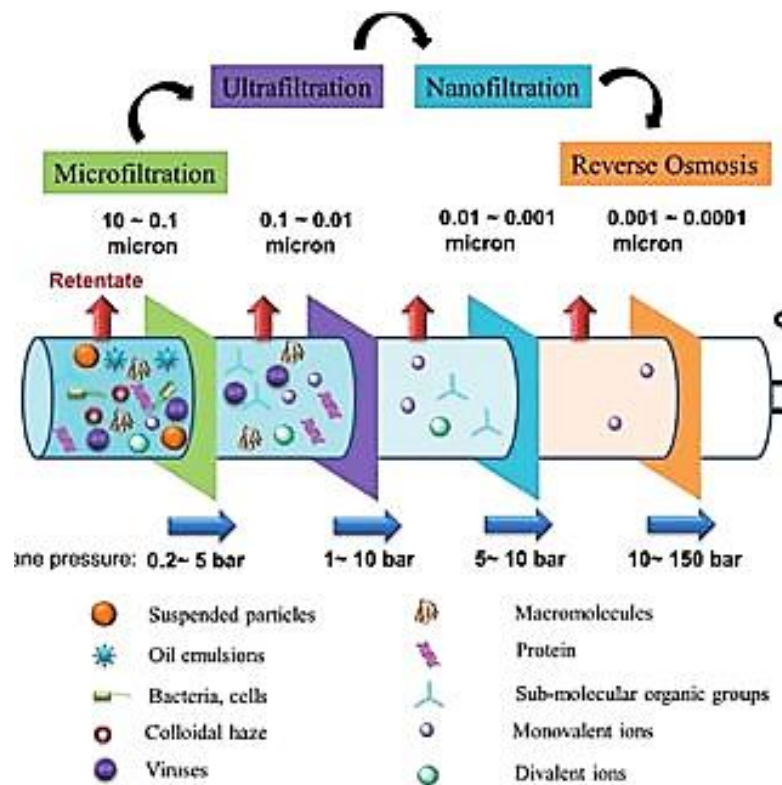


Figure 2.2: Pressure driven membrane processes and the particles rejected from waste water treatment. Reproduced with permission from (Liao et al., 2018). Copyright 2020, Elsevier Science Ltd.

A. Microfiltration and ultrafiltration membrane process

Microfiltration membranes have pore sizes ranging between 5-0.1 μm . thus, only suspended solids are rejected while proteins and other molecules pass through. This membrane is not suitable for removal of heavy metals or micro-organisms hence it is only used for pre-treatment of feed solution. Ultrafiltration membranes have pore sizes in the range of 0.1-0.01 μm and a low transmembrane pressure. They are thus able to reject high molecular weight species such as proteins and suspended solids, while allowing low molecular weight contents like mono- and di-saccharides, salts, amino acids, organics and hydrated metal ions to pass through. To improve the removal efficiency of metals ions by ultrafiltration membranes, polymer-enhanced ultrafiltration membranes (PEUF) were proposed (Fu and Wang, 2011). In PEUFs, water-soluble polymers complex to metallic ions and form macromolecules that have a higher molecular weight than the molecular weight cut-off of the membrane (Fu and Wang, 2011). The polymer-metal complexes are retained when pressure is applied on the ultrafiltration membrane. The polymeric agent can be reused after treatment (Fu and

Wang, 2011). Suitable polymers that can selectively complex with metal ions are polyacrylic acid, polyethyleneimine, humic acid and diethylamino ethyl cellulose, which are selective and have low energy requirements (Fu and Wang, 2011). For instance, Barakat and Schmidt, (2010) used polyethersulphone membrane with carboxyl methyl cellulose as complexing agents to remove Cu (II), Ni (II) and Cr (III) at pH 7. They reported removal efficiencies of up to 97.6%, 99% and 99% for Cu, Ni and Cr respectively. Aroua et al., (2007) investigated the removal of Cr (III) and Cr (VI) ions with chitosan, pectin and polyethyleneimine with almost 100% removal at pH greater than 7.

Table 2.2: Types of polymer-enhanced ultrafiltration membranes and their application in the adsorption of metal ions

Membrane type	Target metals	Experimental conditions	Removal efficiency (%)	Reference
Polyethersulfone (Carboxyl methyl cellulose)	Cu	10 mg L ⁻¹ pH 7	97.6	Barakat and Schmidt, 2010
	Cr(VI)		99	
	Ni		99	
AMICON 8400 (Chitosan, Pectin and Polyethyleneimine)	Cr(III)	5 mg L ⁻¹ pH 6-7	82	Aroua, Zuki and Sulaiman, 2007
	Cr (VI)	50 mg L ⁻¹ pH 5-6	100	
Polyethersulfone (polyethyleneimine)	Cu	50 mg L ⁻¹ pH > 6,	94	Molinari et al., 2008
	Ni	50 mg L ⁻¹ pH > 8	100	
Ceramic (Poly (acrylic acid) sodium)	Cu	160 mg L ⁻¹ pH 5.5	99.5	Camarillo and Llanos, 2010
Polysulfone (Poly (ammonium acrylate))	Cd	112 mg L ⁻¹ pH 6.32 2 bar	99	Ennigrou et al., 2009
Cellulose (Humic acid)	Co	pH 6 2.7 g L ⁻¹ 2 bar	95	Kim et al., 2005
Cellulose Acetate (Poly(diallyl dimethyl ammonium chloride))	As (V)	100 µg L ⁻¹ pH 6.5-8.5	99.9	Pookrod et al., 2010
Polyethersulfone (Poly(acrylic acid))	Cu	10 mol L ⁻¹	93	Ennigrou et al., 2015
	Zn	2.8 Bar	70	
	Ni	pH > 5	80	
Polyethersulfone	Hg	2.9 bar 11 mg L ⁻¹	< 90	Huang et al., 2016

(Polyvinyl amine
and poly (acrylic
acid))

()* Complexing agents

A. Nanofiltration membrane process

Nanofiltration (NF) membranes with pore sizes ranging from 10-1 nm, reject uncharged and dissolved materials based on size, multi-valent ions such as sulphates and phosphates via electrostatic repulsion, and heavy metal ions via electrostatic attraction and size (Wagner, 2001). The membrane allows single charged ions like Na^+ and Cl^- to pass but that is limited to the conditions of the feed solution and whether Na is complexed to a single- or multivalent anion because a salt rejection of up to 50% can be achieved if Na is associated with sulphate ions but 5% if it is complexed to chloride ions (Abhang et al., 2013). The membrane is known for high efficiency of pollutant removal with low energy consumptions.

Examples of nanofiltration membranes used for wastewater treatment: the removal of pentavalent arsenic from synthetic water by spiral wound NF membrane was investigated. The results showed that at higher pH and decreased temperature and feed concentration led to higher As (V) removal. The transmembrane pressure had little effect on removal of As (V) but showed that permeate flux increased when pressure increased. The maximum removal efficiency of As (V) was at pH 8 at $100 \mu\text{g L}^{-1}$. It was found out that the feed concentration played an important role in production of permeate stream that was in agreement with WHO limits imposed because at a high feed concentration the membranes fouled rapidly with no reversibility (Figoli, et al., 2010).

Thin film composite polyamide nanofiltration membranes were applied for the removal of nickel ions from aqueous wastewater. The maximum rejection was found to be 92% for pH > 6 and 98% for pH > 8. Murthy and Chaudhari (2008) also investigated the binary heavy metals (Cd and Ni) separation and found rejection of Cd and Ni ions to be 83% and 99% respectively (Murthy and Chaudhari, 2008).

Zhang et al. (2017) investigated the rejection of Cu, Pb, Cd and Cr by cross-linked graphene oxide composite membranes at pH 7. The results showed decreasing in the metal ion removal with increasing interlayer spacing between the graphene oxide sheets. This suggests that physical sieving had a limited effect on rejection because ion with

smaller radii pass through. They also found that with the introduction of sophorone diisocyanate, the oxygen-containing functional groups on the surface of graphene oxide were consumed, resulting in lower rejection due to reduction in the number of adsorptive sites on the graphene sheets. However, it was suggested that the rejection rate can be improved by increasing the pH of the feed solution.

Gherasim, Cuhorka and Mikulasek, (2013) investigated the rejection of Pb (II) in single and binary (Pb and Cd) solutions using polyamide nanofiltration membrane. At pH 5.7, rejection of Pb from single solutions was found to be 99% and 98% when Cd (II) was present (binary solution). Metal ion rejection was attributed to both size exclusion and electrostatic interaction because the membrane was negatively charged.

In yet another study, functionalisation of halloysites nanotubes membrane with APTES (A-HNTs) increased the rejection of Cu (II), Cr (VI) and Cd (II) from 47.9 to 96, 44.2 to 86.1 and 52.3 to 84.6% respectively. APTES increased the number of active sites on the membrane because amine groups were introduced to provide adsorption sites for metal chelation. Maximum rejection capacity was at pH 5.5 and 5 mg L initial feed concentration. The pore size was determined to be at 2 nm which is for nanofiltration membranes (Zheng et al., 2016).

Zhu et al. (2015) investigated the effect of poly (amidoamine) dendrimer (PAMAM) modification on the removal of metals ions by a hollow fibre membrane. Rejections of Pb, Cd, Cu, Ni and As were recorded at ~99% at pH 7 suggesting functionalization with PAMAM increased rejection by decreasing membrane pore size and having electrostatic repulsion (via the positively charged NH_2 groups). A similar strategy has also been pursued by incorporating metal complexing polymers e.g. bovine serum albumin (BSA) in nanofiltration membranes (Nedzarek et al., 2015). The results showed 93%, 93% and 99% rejection rates of Pb, Cd and Cu respectively, at pH 9. However, the addition of BSA increased membrane fouling.

Removal of Pb, Cd and Cr from water was investigated by covalently grafting 4-amino benzoic acid (ABA) on the surface of a PVC membrane to enhance hydrophilicity and metal rejection. At acidic conditions, nearly 100 % rejection was obtained for all metals. In comparison, the commercial NF membranes only recorded 70–85% rejection rates because they were unmodified. The presence of the $-\text{NH}$ and $-\text{COOH}$ functional groups from ABA contributed to the increased rejection (Nayak et al., 2017).

Recently, (Jia et al., 2019) developed a polyacrylonitrile thin film composite nanofiltration membrane, where the sulfonated polyarylene ether benzonitrile (SPEB) was incorporated into the polyamide layer. The SPEB increased hydrophilicity and smoothness of the membrane while decreasing pore size from 8 to 1.42 nm, resulting in a higher permeability. A rejection of over 93 % towards Pb, Ni and Cd was achieved over a wide acidic pH range. This work provided insightful information on upgrading current nanofiltration membranes for heavy metal removal in harsh acidic conditions.

Table 2.3: Selected nanofiltration studies showing different membranes used, target metals and removal efficiencies.

Membrane Type	Target metals	Experimental conditions	Removal efficiency (%)	References
Commercial NF90 and NF30	As ⁵⁺	pH 8 100 µg L ⁻¹ 6 bar	91-99	Figoli et al., 2010
Thin film composite	Ni	pH 6-8 5 and 250 mg L ⁻¹	92 and 98 ^a	Murthy and Chaudhari, 2013
	Cd	15 atm	82.9 and 98.9 ^b	
Cross-linked graphene oxide composite	Cu, Pb, Cd and Cr	pH 7	< 90	Zhang et al., 2017
Polyamide thin film composite	Pb and Cd	pH 5.7	99 and 98	Gherasim et al., 2013
PVDF/APTES functionalised with halloysites nanotubes	Cu	10 mM 1-3 bar	96	Zheng et al., 2016
Poly (amidoamine) dendrimer (PAMAM) grafted PES	Pb, Cd, Cu, Ni and As ³⁺	pH 7	~ 99	Zhu et al., 2015
BSA complexing agent	Pb, Cd and Cu	pH 9	93, 93 and 99	Nedzarek et al., 2015
PVC covalently grafted with 4-amino benzoic acid (ABA)	Pb, Cd, and Cr ⁶⁺	pH < 7	~ 100 ^c and 70-85 ^d	Nayak et al., 2017
TFN membrane with P[MPC-co-AEMA] in polyamide layer	As ⁵⁺	1000 mg L ⁻¹ 10 bar	98	He et al., 2018
	Se	pH 7.5-8.6	99.8	
Sulfonated polyarylene ether benzonitrile in polyacrylonitrile TFN	Cd	1000 mg L ⁻¹	95	Jia et al., 2019
	Ni	6 bar	97	
	Pb	pH 2-5	96	

^a Ni only in solution, ^b Binary mixture of Ni and Cd, ^c Lab-fabricated membrane, ^d Commercial membrane

B. Reverse and Forward osmosis membranes

Reverse osmosis (RO) is the tightest possible membrane type for liquid-liquid separation. These membranes allow only water molecules through, rejecting all dissolved and suspended materials including monovalent ions. These membranes account for over 20% of all desalination membranes globally. Compared to nanofiltration membranes, they are denser, do not have definite pores and require pressure to force water against the concentration gradient. It has up to 99.9% rejection efficiency of heavy metal removal, but extensive energy requirements are the major drawback of RO membranes (Fu and Wang, 2011). RO membranes have been used for desalination and removal of heavy metal ions from wastewater. Ozaki, Sharma and Saktaywin (2002) found that the rejection of Cu, Cr and Ni from electroplating wastewater to be > 98.8% using low-pressure RO membranes. This study also showed that pH played a role in the rejection because at pH close to the isoelectric point, there was high flux but low rejection due to the repulsion forces between membrane surface and metal ions being weak. The optimum pH was found to be 7-9.

RO membranes have also been tested from a bioreactor (Dialynas and Diamadopoulos, 2009). Approximately 100% of Pb and Ni ions were removed from solution, while removal of Cr and Cu was at 89% and 49%, respectively. The low removal of Cu was linked to its relatively high concentration in the feed solution.

Malamis et al. (2012) used a combination of membrane bioreactor and reverse osmosis membranes to investigate the removal of Pb, Ni, Cu and Cr and the results showed complete removal of the metal ions. The drawback of the study was that the rate of fouling was increased because some of the heavy metals deposited on the membrane surface and interior of bioreactor. Nevertheless, addition of EDTA to chelate Cu and Ni and prevent them from diffusing into the membrane may offer a means to overcome this challenge (Mohsen-Nia, Montazeri and Modarress, 2007).

Comparing RO and NF membranes for treating industrial wastewater at different operating pressures shows that while RO membranes have higher efficiencies for removal of heavy metal ions (> 97% rejection rate), they have a much lower water flux compared to NF membranes. RO membranes are therefore, preferable in treating water to be used for drinking and NF for industrial wastewater treatment (Feini et al., 2008).

Since the active layer of a RO membrane is very dense, almost all the studies have reported high rejection rates of every heavy metal type but considering the high operating pressure and energy required, heavy metal ion removal by these types of membranes is not preferred as other membrane types can also offer similar removal efficiencies (Abdullah et al., 2019).

Forward osmosis (FO) technology has received increasing attention for water treatment because unlike reverse osmosis, external pressure is not required as it uses the osmotic pressure difference between feed and draw solution. It is energy-efficient, applicable to a wide range of contaminants and has reduced membrane fouling, hence it is more preferred for heavy metal-polluted wastewater treatment.

Cui et al. (2014) compared the efficiency of a commercial and that of a lab-fabricated thin film composite reverse osmosis membrane for rejection of Cr, Pb, As, Cd, Cu and Hg ions. It was found that the lab fabricated TFC membrane tested under the FO process had greater rejection for all six ions. The high rejections to heavy metal ions proved to be beneficial to the regeneration of clean draw solution.

Table 2.4: A summary of studies using RO membranes for removal of different target metals from aqueous solution

Membrane type	Target metals	Experimental conditions	Removal efficiency (%)	References
RO membrane	Cu, Cr and Ni	pH 7-9	< 98.75	Ozaki et al., 2002
Membrane bioreactor	Pb and Ni	Not provided	100	Dialynas and Diamadopoulos, 2009, Malamis et al., 2012
	Cr ⁶⁺		89	
	Cu		49	
EDTA as chelate in TFC	Cu and Ni	N/A	85 and 90	Mohsen-Nia et al., 2007
Combination of RO and NF	Cu, Cr ³⁺ , Ni, As ³⁺	35 bar	97	Feini et al., 2008
Lab-fabricated thin film composite (Matrimid substrate)	Cr, Pb, As, Cd, Cu and Hg	2000 mg L ⁻¹	< 99	Cui et al., 2014
PEI and sodium alginate on polydopamine-functionalised polyvinylidene fluoride	Pb, Ni, Cd, Cu and Zn	pH 4 1 g L ⁻¹	> 99	Liu et al., 2017
Commercial thin film composite	Hg	1 mg L ⁻¹ pH 5-8	> 98	Wu et al., 2016
		1 bar		
Polydopamine modified zeolitic imidazolate TFN membrane	Cu, Pb and Ni	pH 6.5 1000 mg L ⁻¹ 5 bar	> 96	Qiu and He, 2019
Thin film inorganic membrane (silica)	Cd, Cu, Pb and Zn	200 mg L ⁻¹ pH 4.5	~ 94	You et al., 2017

C. Nanocomposite membranes

Nanocomposite membranes are simply advanced membranes that contain nanomaterials in the polymer matrices. They are used in several applications such as fuel cells, lithium ion batteries and/or water treatment because they are eco-friendly, low-cost and energy efficient (Bassyouni et al., 2019). Polymer matrix nanocomposite membranes are also ideal for wastewater treatment because they possess- chemical and mechanical stability, improved water permeability, and can be fabricated with selectivity for particular contaminants and improved antifouling properties (Bassyouni et al., 2019; Nasir et al., 2019).

Nanocomposite membranes can be classified into four groups based on the location of the nanomaterials and structure of membrane: 1) conventional nanocomposite; 2) surface located nanocomposite; 3) thin film composite with nanocomposite substrate; and 4) Thin film composite with nanocomposite thin layer.

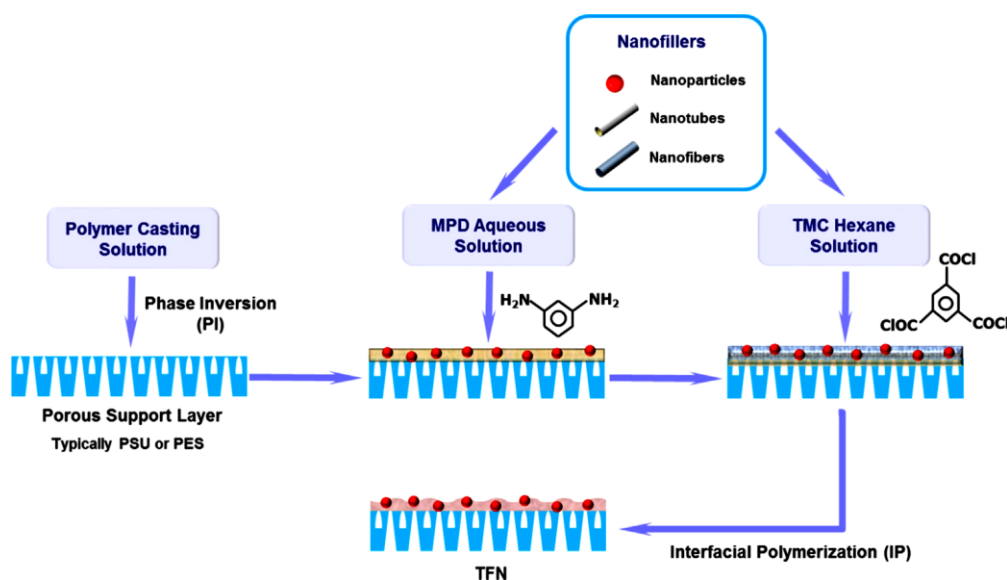


Figure 2.3: Fabrication of thin film nanocomposite membrane through interfacial polymerisation. Reproduced with permission from (Yin and Deng, 2015). Copyright 2020, Elsevier science Ltd.

2.10 Conventional nanocomposite membranes

Conventional nanocomposite membranes are membranes where nanomaterials are dispersed in the polymer matrix. They are used mainly in microfiltration and ultrafiltration processes. The membranes are fabricated by mixing the polymer, solvent and nanomaterial before the phase inversion, blending or electrospinning methods. This

type of membrane is well reported in the literature (Crock et al., 2013; Yin and Deng, 2015).

2.6.4.2 Surface located nanocomposite membranes

As the name suggests, surface located nanocomposite membranes have the nanomaterials localised at their surfaces, which results in their surface properties such as hydrophilicity, pore size and/or roughness being modified. Preparation of these membranes can be by various processes, example, self-assembly where nanoparticles interact via H-bonding and coordination or coating/deposition where dip-coating or filtration-deposition are applied to place nanomaterials on the surface. Incorporation of the nanomaterials on the surface of the membrane does not affect the intrinsic structure of the polymer (Yin and Deng, 2015).

2.6.4.3 Thin film composite with nanocomposite substrate

This third class of nanocomposite membranes have nanomaterials embedded in the polymer substrate, and an ultra-thin barrier layer atop this substrate. The membranes have higher water permeability because of the hydrophilic nanoparticles, mechanical stability, less flux decline and could mitigate internal concentration polarization i.e. there won't be a build-up of concentration gradient on both sides of the membrane. Fabrication of these membranes involves two steps, phase inversion to generate the substrate, and interfacial polymerization to fabricate the thin film layer (Sirinupong et al., 2018)

All the three classes of nanocomposite membranes have drawbacks in terms of the difficulty to fabricate a membrane with a definite membrane technology process. The nanomaterials embedded have the potential to leach out because their interaction is based on electrostatic attraction between polymer and nanoparticle. Incorporating nanomaterials directly into the polymer has the potential to affect the membrane's intrinsic properties such as porosity and hydrophilicity and there is difficulty in overcoming the trade-off relationship between permeability and selectivity (Yin and Deng, 2015). Even though some of the disadvantages affect the thin film nanocomposite membranes, they have been reported to be better than all the other three (Nasir et al., 2019).

2.6.4.4 Thin film nanocomposite membranes

In thin film nanocomposite (TFN) membranes, the nanomaterials are embedded in an ultra-thin barrier layer, commonly made of polyamide, atop a porous substrate (Figure 2.3). The common fabrication methods are the phase inversion and in-situ interfacial polymerization. The phase inversion method involves a mixing process that forms a uniform solution between a polymer and nanomaterial that solidifies and precipitates after immersion in non-solvent coagulation bath (Nasir et al., 2019). Interfacial polymerization is then done to form the thin film layer. In this process, the polyamide layer is formed when the substrate is immersed in the aqueous m-phenylenediamine solution then immersed in the organic trimesoyl chloride. The polymerization occurs at the interphase of the two monomers (Figure 2.3). The nanomaterials can be incorporated in either the aqueous or organic phase prior to the polymerization process (Nasir et al., 2019).

The surface located nanomaterials improve the membrane's performance by increasing hydrophilicity and/or permeability, fouling resistance, and selectivity. Thin film nanocomposite membranes have numerous applications such as in fuel cells or sensors but have also attracted interest in water purification and wastewater treatment. They have been proven to be better at wastewater treatment. However, a balance needs to be struck between permeability and selectivity. The polyamide thin film layer controls the membrane's permeability, fouling resistance and selectivity because of the nanomaterials embedded in the layer. Increasing the loading of nanomaterials would therefore increase the hydrophilicity of the membrane and decrease the water contact angle, that helps facilitate water solubilisation and diffusion, thus improving membrane's permeability. However, too high a loading of nanomaterials can also result in agglomeration and pore blockage, thus reducing permeability.

Some of the studies include adding nanomaterials like zeolite, mesoporous silica or multi-walled carbon nanotubes (Amini et al., 2013; Vatanpour et al., 2017; Wu et al., 2013b, 2013a). Adding or increasing hydrophilic nanoparticles can also sometimes affect the selectivity of the membrane. Fortunately, the trade-off relationship doesn't apply to antifouling properties. Anti-biofouling properties require incorporation of biocidal nanomaterials such as silver nanoparticles which prevent bacterial growth on the

membrane surface by disrupting the metabolism and replication processes of pathogens (Faria et al., 2017; Park et al., 2016).

Studies have been done on removal of heavy metal ions by TFN membranes and that include Di et al. (2015) investigating the removal of Cr (III) using TFN membranes with cerium oxide carbon nanotubes incorporated while, Nayak et al. (2015) used polyvinyl chloride thin film nanocomposite membrane for complete removal of Cr (VI). The approach to this study was to reduce Cr (VI) to Cr (III) before adsorption and the medium was maintained at pH 4 to facilitate the formation of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$.

Anirudhan and Ramachandran, (2015) synthesised a TFN membrane with polyacrylonitrile and bentonite functionalised with amidoxime for removal of Cu, Zn and Cd at pH 6 and initial concentration of 25 mg L^{-1} . The maximum adsorption efficiencies observed were 99.8, 98.9 and 97.4% for Cu, Zn and Cd respectively. The study showed that the mechanism of removal is first ion exchange followed by metal chelation with amidoxime.

A humic acid-immobilised amine modified polyacrylamide TFN membrane was fabricated and tested for adsorption of Cu, Zn and Co ions. At initial concentration of 25 mg L^{-1} , the amounts of Cu, Zn and Co adsorbed were 11.47, 11.15 and 10.98 mg g^{-1} respectively. When the initial concentration was increased to 100 mg L^{-1} , the adsorption capacities tripled (Anirudhan and Suchithra, 2010). In another study a thin film nanocomposite membrane incorporated with zeolite for removal of Pb was investigated. The results showed adsorption capacity of 66.32 mg g^{-1} at an initial concentration of 200 mg L^{-1} . The Pb uptake was attributed to the interaction between the metal and the silanol (Si-OH) group (Msaadi et al., 2017).

Recently, (Jia et al., 2019) developed a polyacrylonitrile thin film composite membrane, where the sulfonated polyarylene ether benzonitrile (SPEB) was incorporated into the polyamide layer. The SPEB increased hydrophilicity and smoothness of the membrane while decreasing pore size from 8 to 1.42 nm, resulting in a higher permeability. A rejection of over 93% towards Pb, Ni and Cd was achieved over a wide acidic pH range. This work provided insightful information on upgrading current nanofiltration membranes for heavy metal removal in harsh acidic conditions.

Qiu and He (2019) synthesised a polydopamine modified zeolitic imidazolate TFN membrane for removal of Cu, Pb and Ni at pH 6.5. The removal efficiency was > 96%

for all the three ions. Wang and Wang, (2010) fabricated a chitosan modified thin film nanocomposite membrane for removal of Hg ions and reported a maximum adsorption capacity of 785.2 mg g⁻¹.

The use of magnetic nanoparticles incorporated in TFN membranes has also been investigated. Magnetite (Fe₃O₄) has been used in TFN for adsorption of Cu and Pb. Adsorption capacities of 158.7 and 301 mg g⁻¹ respectively, were reported at pH 5 (Mahdavinia et al., 2016; Msaasi et al., 2017). A TFN membrane modified with zerovalent iron titanium dioxide nanoparticles were used for the removal of Cr (VI) with removal efficiency of 99.49% at 5 bar. The study showed that Cr (VI) removal decreased with increasing pH and feed concentration (Kazemi et al., 2018). Bisphosphonate-modified magnetite particles have been incorporated in thin film nanocomposite membrane for removal of uranium dioxide UO₂²⁺ from wastewater (Wang et al., 2016).

Finally, it is important to note that TFN membranes have some challenges which include the uneven distribution of nanoparticles in the polyamide layer, and the possibility that they can leach out during membrane use. One way to mitigate against nanomaterial agglomeration is by incorporating functional groups on the nanomaterials to form stable, uniform dispersions, thus minimising precipitation in either the aqueous or organic solvent during polymerisation. In addition, material loss can be controlled by covalently binding the thin film layer to the polyamide layer (Bassyouni et al., 2019; Lau et al., 2015).

Table 2.5: Summary of studies involving the use of thin film nanocomposite membranes for removal of metal ions

Nanomaterials embedded on the polyamide layer	Target metals	Experimental conditions	Adsorption capacity (mg g ⁻¹), Removal efficiency (%)	Reference
Cerium oxide modified carbon nanotube	Cr	Not provided	90	Di et al., 2015
Bentonite	U	pH 3-5	21.3	Simsek and Ulusoy, 2012
	Pb	50-100 mg L ⁻¹	10	
Fe ₃ O ₄	Cu	pH 5	159	Mahdavinia et al., 2016; Msaasi et al., 2017
	Pb	25 mg L ⁻¹ .	301	
Bentonite functionalised with amidoxime	Cu	pH 6 25 mg L ⁻¹ .	99.8	Anirudhan and Ramachandran, 2015
	Zn		98.9	
	Cd		97.4	
Amine functionalised humic acid	Cu	25 mg L ⁻¹	11.47	Anirudhan and Suchithra, 2010
			11.15	
	Zn		10.98	
	Co			
Zeolite	Pb	200 mg L ⁻¹ 10 bar	66.32	Msaadi et al., 2017.
Chitosan	Hg	100 µg L ⁻¹ 5 bar	785.2	Wang and Wang, 2010
Bisphosphonate-modified magnetite particles	U	pH 5-8 10 bar	93	Wang et al., 2016
Polydopamine modified zeolitic	Cu, Pb and Ni	pH 6.5 1000 mg L ⁻¹	> 96	Qiu and He, 2019

imidazolate TFN membrane		5 bar		
Sulfonated polyarylene ether benzonitrile	Cd, Ni and Pb	1000 mg L ⁻¹	< 94	Jia et al., 2019
		6 bar pH 2-5		
Iron titanium dioxide	Cr (VI)	5 bar	99.49	Kazemi et al., 2018

2.11 Thin film nanocomposite (TFN) membranes with graphene oxide

Graphene oxide (GO) is a two-dimensional single layer material consisting of sp²-hybridized carbon atoms in a hexagonal honeycomb lattice (Figure 2.4). It contains strongly oxygenated groups such as epoxide, carboxyl, hydroxyl and ketones on the surface and is a highly hydrophilic layered material. In addition, it can be easily exfoliated in water to yield very stable dispersions and, has a theoretical surface area of about 2600 m² g⁻¹ and high mechanical strength of >1060 Gpa. It is a non-toxic and biodegradable material that is easily obtained in bulk quantities from cheap natural graphite.

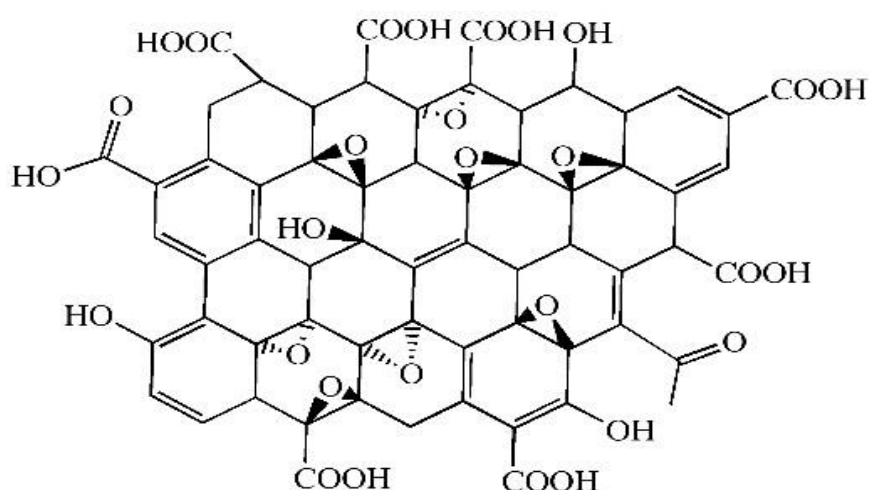


Figure 2.4: Structure of graphene oxide showing its different reactive groups (Wilkinson, 2016)

Due to its hydrophilic properties, graphene oxide has attracted attention for several biological and electronics applications, as well as wastewater treatment. Examples

include adsorption of fluoride ions, heavy metals such as Hg, As, Pb, Cu, etc. (Awad et al., 2020; Tang et al., 2016; White et al., 2018). Recently, GO has been widely used in polymeric nanocomposite membranes for reverse osmosis and nanofiltration processes to enhance hydrophilicity thus increase water flux, and act as an antifouling agent. Because of electron dense carbons and oxygenated functional groups, graphene oxide can also be easily functionalized in order to increase its selectivity for contaminants. Some of the functionalisation of graphene oxide include adding metal oxides such as Fe-Mn to GO for Hg(II) removal (Awad et al., 2020), triethoxysilane to GO for removal of Cr (VI) (Tang et al., 2016), carboxylic acid groups to GO for Cu (II) and Hg(II) removal (White et al., 2018), zeolite in GO composite for As (III) removal (Amini et al., 2013). In this study L-Cysteine and phosphate have been used to functionalise GO for removal of As (III), U(VI) and Hg(II).

L-cysteine is an amino acid that has many applications in medicine and wastewater treatment because of its high affinity towards metal ion chelation. This amino acid is easily accessible, cost effective and non-toxic to the environment. Following the Pearson's hard-soft acid-base interaction principle, the β -thiol groups (-S-H) on Cysteine have a high affinity towards soft and intermediate metal ions such as Cd, Pb, Zn and Hg while the amine moieties have affinity towards hard and intermediate metals such as Cr, As, Sn and Pb. There are several studies where cysteine-GO composites were used to either detect or remove heavy metals in wastewater (El Adraa et al., 2017; Seenivasan et al., 2015). However, there are no studies on the cysteine-functionalised GO thin film nanocomposite membranes for heavy metal removal.

Phosphate groups are used in wastewater treatment because they can convert soluble toxic heavy metals into insoluble orthophosphates. Phosphate groups to GO bind strongly to uranium which exists in its aqueous hexavalent form. Triethylphosphate acts as a strong ligand to coordinate to UO_2^{2+} . Hg(II) and U(VI) are the most toxic ions found in AMD and will be investigated in this study.

The use of membranes for AMD remediation is not a common method because of high costs of membrane process and high risk of membrane fouling due to susceptibility of membrane to the low pH of AMD (Liu et al., 2011). Recently, the high membrane fouling, and risk of performance failure have been reduced by pre-treating AMD feed solution. TFN membranes in AMD treatment will provide increased surface area for

removal upon functionalisation compared to the conventional methods such as nanoparticles. There is also less risk of toxicity towards aquatic systems from nanoparticles because they are bound.

The fabrication of functionalised GO thin film nanocomposite membranes in remediating AMD-contaminated waters has not been studied yet, so this study is aiming on giving more insight on the adsorption capacity of the membranes under AMD conditions.

2.12 Instruments used in the characterization of nanocomposite membranes

The various properties of the Cysteine and phosphate functionalised graphene oxide TFN membranes were evaluated using several techniques and instruments. Characterization was performed for bare GO, functionalised GO, and the thin film layer of the composite membranes. The characterization techniques include CHNS elemental analysis, transmission electron microscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDX), atomic force microscopy (AFM), Raman spectroscopy. The following sections describe these techniques in detail.

A. Scanning Electron Microscopy

Scanning electron microscopy involves using the microscope's electron beam to analyse the surface of membranes. A scanning electron microscope consists of an electron gun, a series of electromagnetic lenses such as condenser and objective lens, a column, scanning coil and a detector (Figure 2.5). These components work together to provide the 3-D surface topography.

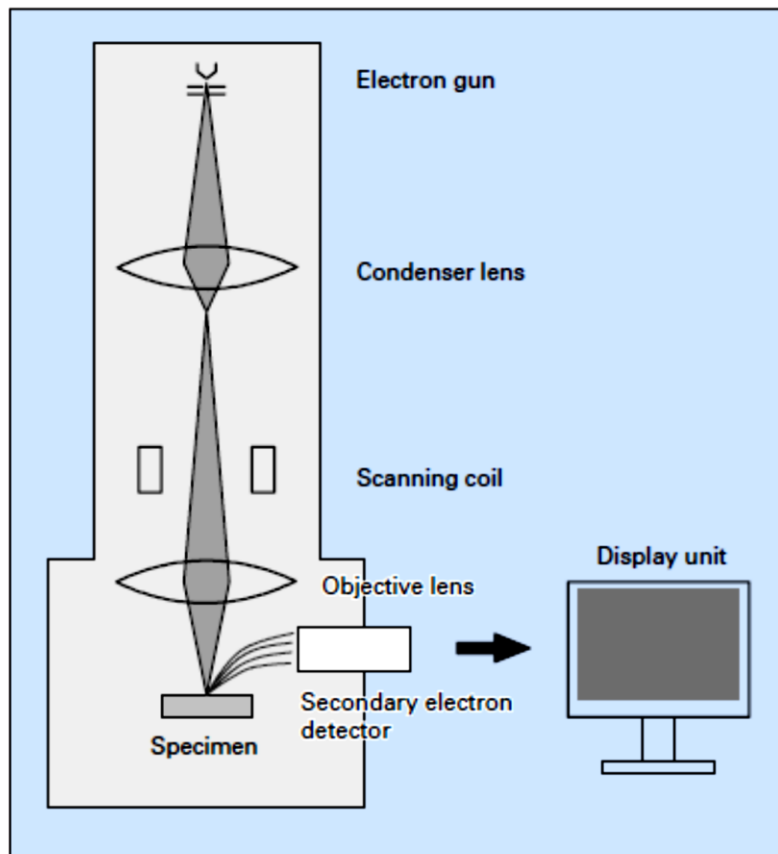


Figure 2.5: The basic components of SEM (Leng, 2008)

SEM works by focusing electron beam on the surface of the sample, where emission of back scattered and secondary electrons happens. These emitted scattered electrons are collected and amplified to give the composition of the sample as well as the topography of the image. The magnification of SEM can be as high as $\times 30\,000$ and the resolution in the range of 2-5 nm or higher (Leng, 2008). Chemical information about specimens is obtained via energy dispersive X-ray.

The basic components of SEM are:

- i. **Electron guns:** Electrons guns are also referred to as electron sources where the electron beams are produced by thermionic heating. The generated electrons are accelerated to a voltage of 1-40 kV and condensed into a narrow beam that is used to scan the sample surface. There are three commonly used types of electron sources which are the tungsten filament, solid state crystal (cerium hexaboride or lanthanum hexaboride) and Field emission gun (FEG) which is the most used electron gun. FEG is a wire of tungsten with a sharp tip $< 100\text{ nm}$ is used to generate the electron beam

by using field electron emission, the small tip radius helps improve focus and emission.

- ii. Lenses: the lenses present in SEM demagnify the image of the emission source thus obtaining a narrow probe on the sample surface. These lenses are the condenser and objective, where the condenser lens focus the electron beam into a parallel stream as it moves from the source, which diverges the beam, down the column. Where the objective lens also converges or focus the beam down the condenser into a narrow probe on the surface of the sample.
- iii. Column: the column contains the aperture and stigmator, where the aperture removes the scattered electrons and makes sure blurry images are not produced by controlling the spherical aberrations. The stigmator is a string of coils that surround the electron beam and used to correct astigmatism to produce good resolution images.
- iv. Scanning coils: the scanning coils are used after the beam is focussed by deflecting the beam in the x- and y-axes to scan the surface of the sample.
- v. Detector: there are several types of detectors used to detect the various signals which come from different penetration depths in SEM. The detectors are (Barron, 2012):
 - Secondary electron detector which detects inelastic scattered electrons close to the surface.
 - Back scattered electron detector detects elastically scattered electrons which are higher in energy from atoms below the sample surface.
 - Energy dispersive X-ray detects X-rays that are emitted.

In this study, a Carl Zeiss Sigma FESEM equipped with oxford x-act EDX detector was used to characterise the surface of the thin film nanocomposite membranes, comparing modified and unmodified thin film nanocomposite membranes. The samples were prepared on a SEM disc and coated with gold/palladium prior to analysis. Using SEM with EDX addresses the need for elemental analysis because obtaining only imaging data is not enough.

B. Energy Dispersive X-ray

Most SEM instruments are equipped with the energy dispersive X-ray component which is useful because the microscope emits x-rays when the electron beam displaces the inner shell electron which is replaced by an outer shell electron. An EDX is a semiconductor detector with a collimator and electron trap, where the collimator is used to collect X-

rays from the interaction between the primary electron beams and sample. Since each element has a signature energy difference between the outer and inner shell electrons, the x-rays emitted are detected and provide elemental identification. The data can be obtained for specific points on the membrane surface or over a large area of the sample. An electron trap on the other hand is used to only allow X-rays and not electrons to enter the detector. It is limited by not detecting hydrogen, helium and lithium.

C. Transmission Electron Microscopy

Transmission electron microscopy is where the beam of electrons (rather than optical light) transmits through a thin specimen by interacting with the specimen when passing through. The image formed from the interaction of the electrons with the specimen, is magnified and focused onto an imaging device that can detect electrons such as the charged coupled device (CCD) camera. The resolution of TEM is higher than that of scanning electron microscopy and light microscopes because the electrons have a shorter de Broglie wavelength than visible light. The size and shape of GO particles used in modification of the thin film composite membranes were determined using TEM.

Limitations of TEM are that the specimen needs to be significantly thin for the electron beam to pass through and provide more forward scattering of the electrons than the backscattering, it only provides 2-D images of a 3-D specimen meaning a TEM instrument is not depth sensitive where the bottom and top part of the specimen are not viewed and lastly, TEM ionization radiation can damage the specimen. The difference between SEM and TEM is illustrated in the table below.

Table 2.6: Differences between SEM and TEM

SEM	TEM
Images the surface of the specimen	Images ultrathin structure of specimen
The electron beam scans the specimen surface	Electron beam penetrates the specimen
Lower resolution	Higher resolution
Three dimensional images are produced	Produces two dimensional images

D. Atomic Force Microscopy

Atomic force microscopy was used to scan the nanocomposite membranes' topography by using a sharp tip to probe and map. It detects near-field forces between the tip and sample and these forces are short range forces which are between atoms when their distance is close to atomic spacing. Because a variation of these forces on the atomic scale allows AFM to obtain topographic images of atoms, Van der Waals forces are dipoles of molecules, electrostatic forces which are electric charges of the tip and sample and capillary forces which result from water vapour condensation between tip and sample (Leng, 2008).

AFM is composed of

- A sharp tip on the back of the cantilever
- A split photodiode detector to sense the deflection of the cantilever
- A feedback system that monitors and controls the deflection
- A scanning system that moves the sample with respect to the tip in a raster pattern
- A computer that converts the data measured into an image.

The principle of AFM is when the tip, which is at the end of the cantilever touches or is near the surface of the sample, the forces generated due to the interaction lead to the deflection of the cantilever. The deflection is then measured by reflecting the laser beam off the back of the cantilever into the split photodiode detector (SPD). The two most used modes of operation are contact mode AFM and tapping mode AFM. Contact mode AFM scans the sample while monitoring the change in cantilever deflection with the detector. A loop maintains cantilever reflection by vertically moving the scanner to get a constant signal. The distance the scanner travels at each x, y data points is stored by the computer to form topographic image of the sample's surface. While the tapping mode AFM

oscillates the cantilever at its resonance frequency and lightly taps the surface with the tip during scanning. The electrostatic forces increase when the tip gets closer to the surface and decreasing the amplitude of oscillation which is detected by the laser deflection method. It is like the contact mode AFM where the data points at x, y vertical scanning are used to form a topographical image. The difference between the two is that tapping mode eliminates the shear forces present in contact mode meaning it can be used to image soft, fragile and adhesive surfaces without damage whereas contact mode allows damage to occur (Barron, 2012).

The AFM analysis was performed on the modified and unmodified membranes to get the surface roughness and it was carried out by the Veeco Di3100 AFM. The graphical images were presented in 3D form while the quantitative measurements consisted of the average roughness (R_a) and the root mean square of the roughness (R_{RMS}).

E. Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS is currently the most useful instrument used in the detection of trace multi-elemental and isotopic concentrations in liquids, solids or gaseous samples with a wide linear dynamic range, low detection limit, and ability to measure isotopic ratios. ICP-MS measures elements in concentrations as low as parts per billion (ppb), and parts per trillion (ppt). The principle of the technique involves ionization of the atoms of the elements in the sample, and then the ions are separated and detected according to their mass-to-charge ratio. The source of the ionization is inductively coupled plasma, while the separation and detection of the ions are done by a mass spectrometer. The basic components of an ICP-MS include

- Nebulizer and spray chamber
- Plasma torch (ICP source)
- Differentially pumped interface with ion-focusing system and mass separation device
- Mass spectrometer
- Detector

The analysis of a sample using ICP-MS involves introducing the sample to the instrument using the peristaltic pumps. The solution is then pumped to the nebulizer where it is converted into spray. Large drops are filtered out while the small drops continue into the plasma torch (the inductively coupled plasma source). The plasma is produced in a stream

of hot gas (mainly argon gas) flowing through a set of three concentric quartz tubes known as the plasma torch.

In the plasma, the solvent in the spray evaporates thereby leaving particles which are vaporized and ionised. A positive ion beam is formed as the electrons diffuse and charge separation occurs. The positive ions are focused into the mass spectrometer by a series of ion optics. Ions of same mass-to-charge ratio leave the mass spectrometer and they are detected by the detector which converts these ions into electric signals (Barron, 2012).

ICP-OES is also used to detect heavy metal ions in solution but the difference is that the ions in ICP-OES are excited by vertical plasma that emits photons which are separated based on their wavelength emission hence the optical part of the detector. ICP-MS is more expensive because of the magnitude of sensitivity (lower) and detection (higher) which is better than for ICP-OES which has a low detection limit and high potential for spectral interference.

The ICP-MS was used to detect trace levels of U and Hg after adsorption by the thin film nanocomposite membranes.

CHAPTER 4

MATERIALS AND METHODS

This chapter describes the materials and methods used to synthesise the nanosheets and thin film composite membranes. Characterisation of the materials, batch adsorption studies and application studies

3 Materials and Methods

3.1 Materials

A. Glassware

All the glassware and apparatus used in this work were thoroughly washed with detergent, soaked in a 5% HNO_3 bath for 48 hours, followed by rinsing with deionised water from Milli-Q-RO4 system (Millipore, Bedford, MA, USA) and oven drying. The pH of the solutions was measured using a Five easy FE20 pH meter purchased from Mettler Toledo (Johannesburg, South Africa).

B. Chemicals

Graphite, L-cysteine and triethylphosphite, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Polysulphone pellets (MW= 35 000), dimethylformamide (DMF), trimesoyl chloride (TMC) and m-phenylenediamine (MPD) were purchased from Sigma-Aldrich. KmnO_4 (%), HNO_3 (55%), H_2SO_4 (95%), H_3PO_4 (85%), H_2O_2 (50%), HCl (32%) and Ethanol (99%) were purchased from ACE chemicals.

3.2 Synthesis and characterisation of graphene oxide and derivatives

A. Synthesis of graphene oxide

Graphene oxide was synthesised using the improved Hummer's method (Xia et al., 2015). For this, 120 mL sulphuric acid (H_2SO_4) and 13 mL phosphoric acid (H_3PO_4) were mixed in a 9:1 volume ratio. One gram of graphite powder followed by 6 g potassium permanganate (KmnO_4) were then slowly added to this solution under stirring. The mixture was left to stir in an oil bath for approximately 12 hours at 50 °C until the solution turned dark green. The product was cooled at room temperature and then placed in an ice bath before 1 mL of 30 % hydrogen peroxide (H_2O_2) was added dropwise to stop the oxidation reaction. The mixture was then centrifuged for 60 minutes at 4000 rpm. The supernatant was discarded, and the precipitate washed suspended in a 1:1 mixture of hydrochloric acid (HCl), deionised water (DI) and ethanol, and centrifuged at 4000 rpm for 60 minutes. This procedure was repeated five times after which the solid was dried overnight in an oven at 70°C and crushed to a fine powder. The powder was characterised using TEM, XRD, CHNS and FTIR to determine the morphology, elemental composition, inter-sheet spacing and functional groups. Samples for TEM analysis were sonicated in methanol for 10 minutes before analysis.

B. Synthesis of L-cysteine-functionalised GO (rGO-SH)

For GO reduction, Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (0.25 g) was added to 50 mL GO aqueous dispersion (10 mg mL^{-1}) and mixed for 30 minutes. Separation of GO/EDC was done by adding 0.3 g L-cysteine and stirred for 24 hours at room temperature. The rGO-SH was collected after centrifugation at 4000 rpm, washed with DI water several times to remove excess cysteine and EDC. The sample was dried in an oven at 70°C for 12 hours (Yan, 2017)..

C. Synthesis of phosphate-functionalised GO (GO-PO₄)

Phosphate-functionalised GO was synthesised using the Arbuzov reaction (Liu et al., 2015). For this, 0.5 g of GO was dispersed in 50 mL triethylphosphite and ultrasonicated for 1 hour. LiBr (1.4 g) was then added to the reaction mixture and sonication continued for 30 more minutes. The resulting solution was refluxed at 130°C under stirring and N_2 (inert reaction) for 36 hours. When the reaction was complete the product was filtered and dried under vacuum for 24 hours at 60°C . The dried product was pulverised, dispersed in 50 mL tetrahydrofuran (THF) and ultra-sonicated for 10 minutes. The dispersion was centrifuged at 4000 rpm, washed with THF and DMF five times and dried in an oven at 80°C for 12 hours (Goods et al., 2014; Liu et al., 2015).

D. Characterisation of GO and functionalised derivatives

Fourier transform infrared spectra were recorded in the range $4000\text{--}500 \text{ cm}^{-1}$ using a Tensor 27 Infrared Spectrometer (Massachusetts, USA). X-ray diffraction analysis was by a Bruker D2 phaser diffractometer ($\text{Cu-K}\alpha$) (Johannesburg, South Africa) at a scanning range of $10^\circ - 90^\circ$ (2θ), a step size of 0.026 and step time of 37 seconds. The morphology of nanosheets was determined using a FEI Tecnai G² Spirit transmission electron microscope (Hillsboro, USA) at an acceleration voltage of 120 kV and sample preparation was sonication for 10 minutes in methanol. Carbon hydrogen nitrogen and sulphur (CHNS) elemental analysis was done by varioELcube v4.0.13 (Elementar, Germany)

3.3 Adsorption of Hg and U ions using GO nanosheets and its derivatives

The synthesised GO, rGO-SH and GO-PO₄ were applied for the removal of Hg(II) and U(VI). For these studies, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salts were used. The

effects of contact time, element concentration, pH, and adsorbent concentration were examined.

The effect of contact time was studied at 0, 5, 10, 15, 20, 30, 50, 90, 120 and 150 minutes to determine the rate at which the adsorbent reaches equilibrium, where 20 mg of GO, rGO-SH and GO-PO₄ nanosheets were added to a 15 mL centrifuge tube with 100 µg L⁻¹ solution of Hg(II) and U(VI) with pH adjusted to 4 using 1% HNO₃ and NaOH. The resulting solutions were shaken in a rotor shaker at 150 rpm

The effect of pH on adsorption was studied with pH of 1, 2, 4, 6 and 8, where 20 mg of GO, rGO-SH and GO-PO₄ was added in a 15 ml centrifuge tube with 100 µg L⁻¹ of elemental solution of Hg(II) and U(VI) and shaken in the rotor shaker at 150 rpm for 150 minutes. The effect of element concentration was investigated using solutions of 2, 5, 10, 50 and 100 µg L⁻¹ for U(VI) and Hg(II). The solution pH was adjusted to 4 before adding to 20 mg of GO, rGO-SH and GO-PO₄ nanosheets in 15 mL centrifuge tubes, the solutions were mixed in a rotor shaker for 150 minutes at 150 rpm. The solutions' pH was adjusted using 1% NaOH and 1% HNO₃.

The resulting solutions were centrifuged for 5 minutes and the supernatant was acidified with 1 % HNO₃. Concentrations of Hg(II) and U(VI) were determined using an Agilent 7700 series ICP-MS. Removal efficiencies and adsorption capacities of the GO, rGO-SH and GO-PO₄ nanosheets were determined using the following equations (Nekhunguni et al., 2017a):

$$\text{Removal efficiency} = \frac{C_o - C_e}{C_o} \times 100\% \quad (5)$$

$$\text{Adsorption capacity (qe)} = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \quad (6)$$

Where C_o and C_e represent the concentrations (µg L⁻¹) before and after adsorption, V (mL) represents the volume of the adsorbate and m (g) is the mass of adsorbent (Sadegh et al., 2017).

3.4 Application of GO nanosheets and functionalised derivatives on actual AMD-contaminated water.

To determine how effective the prepared adsorbents were on actual AMD-contaminated water, adsorbents were applied to water samples collected from the Donaldson dam in Bekkersdal, south of Randfontein, Gauteng (26°16'47.5"S 27°41'11.4"E). This dam

receives effluent from mine dumps in the West Rand of Johannesburg. Water samples were collected in acid-rinsed polypropylene bottles. The pH and conductivity of the water were measured immediately after collection, after which the water was acidified using 1% HNO₃. In the laboratory, the water samples were analysed for total metal concentrations using ICP-OES. To test Hg(II) and U(VI) removal capacities of the synthesised adsorbent, 10 mL of the water sample that was filtered with 0.25 µm filter was put in 15 mL centrifuge tubes containing 20 mg of adsorbent and agitated for 24 hours at 150 rpm. Samples were then centrifuged, filtered, acidified with 1% HNO₃ and stored in 15 mL centrifuge tubes in the fridge until analysis for total metal concentrations using ICP-OES.

3.5 Synthesis of membranes

A. Synthesis of support polymer

The PSF support layer was fabricated by phase inversion method. For this, 2.g polysulphone pellets were added to 20 mL DMF, stirred at 50 °C for 12 hours and degassed. The resulting clear solution was spread on a glass plate and cast at 50 µm thickness using an Electrometer 4843 automatic film applicator (Manchester, UK). The film was immersed in a deionised water bath for coagulation and precipitation and then stored in DI water for further use (Xia et al., 2015).

B. Synthesis of polyamide layer containing graphene oxide nanosheets and the functionalised derivatives

To make the TFN membranes, 20 mL of 2 wt.% (0.20 g) of *m*-phenylenediamine-water solution was prepared. The mixture was then vacuum filtered onto the PSU support membrane for 5 minutes, followed by 20 mL of 0.2 wt.% (0.020 g) TMC-hexane solution to obtain one side of the functional membrane. The polyamide thin film layer was formed at the interface of the two solutions. A mass of 0.03 g of GO, rGO-SH and GO-PO₄ was added to 10 mL ethanol and sonicated for 30 minutes before the mixture was vacuum filtered onto the polyamide layer followed by the TMC mixed in hexane solution for introduction of acyl chloride groups to react with incoming nanoparticles. The procedure was repeated 3 times with GO, rGO-SH and GO-PO₄ -ethanol mixture and TMC-hexane solution. The membrane was rinsed with pure hexane and dried at room temperature overnight. The membranes were stored in Ziploc bags until use (Choi et al., 2017; Mahdavi and Rahimi, 2018; Xu et al., 2018).

3.6 Membrane characterisation

Four membranes were prepared: one without nanomaterials (TFC only), one with unfunctionalised GO (GO-TFN), one with Cysteine-functionalised GO (rGO-SH TFN) and lastly, one with phosphate-functionalised GO (GO-PO₄ TFN). Membrane thickness was determined using SEM and the thickness were found to be 180.4, 113.5, 84.8 and 85.9 μm for TFC, GO-TFN, rGO-SH TFN and GO-PO₄ TFN respectively.

Membranes were characterised using Fourier transform infrared spectra recorded in the range 4000–500 cm^{-1} using a Tensor 27 Infrared Spectrometer (Massachusetts, USA). Carbon hydrogen nitrogen and sulphur (CHNS) elemental analysis was done by varioELcube v4.0.13 (Elementar, Germany) where WO_2 was added to facilitate combustion. A Carl Zeiss Sigma 03-39 FESEM (Jena, Germany) equipped with oxford x-act EDX detector was used to characterise the surface of the thin film nanocomposite membranes. The samples were prepared on a SEM disc and coated with gold/palladium prior to analysis.

3.7 Membrane performance experiments

All the filtration experiments of the prepared membranes were carried out in a Sterlich dead-end stirred cell (Figure 3.1).

A. Leaching and Pure water flux

Before experiments, leaching studies were conducted to determine GO leaching from membranes and determine the number of times the membranes need to be washed before adsorption experiments to ensure that no unbound GO / derivatives do not escape into treated water. GO loss was determined using UV-Vis spectrophotometry. Membranes were pressure-washed in a dead-end filtration system with deionized water at 200 Kpa for 18 hours at which 50 mL volume of the sample was collected. The presence and concentration of GO in filtered water was determined at 200-300 nm where GO has the maximum absorbance (Goodwin et al., 2018). When the wavelength was determined, the standard concentrations of GO and functionalized GO were prepared to plot a calibration curve. The curve was then used to get the unknown concentrations of the leached GO and its derivatives. A graph of volume versus concentration was plotted to determine the number of washes after which it was appropriate to employ the membrane without GO loss.

The flux of membranes was determined using deionized water at a feed pressure of 200 kPa for 30 minutes until permeate flux became constant. The process was repeated 3 times for each membrane type. The stable flux (J) was determined by the following equation:

$$J = \frac{V_P}{A \times T} \quad (14)$$

Where J ($\text{L m}^{-2} \text{h}^{-1}$) represents flux, V (L) is the volume of the permeated liquid at that specific pressure, T (h) is the time of permeation and A (m^2) is the filtration area (Mahdavi and Rahimi, 2018).

B. Membrane hydrophilicity

The surface hydrophilicity of the prepared membranes was evaluated by contact angle experiments using a Kruss Drop Shape Analyzer, DSA30 (GmbH, Germany) to determine hydrophilicity of the membranes at room temperature. Ten replicates were done, and three most precise measurements were averaged.

C. Membrane fouling resistance

Fouling experiments were carried out with AMD-contaminated water collected from the Donaldson dam in Bekkersdal, ($26^{\circ}16'47.5''\text{S}$ $27^{\circ}41'11.4''\text{E}$) at pH 4.78 after the pure water flux studies. The fouling resistance of the flat sheet was evaluated by decrease in water flux over 30 minutes time intervals for 5 hours with adjusted pH of 2.97.

3.8 Removal of Hg(II) and U(VI) ions by TFN membranes

The performance of GO, as part of a TFN membrane was carried out using membranes that had been leached according to the results of the leaching study described above, using a dead-end filtration system under N_2 gas (Figure 6). The membranes used were pressured washed with deionised water before adsorption. Experimental conditions were as follows:

Effect of pH: Removal of $100 \mu\text{g L}^{-1}$ of Hg and U, from solutions by the three membranes was investigated at pH 1, 2, 4, 6 and 8. respectively.

Effect of concentration: Hg and U solutions ($2, 5, 10, 50$ and $100 \mu\text{g L}^{-1}$) were stabilised at pH 4.

Effect of contact time: the analyte concentration and pH were kept at $100 \mu\text{g L}^{-1}$ (Hg and U) and 4 respectively.

Application studies: Water from the Donaldson dam in Bekkersdal (100 mL), (pH was 6.78) was put in the dead-end cell containing a membrane, and the feed stirred for 24 hours.

For each experiment, the column of the dead end stirred cell was filled with 100 mL of the analyte. A pressure of 100 kPa (~ 1 bar) was then applied under stirring conditions to allow the analytes to interact with the membrane. The permeate was collected, acidified with 1 % HNO_3 , stored in 50 mL centrifuge tubes and analysed in ICP-OES or ICP-MS.

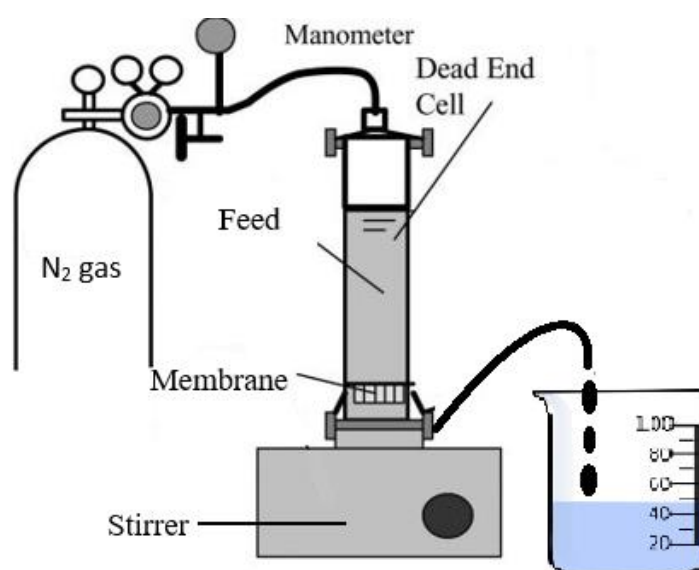


Figure 3.1: Schematic diagram of the dead end filtration system (Koyuncu and Wiesner, 2007)

CHAPTER 4

Batch adsorption studies

This chapter presents the results of adsorption experiments using graphene oxide nanosheets and its *L*-cysteine and phosphate-functionalised derivatives. The journal articles in which these results have been published are listed below.

Contribution to the first paper: Lead author, conducted the experimental work, analysed and interpreted the results.

Contribution to the second paper: Second author, conducted the experimental work, assisted in analysing and interpreting the results.

1. **Nhlane D.**, Richards H. and Etale A. (2020). *Facile and green synthesis of reduced graphene oxide for remediation of Hg(II)-contaminated water*. Materials Today: Proceedings. [Doi.org/10.1016/j.matpr.2020.04.163](https://doi.org/10.1016/j.matpr.2020.04.163)
2. Etale A., **Nhlane D.**, and Richards H. (2020). *Graphene oxide nanosheets for treatment of mine drainage contaminated water: The effect of phosphate functionalisation on U(VI) removal*. Materials Today: Proceedings. [Doi.org/10.1016/j.matpr.2020.03.549](https://doi.org/10.1016/j.matpr.2020.03.549)

4 Adsorption of Hg(II) and U(VI) by graphene oxide and functionalised derivatives

4.1 Cysteine-functionalised graphene oxide (rGO-SH)

A. TEM characterisation of nanosheets

TEM images showed that the lateral sizes of GO and rGO-SH nanosheets ranged from nano to micron scale sheets with creases and folds (Figure 4.1A). These folds are thought to be due to the abundant oxygen functional groups in GO (Meyer et al., 2007). Functionalized GO (Figure 4.1B) showed no obvious differences except for their darker shade which may be interpreted as being due to greater stacking from crosslinking by cysteine groups as well reduced numbers of intercalating hydroxyl and epoxide moieties (Vorrada et al., 2013).

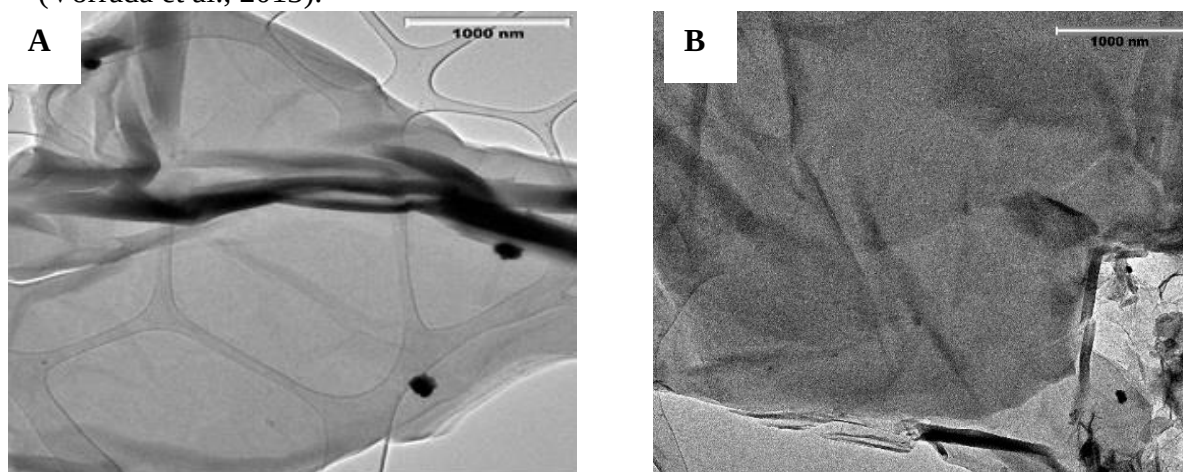


Figure 4.1: TEM images of (a) GO, (b) rGO-SH.

B. XRD analysis

The X-ray diffractogram of GO (Figure 5.2) showed the characteristic diffraction peaks located at $9.2^\circ 2\theta$ corresponding to the (002) reflection of GO, and a weak peak at $43^\circ 2\theta$ which is attributed to the (100) reflection of GO. Reduced GO had a peak at 11.5° and $19.9^\circ 2\theta$, suggesting a reduction in interlayer spacing from 0.48–0.39 nm due to removal of the intercalating carbonyl and hydroxyl moieties present in GO (Pham et al., 2011). It is postulated that this reduction in interlayer spacing despite intercalation of cysteine is because the cysteine moieties are in plane (Bourlinos et al., 2003). Further proof that cysteine was incorporated into reduced GO adsorbent was determined by FTIR.

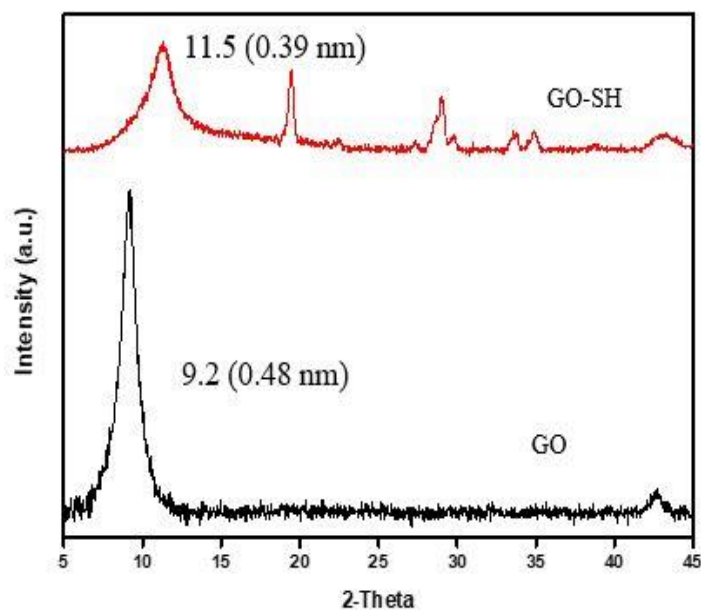


Figure 4.2: XRD pattern of A) GO and B) rGO-SH nanosheets

C. FTIR analysis

Functionalization of GO by cysteine was confirmed by FTIR spectroscopy (Figure 4.3). The FTIR spectra for unfunctionalized GO show a broad peak centered at 3350 cm^{-1} which is due to the stretching vibrations of OH groups on GO. The GO spectra also show peaks at $2250\text{--}1995\text{ cm}^{-1}$, 1750 cm^{-1} , 1600 cm^{-1} , 1050 cm^{-1} and 850 cm^{-1} which correspond to C=C, carbonyl, carboxyl and epoxy groups, respectively (González et al., 2012). Cysteine functionalization is confirmed by the weakened epoxy peak at 850 cm^{-1} and emergence of peaks at 950 and $1200\text{--}1400\text{ cm}^{-1}$ corresponding to C-N in-plane vibrations, this proves that a nucleophilic substitution of NH_2 to carboxyl groups to form an amide bond was successful (Muralikrishna et al., 2014).

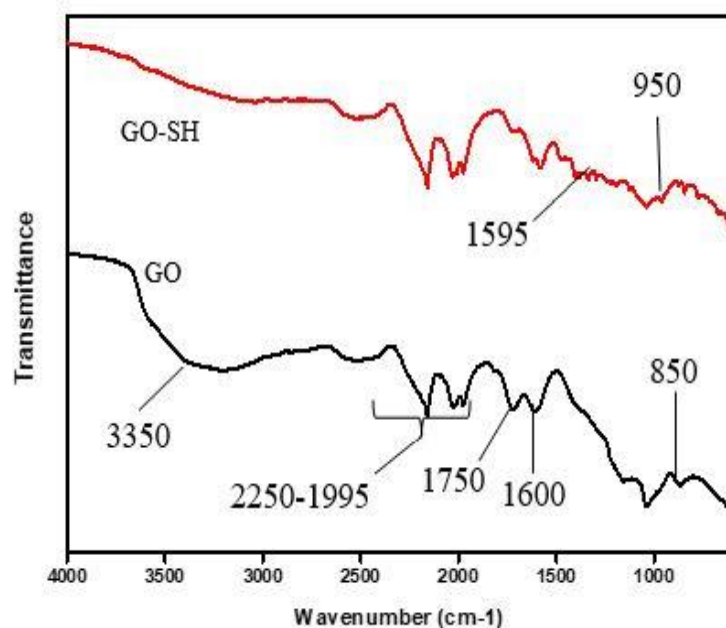


Figure 4.3: FTIR spectrum of A) GO and B) Cysteine functionalised GO nanosheets

D. Elemental analysis of nanosheets

The CHNS elemental analysis in (Table 4.1) also shows that the one step reduction and functionalisation of GO was successful because of the decrease in the oxygen content and an increase in percentage of sulphur and nitrogen after the incorporation with L-Cysteine because the carbodiimide formed an amide bond between a primary amine in cysteine and carboxyl group (Mahdavi and Rahimi, 2018). The 5 % of sulphur content in graphene oxide comes from the sulphuric acid used to oxidise graphite.

Table 4.1: Elemental composition of GO and rGO-SH

Sample	Elements (%)				
	C	H	N	S	O
GO	30.80	2.60	0	5.36	61.24
rGO-SH	38.90	4.29	9.60	21.29	25.92

4.2 Hg adsorption studies between graphene oxide and Cysteine-functionalised graphene oxide (rGO-SH)

A. Effect of adsorbent concentration

The effect of adsorbent concentration on Hg and U removal was examined using rGO-SH and GO-PO₄ concentrations ranging from 10-100 mg at pH 4. The Hg and U removal efficiency increased with adsorbent amounts due to the increase in active sites on the adsorbents (Figure 4.4), the removal efficiency of Hg(II) and U(VI) was optimal (82 and 85 % for GO and functionalized GO, respectively) at 20 mg of adsorbent and so this mass was used for subsequent batch studies. A closer look at the results show that the adsorption efficiency of Hg(II) and U(VI) remained at a maximum after 20 mg dosage, however Krishna Kumar et al., 2016 experienced a decrease in removal efficiency because of the desaturation of active sites in the process of adsorption, meaning that the adsorbent agglomerates at higher dosage.

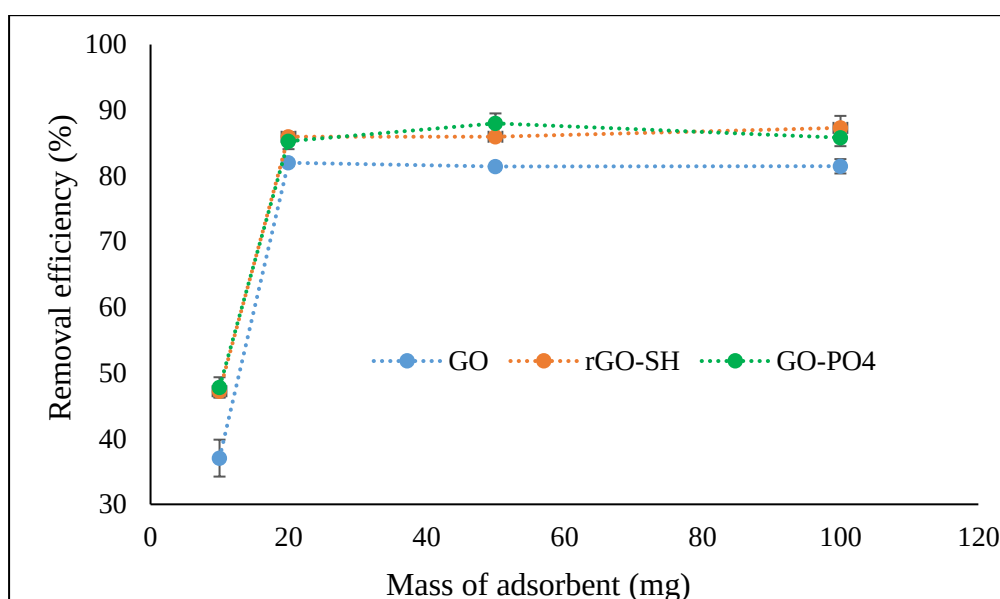


Figure 4.4: The effect of varying dosage amount of GO, rGO-SH and GO-PO₄ on removal

B. Effect of contact time

The effect of contact time on the adsorption of Hg(II) ions by GO and rGO-SH was examined at pH 4, from 0-150 minutes. As shown in (Figure 4.5), adsorption of Hg(II) ions by both GO and rGO-SH was rapid in the first 30 minutes with removal efficiencies of (74.3 and 78.1 %) for GO and rGO-SH respectively, then reached equilibrium after 30 minutes. This rapid increase in adsorption is known to be due to the concentration gradient and the high availability of adsorption sites at the initial stages of reactions. The removal efficiency reaches equilibrium because as contact time increases, the number of

available sites decreases. The removal efficiency is higher for rGO-SH because of the additional active sites sulfhydryl and amine functional groups on the surface of rGO-SH that can complex with Hg(II) ions.

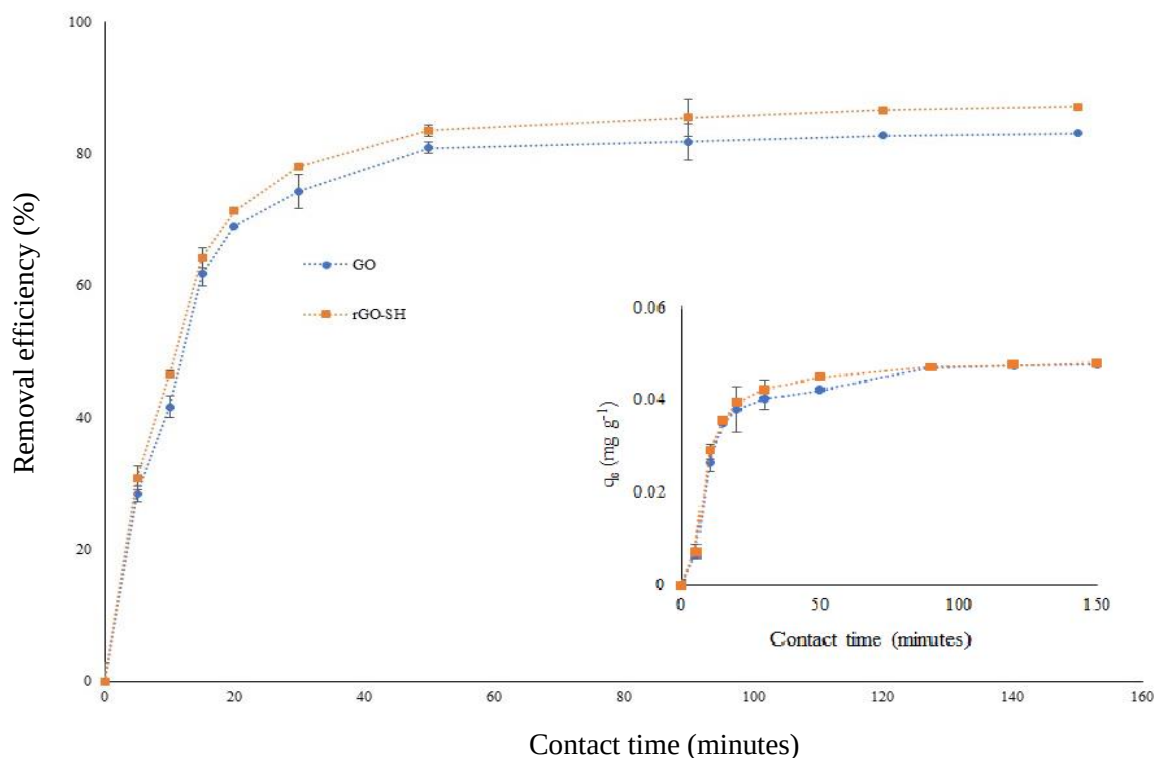


Figure 4.5: The effect of contact time on removal of Hg(II) by GO and rGO-SH

Adsorption of Hg to both GO and rGO-SH followed the pseudo-second-order model (Table 4.2) suggesting that adsorption of Hg(II) to the two adsorbents was by chemisorption. At the experimental pH and concentration i.e. pH 4 and $100 \mu\text{g L}^{-1}$, Hg ions (Figure 4.6) exist as $\text{Hg}(\text{OH})_2$, Hg^{2+} and $\text{Hg}(\text{OH})^+$ where the $\text{Hg}(\text{OH})_2$ is dominant meaning that precipitation is likely happening compared to adsorption, however the $\text{Hg}(\text{OH})^+$ species is adsorbed via chemisorption with the interaction of the negatively charged functional groups on the adsorbents.

Table 4.2: Kinetic parameters of Hg(II) sorption at 298 K

Adsorbent	Pseudo-second-order			Pseudo-first-order
	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2	R^2
GO	216.46	0.0401	0.94	0.83
rGO-SH	281.55	0.0602	0.96	0.93

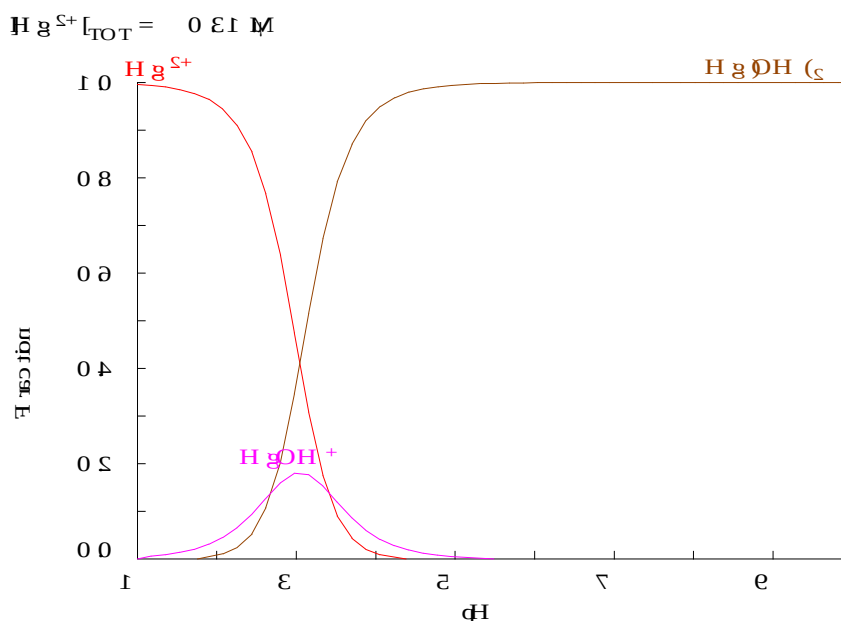


Figure 4.6: Species distribution of Hg(II) across pH 1-10

C. Effect of pH

The pH at which maximum removal efficiency of Hg(II) using GO and rGO-SH was examined and reported (Figure 4.7) with adsorbate solutions of 100 $\mu\text{g L}^{-1}$ (preliminary investigations showed this to be the optimal concentration). Overall, Hg(II) removal was higher for rGO-SH than GO (74.9 % and 88.2 % for GO and rGO-SH respectively). The removal efficiency increased from pH 1 to pH 4 and attained maximum at pH ~4. The adsorption efficiency is dependent on Hg(II) speciation (Figure 5.6) and functional groups as a function of pH. The low adsorption capacity of Hg(II) ions at low pH values can be attributed to competition between Hg(II) ions and hydrogen ions for the adsorption and the electrostatic repulsion between Hg(II) ions and the surface of the adsorbent. Hydrogen ions are strong competitors due to their smaller ionic radius (1.2 pm compared to 102 pm for Hg^{2+}). Competition from H^+ ions decrease with increasing pH, and by pH 4, adsorption increased by up to 30 % for both adsorbents. Subsequent experiments were conducted at pH 4.

A close look at the data showed that cysteine functionalization increase Hg(II) removal due to the affinity of these ions for thiol groups (Awad et al., 2020; Saad and Cukrowska, 2013) compared to the electrostatic interaction, where graphene oxide functionalized-thiol groups have a pKa value of 6.59 (Orth et al., 2016), which means that at the experimental pH, thiol groups are protonated. The reason for the high affinity is because of the Pearson's hard-soft acid base concept, where thiol groups are soft bases and can interact with the soft acid, Hg(II). Krishna Kumar et al., 2016 also reported that the electron lone pairs on nitrogen can donate to the empty orbital of Hg(II) ions. Another reason could be that at pH 4, $\text{Hg}(\text{OH})_2$ is dominant in solution, therefore precipitation is occurring instead of adsorption.

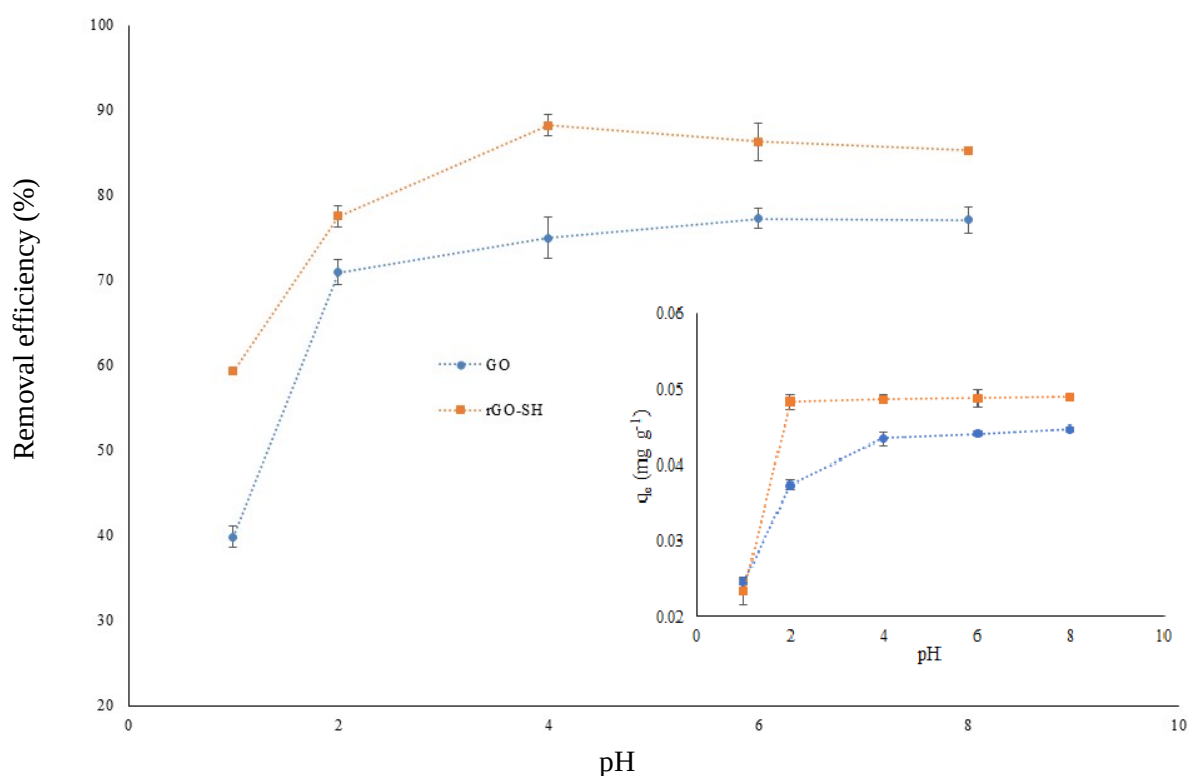


Figure 4.7: Effect of change in pH on adsorption of Hg(II) ions onto GO and rGO-SH

D. Effect of initial concentration

Hg(II) solutions of varying concentrations were exposed to 20 mg of GO or rGO-SH at pH 4, for 150 minutes and the effect of concentration on adsorbate performance evaluated. Removal efficiency increased with increasing initial Hg(II) concentration (Figure 5.8) and functionalisation with L-cysteine increased removal of Hg by GO from 80.7 to 85.3 %. In addition to the fact that Hg(II) is a chalcophile, (Krishna Kumar et al., 2016b) recently showed that binding of Hg(II) via surface complexation by GO occurs via electron pair sharing with oxygen moieties of oxygen-containing functional groups. Increasing the concentration of these groups such as thiols and amides increases the chances of lone pair sharing with Hg(II).

From figure 4.8 (insert), the adsorption capacity increases with increasing initial Hg(II) ion concentration, from 5.129×10^{-4} - 0.0374 mg g^{-1} and from 7.15×10^{-4} - 0.0421 mg g^{-1} for GO and rGO-SH respectively. This can be attributed to the fact that the higher the initial Hg(II) ion concentration, the higher the driving force of the concentration gradient at solid-liquid interface which causes an increase in the amount of Hg(II) ions adsorbed on the functionalised graphene oxide. With more Hg(II) ions present in solution, a larger fraction of the active sites is involved in the adsorption process. The effect doesn't indicate saturation of the available binding sites.

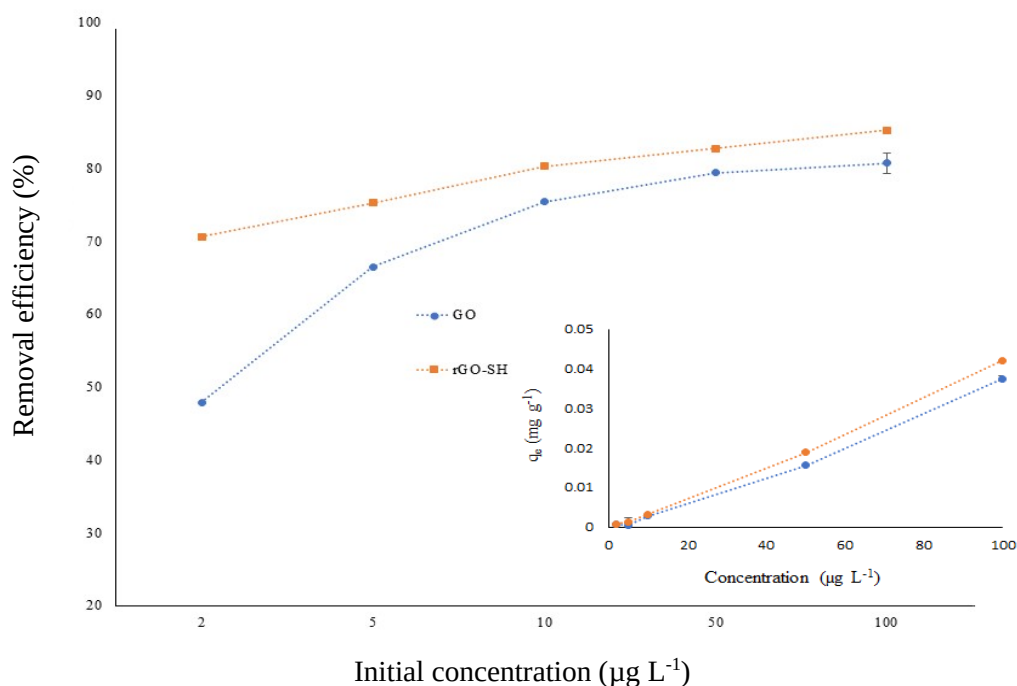


Figure 4.8: Effect of Hg(II) concentrations on removal.

The distribution of Hg(II) ions onto the adsorbent surface at equilibrium is best described by adsorption isotherms. The experimental data for Hg(II) adsorption by GO and rGO-SH was fitted with the Langmuir and Freundlich isotherms models, the model parameters for the experimental data were obtained and given in (Table 4.3). The isotherm data were better fitted by the Freundlich model suggesting that for both adsorbents, adsorption of Hg(II) took place on a heterogeneous surface by multi-layer adsorption. The value of $n > 1$ showed that the adsorption of Hg(II) by GO and rGO-SH was favorable at the operating conditions studied. The D-R model was also fitted to the data and a mean free energy of 9.74 kJ mol^{-1} was determined, which is greater than 8 kJ mol^{-1} proving that chemisorption or chemical ion exchange is the adsorption mechanism favored (Largitte and Pasquier, 2016; Nethaji et al., 2013).

Table 4.3: Langmuir and Freundlich adsorption isotherm constants for Hg(II) sorption

Adsorbent	Freundlich isotherm			Langmuir
	$K_F (\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$	n	R^2	R^2
GO	1.06	1.65	0.92	0.49
rGO-SH	1.07	1.69	0.92	0.23

4.3 Phosphate functionalised graphene oxide

A. XRD analysis

The X-ray diffractogram of GO showed the characteristic diffraction peaks located at 2θ 9.2 corresponding to the (002) reflection of GO, and a weak peak at 2θ 43 which is attributed to the (100) reflection of graphite. Functionalized GO had a peak at a smaller diffraction angle of 7.1, suggesting that phosphate functionalization increased the interlayer spacing of GO from 0.96 – 1.24 nm. The XRD pattern also shows a distorted structural order of the GO planes because there is a peak at 20° for the phosphorylated graphene oxide (Ghafuri and Talebi, 2016).

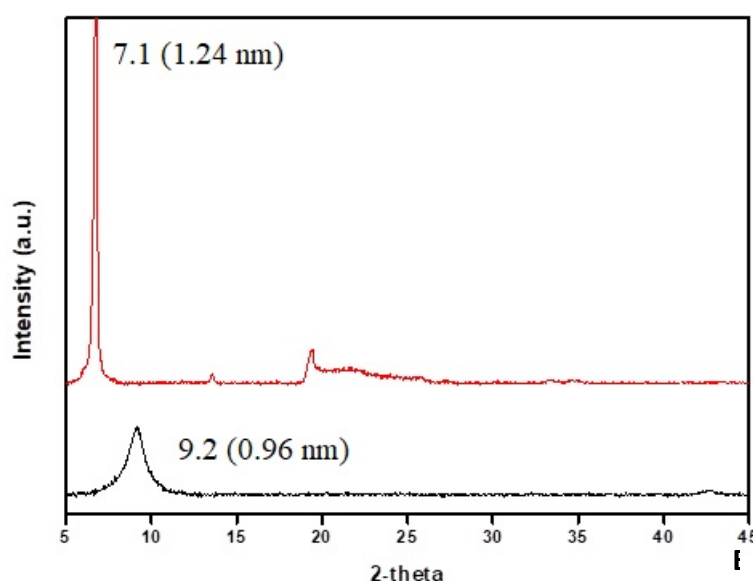


Figure 4.9: XRD pattern of GO (A) and GO-PO₄ (B) nanosheets

B. FTIR

Phosphate functionalization of GO was confirmed by FTIR spectroscopy (Figure 4.10). The FTIR spectra for unfunctionalized GO show a broad peak centered at 3200 cm^{-1} which is due to the stretching vibrations of OH groups on GO. The GO spectra also show peaks at $2250\text{--}1995\text{ cm}^{-1}$, 1750 cm^{-1} , 1600 cm^{-1} , 1050 cm^{-1} and 915 cm^{-1} which correspond to C=C, carbonyl, carboxyl and epoxy groups, respectively (González et al., 2012; Liu et al., 2015). Phosphate functionalization is confirmed by the weakened epoxy peak at 915 cm^{-1} and emergence of a peak at 960 cm^{-1} corresponding to P-O vibrations (Ghafuri and Talebi, 2016; Liu et al., 2015). The successful functionalization of GO with

phosphate is also confirmed by peaks at 2950 cm^{-1} corresponding to P-O-H stretch and P=O at 1130 cm^{-1} (Ghafuri and Talebi, 2016)

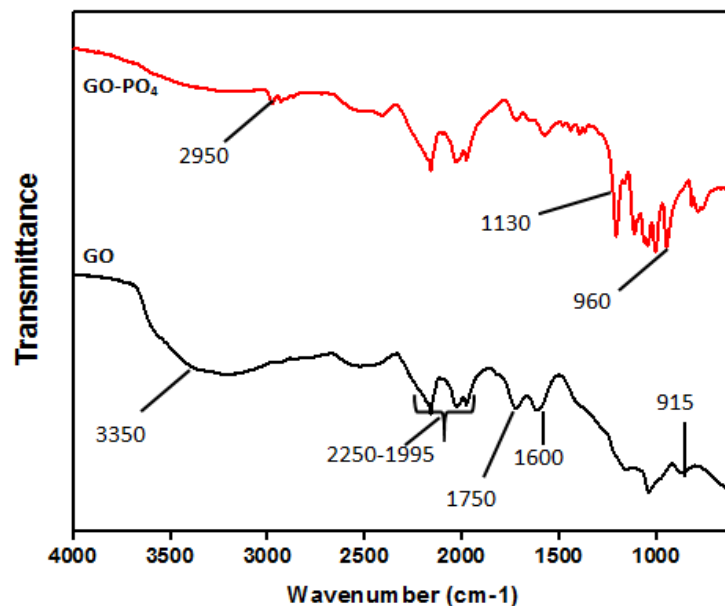


Figure 4.10: FTIR spectra of GO and GO-PO₄

C. TEM

The morphology of phosphate-functionalised graphene oxide is the same as cysteine functionalised GO with flat sheet-like structure stacked together (Appendix 3). Functionalized GO showed no obvious differences except for their darker shade due to greater stacking from crosslinking by phosphate groups. The proposed reaction scheme (Figure 4.11) suggests that phosphorylation occurs via a nucleophilic attack by triethyl phosphite on carbon electrophile e.g. epoxide groups of GO (Goods et al., 2014).

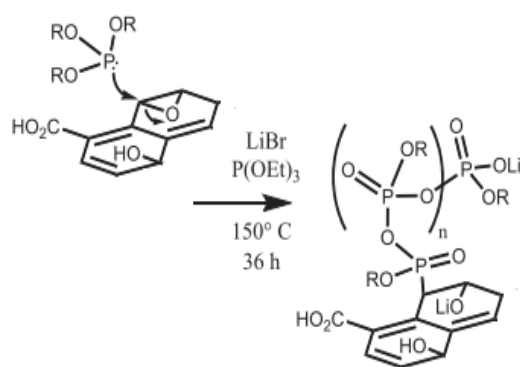


Figure 4.11: Reaction scheme for the synthesis and phosphorylation of GO

4.4 U(VI) adsorption studies

A. Effect of contact time

The effect of contact time against the removal efficiency of U(VI) by GO and GO-PO₄ was observed at pH 4 and initial concentration of 100 µg L⁻¹. As shown in (Figure 4.12), a rapid adsorption of U(VI) on GO and GO-PO₄ surface was observed for the first 20 minutes but higher for the functionalised material. The rapid increase in adsorption is known to be due to the high concentration gradient and more availability of active sites at the initial stage. During the reaction time, removal efficiencies of the adsorbents increased from 33.1 to 89.5 % for GO and 46.0 to 98.9 % for GO-PO₄. Prolonging the contact time to over 20 minutes showed no major improvement on the adsorption capacity (Figure 4.12 insert). This relatively fast adsorption equilibrium indicated either strong chemisorption or surface complexation for the adsorption of U(VI) on GO and GO-PO₄ surfaces. To prove whether the mechanism was chemisorption, kinetic models to fit the data were done. (Liu et al., 2015)

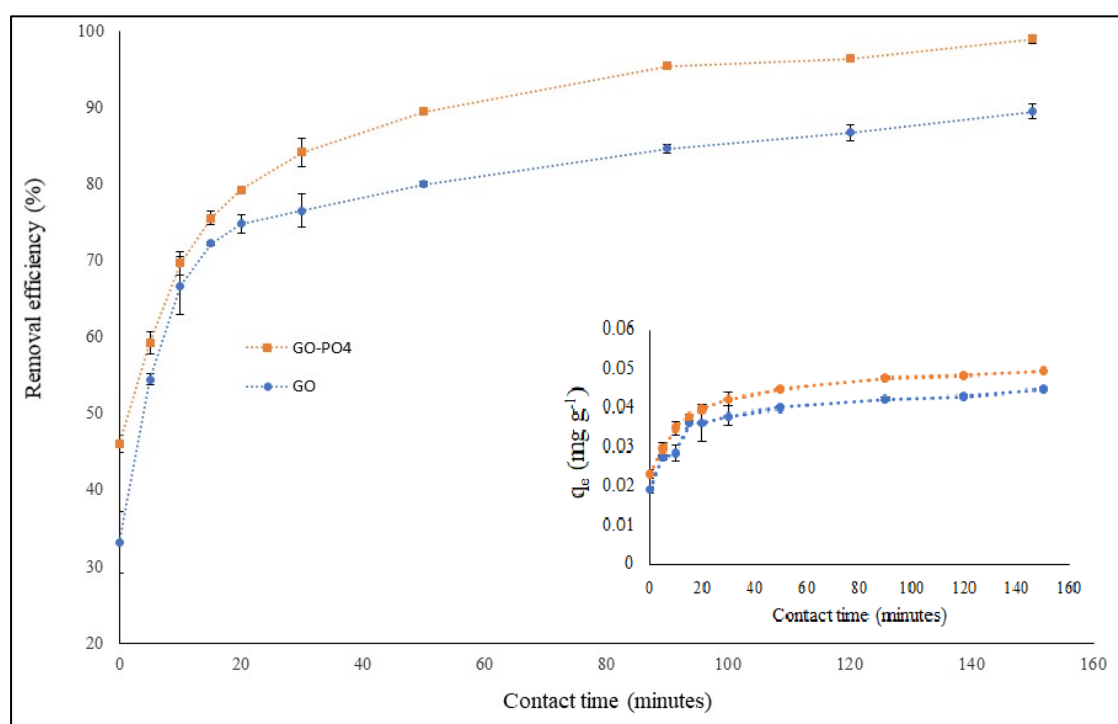


Figure 4.12: Effect of contact time on the adsorption of U(VI) ions onto GO and GO-PO₄

The data for contact time were fitted on selected models to determine mode of U(VI) removal by the adsorbents. The data for GO and GO-PO₄ showed that the mechanism of U(VI) removal followed the pseudo-second order model ($R^2 = 0.91$ and 1.00 respectively) suggesting that the mechanism of removal is by chemisorption (Table 4.4).

The mechanism of U(VI) removal is similar to several studies for removal of U(VI) by materials such as chitosan-tripolyphosphate beads (M.K. Sureshkumar et al., 2010), ferric oxide-modified zeolite (Nekhunguni et al., 2017a), phosphate-functionalized graphene oxide (Liu et al., 2015).

Table 4.4: The fit of kinetics models to data for adsorption of U(VI) by GO and GO-PO₄

Adsorbent	Pseudo-second-order			Pseudo-first-order
	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2	R^2
GO	746.55	0.0239	0.91	0.90
GO-PO ₄	566.70	0.0239	1.00	0.97

B. Effect of pH

The effect of pH on adsorption of GO and GO-PO₄ for U(VI) was examined with adsorbate solutions of 100 µg L⁻¹. The removal efficiencies increased from pH 1 to 4 and attained maximum at pH~4 (Figure 4.13). The efficiencies were higher for GO-PO₄ than GO due to the U(VI) ions binding strongly with phosphorus-related functional groups compared to carboxyl groups, this is due to the U–O–P ligand formed (Liu et al., 2015). Removal is also affected by U(VI) speciation at varying pH values. At low pH, U(VI) exists in solution predominantly as UO₂²⁺ ions (Figure 4.14), which are suited for adsorption to negatively charged surfaces provided by GO and GO-PO₄. However, H⁺ ions are also abundant at low pH, and because of their small radius, they are preferably adsorbed, hence the low adsorption at low pH. Although competition from H⁺ ions decreases with increasing pH, adsorption increases very slightly for both adsorbents above pH 4 because of the competition of available active sites between UO₂²⁺, UO₂(OH)⁺ and (UO₂)₃(OH)₅⁺ ions, so subsequent experiments were conducted at this pH.

At pH beyond 6, the adsorption efficiency decreased because from the speciation diagram in (Figure 4.14), solution pH beyond 7 results in polymerization of the hydrolysed uranyl species such as: UO₂ (OH)₃⁻, which are negatively charged and are repelled by the negatively charged surface of GO and GO-PO₄, resulting in low adsorption affinity. The optimal adsorption capacity could be attributed to precipitation, since uranium can precipitate as schoepite (UO₂ (OH)₂.H₂O (s)) which can be implicated as increased adsorption (Tutu *et al*, 2009).

A close look at the data showed that not only did phosphate functionalization increase U(VI) removal (Sandino and Bruno, 1992), GO-PO₄ also attained maximum adsorption before unfunctionalized GO. Liu et al. (2015) showed that this is because phosphate functionalization leads to a shift in the p*H*_{pzc} of GO, from pH 3 to pH 2, which results in earlier attainment of sorption equilibrium. In sum, phosphate functionalization affects U(VI) removal both due to the affinity of U(VI) ions for phosphate groups, and by modifying the adsorbent surface allowing for adsorption at even lower pH.

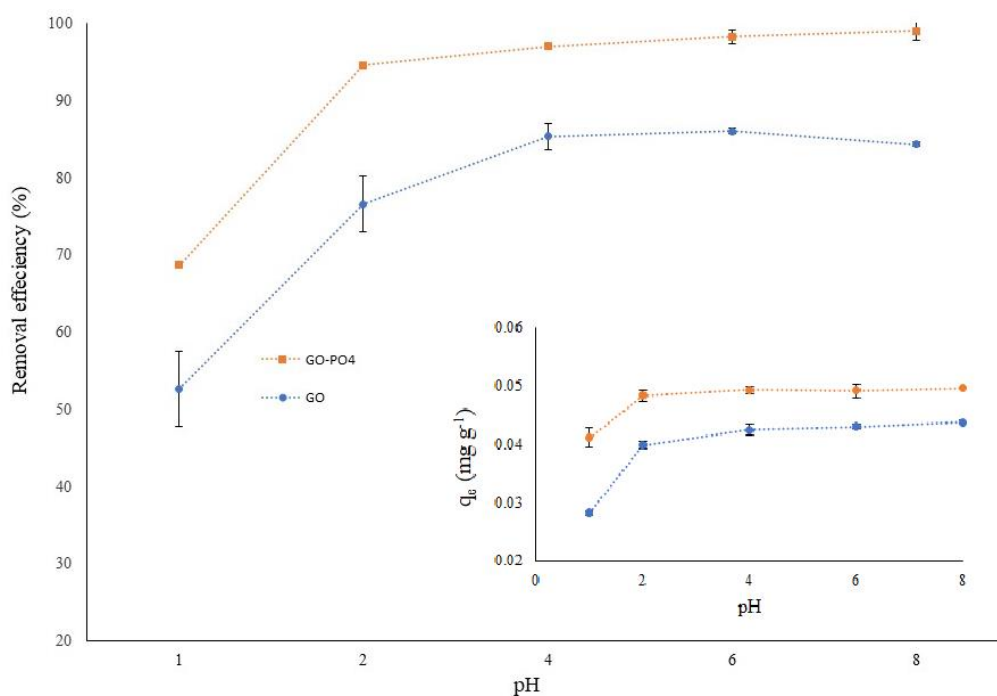


Figure 4.13: Effect of pH on adsorption of U (IV) ions onto GO and GO-PO₄

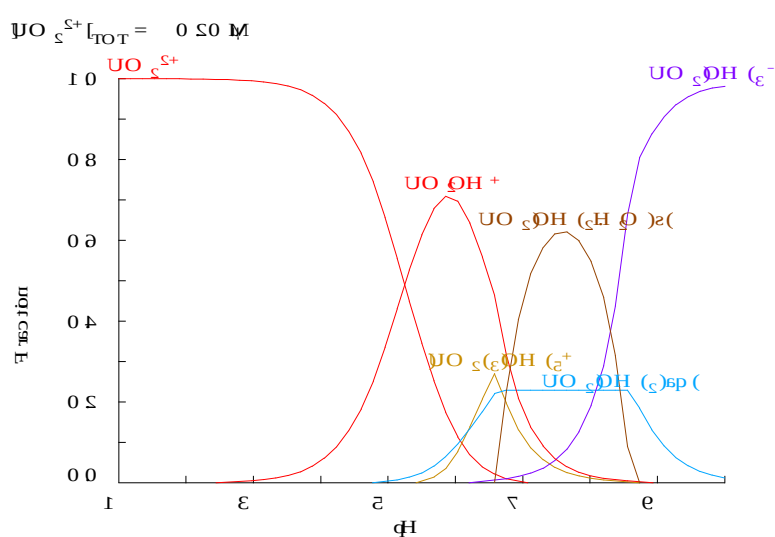


Figure 4.14: Species distribution of U(VI) through pH 1-10 at experimental concentration of 100 µg L⁻¹

C. Effect of initial concentration

U(VI) solutions of varying concentrations were exposed to 20 mg of GO or GO-PO₄ at pH 4, for 150 minutes and the effect of concentration on adsorbate performance evaluated. The results showed that phosphate functionalization generally increased removal by >30 % (Figure 4.15). Removal of U(VI) by unfunctionalized GO reached a maximum at 50 $\mu\text{g L}^{-1}$ adsorbate concentration and began to decline after this concentration. In contrast, adsorption by GO-PO₄ remained constant at ~100% even when adsorbate concentration was increased to 100 $\mu\text{g L}^{-1}$, this could be attributed to fact that the sorbent does not provide resistance for mass transfer towards solution medium (Nekhunguni et al., 2017a). Ai et al. (2018) recently showed, using density function theory calculations, that binding of U(VI) by GO occurs by electrostatic bonding with oxygen moieties of oxygen-containing functional groups. Increasing the concentration of these groups on the adsorbent surface may therefore enhance the adsorption of U(VI). Finally, there is also evidence to suggest a contribution from cation- π interactions in the bonding of positively charged ions by GO.

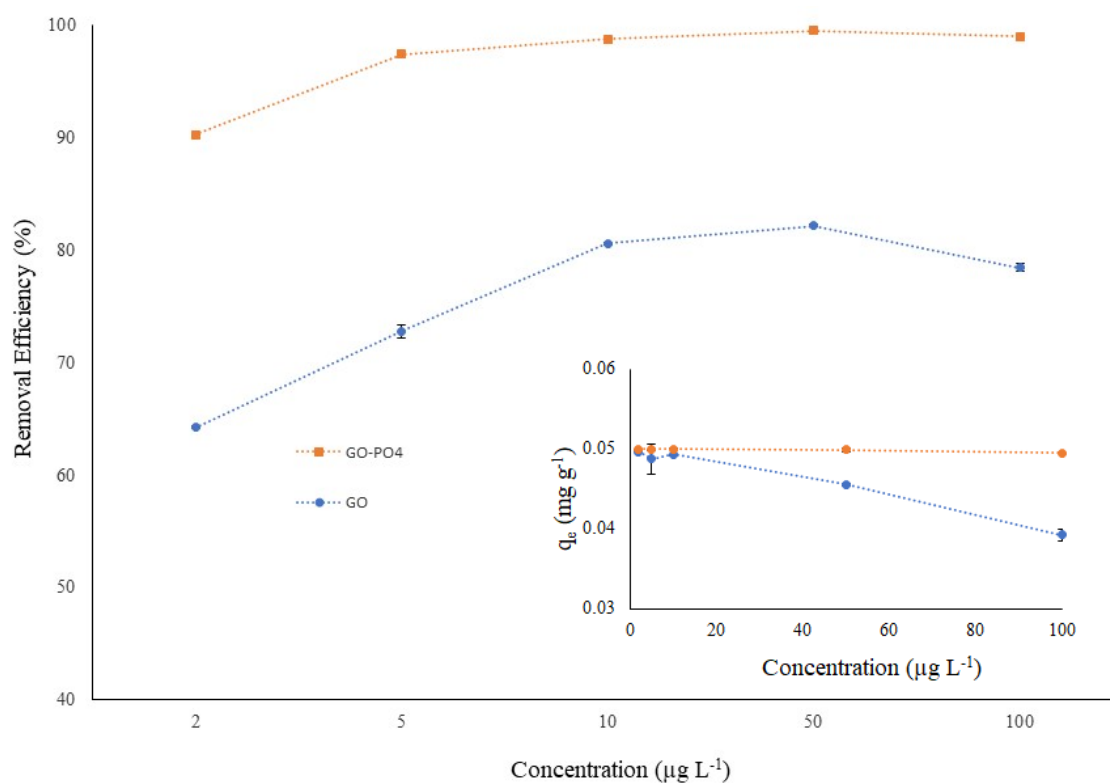


Figure 4.15: Removal efficiency of U(VI) onto GO and GO-PO₄ with change in initial concentration

The distribution of U(VI) ions onto the adsorbent surface at equilibrium is best described by adsorption isotherms. The experimental data for U(VI) adsorption by GO and GO-PO₄ were fitted with the Langmuir and Freundlich isotherms models, the model parameters for the experimental data were obtained and given in (Table 4.5). Freundlich isotherm best fitted the data ($R^2 = 0.99$ and 0.98 for GO and GO-PO₄ respectively), which could imply that adsorption of U(VI) takes place on a heterogeneous surface by multi-layer adsorption. The value of $n > 1$ showed that the adsorption of U(VI) by GO and GO-PO₄ was favourable at the operating conditions studied. The mechanism of removal was also confirmed by the mean free energy (11.5 kJ mol^{-1}) determined from the D-R model proves that chemisorption or rather chemical ion exchange is the adsorption mechanism favoured (Largitte and Pasquier, 2016; Nethaji et al., 2013).

Table 4.5: The fit of isotherm models to adsorption data

Adsorbent	Freundlich isotherm			Langmuir isotherm	
	$K_F (\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$	n	R^2	$q_m (\text{mg g}^{-1})$	R^2
GO	1.84	1.07	0.99	0.096	0.45
GO-PO ₄	2.02	1.05	0.96	0.15	0.70

4.5 Application studies

The potential of GO, rGO-SH and GO-PO₄ as adsorbents for removal of Hg (II) and U(VI) were tested on actual mine-drainage contaminated water, to evaluate their applicability in the treatment of real samples. As shown in (Figure 4.16) below, aluminium, chromium (III), arsenic (III), vanadium and magnesium, which are hard metals were better adsorbed by the rGO-SH and GO-PO₄ because of the Pearson hard-soft acid-base concept. It shows that functionalization increases adsorption of these ions because the adsorbents are hard bases due to the nitrogen groups in rGO-SH and phosphate groups in GO-PO₄. The intermediate metals such as lead, zinc, nickel and iron were removed by all three adsorbents. The softer metals like nickel and copper were better adsorbed by GO with removal efficiencies of 100 % and 90 % respectively.

All three adsorbents were able to remove U(VI) from AMD-water but the performance of GO-PO₄ was still superior to that of GO and rGO-SH. The former attained 100 % removal whereas the latter achieved 21 and 26 % removal respectively. We note, also, that for all three adsorbents, the q_e was higher in AMD than synthetic water e.g. 0.096 mg g⁻¹ versus 0.406 mg g⁻¹ for removal of U(VI) by GO, and 0.15 mg g⁻¹ versus 1.91 mg g⁻¹ for GO-PO₄. This could be explained by the presence of phosphate groups forming U-O-P ligands.

The high concentrations of Fe as iron oxides on the surface of each adsorbent could be the reason for an increased removal efficiency, it could be facilitating the adsorption of almost all the metal ions by forming Fe-metal complexes (Ulrich et al., 2006; Yoon et al., 2016).

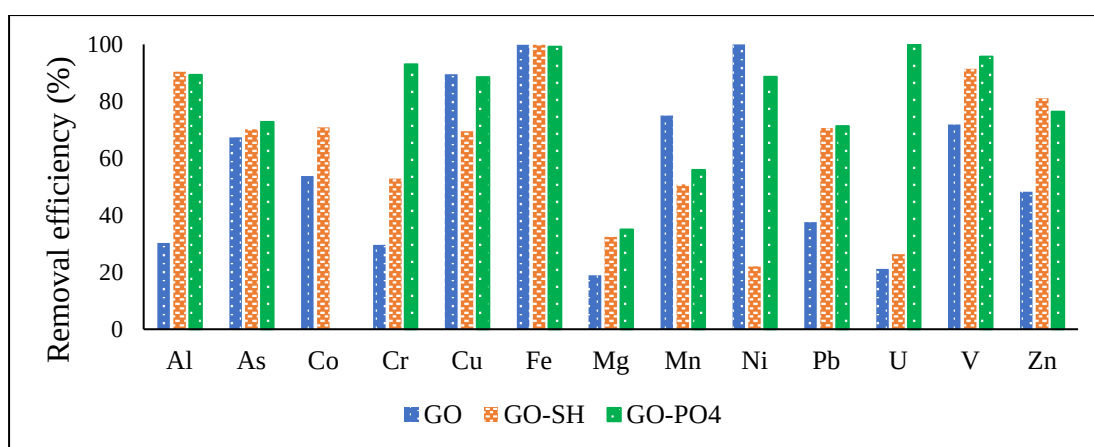


Figure 4.16: Graphene oxide and functionalised derivatives on treatment of real AMD-contaminated water

4.6 Comparison on performance between the rGO-SH and GO-PO₄ nanosheets compared to GO

Graphene oxide nanosheets and functionalized derivatives were successfully synthesised and used for adsorption of Hg(II) and U(VI) ions in aqueous solutions.

The reduction and functionalization of GO by L-cysteine was performed in a one-step synthesis and found that rGO-SH has a lower interlayer spacing because of the collapse of the graphene structure and the in-plane addition of cysteine groups. The presence of cysteine groups was confirmed by FTIR and CHNS elemental analysis, where there was C-N stretch and an increase in the nitrogen and sulphur content respectively. The adsorption studies found that rGO-SH removed Hg(II) better than GO and not only because of the added functional groups such as thiol groups which prefer to complex with Hg(II) ions but also the increased electron density from the nitrogen and oxygen groups in cysteine which can donate their lone pairs to the vacant orbitals of Hg and also the cation- π interaction played a role in the increased removal. The method for reduction has also proven to be greener and cheaper than other methods reported.

The functionalization of GO by phosphate groups for removal of U(VI) ions was also successful because of the presence of P-O and P=O groups in the FTIR spectrum and the increase in the interlayer spacing because of the nucleophilic attack of the phosphate groups on the out-of-plane epoxy groups in GO. The adsorption studies showed that GO-PO₄ adsorb U(VI) ions better than GO with ~100 % removal efficiency, this is because of GO-PO₄ is a hard base due to the phosphate groups hence it attracts UO_2^{2+} which is a hard acid. But also because of the increased amount of oxygen moieties, an electrostatic interaction is increased by forming U-O-P ligands.

In conclusion, the presence of other ions in solution like in AMD-contaminated water samples, the adsorbents performed exceptionally well with increased removal efficiencies and adsorption capacities. For example, U(VI) ions were removed by GO-PO₄ with 100 % efficiency. This shows that functionalization improves the capabilities of the adsorbents to selectively remove ions in a mixed matrix.

CHAPTER 6

Thin film nanocomposite membranes

This chapter focuses on thin film nanocomposites membranes, their performance and removal of targeted metal ions.

5 Removal of Hg(II) and U(VI) using membranes containing graphene oxide and its functionalised derivatives

This section presents results on removal of Hg(II) and U(VI) by TFN membranes functionalised with GO nanosheets and its functionalised derivatives in the PA layer. Membranes with unfunctionalized GO and functionalised GO (rGO-SH and GO-PO₄) were pressure washed with deionized water before characterisation and removal experiments, to remove excess GO. Membranes were characterised using SEM-EDX, CHNS, AFM and FTIR. Membrane performance was determined by pure water flux experiments and surface hydrophilicity by contact angle measurements. Membrane fouling resistance tests were determined using AMD-contaminated water. The membranes' removal efficiencies of Hg(II) and U(VI) were determined by investigating the effect of pH, concentration and contact time. Applications studies are also reported based on field samples of AMD-contaminated water.

5.1 Cysteine functionalized graphene oxide thin film nanocomposite membrane (rGO-SH TFN)

5.1.1 Characterisation

A. SEM

The morphology of the TFC and TFN membrane containing GO and rGO-SH is shown in Figure 5.1. (Xia et al., 2015; Yin et al., 2016). The GO-functionalised TFN membrane (Figure 5.1B) shows a leaf-like morphology formed when GO nanosheets reacted with the acyl chloride of TMC but rGO-SH functionalised membrane (Figure 5.1C) showed the nodular surface (ridge and valley morphology) found in TFC only (Figure 5.1A). The morphology improved water permeability of the membranes by increasing flux when GO and rGO-SH were added. The increase in flux is because of the channels introduced when GO and rGO-SH disrupted the polyamide layer formation. The surface of the GO and rGO-SH functionalised TFN membranes is denser than the bare TFC membrane, this behaviour is consistent with studies on the polyamide thin film membranes formed via interfacial polymerization (He et al., 2015; Xie et al., 2012).

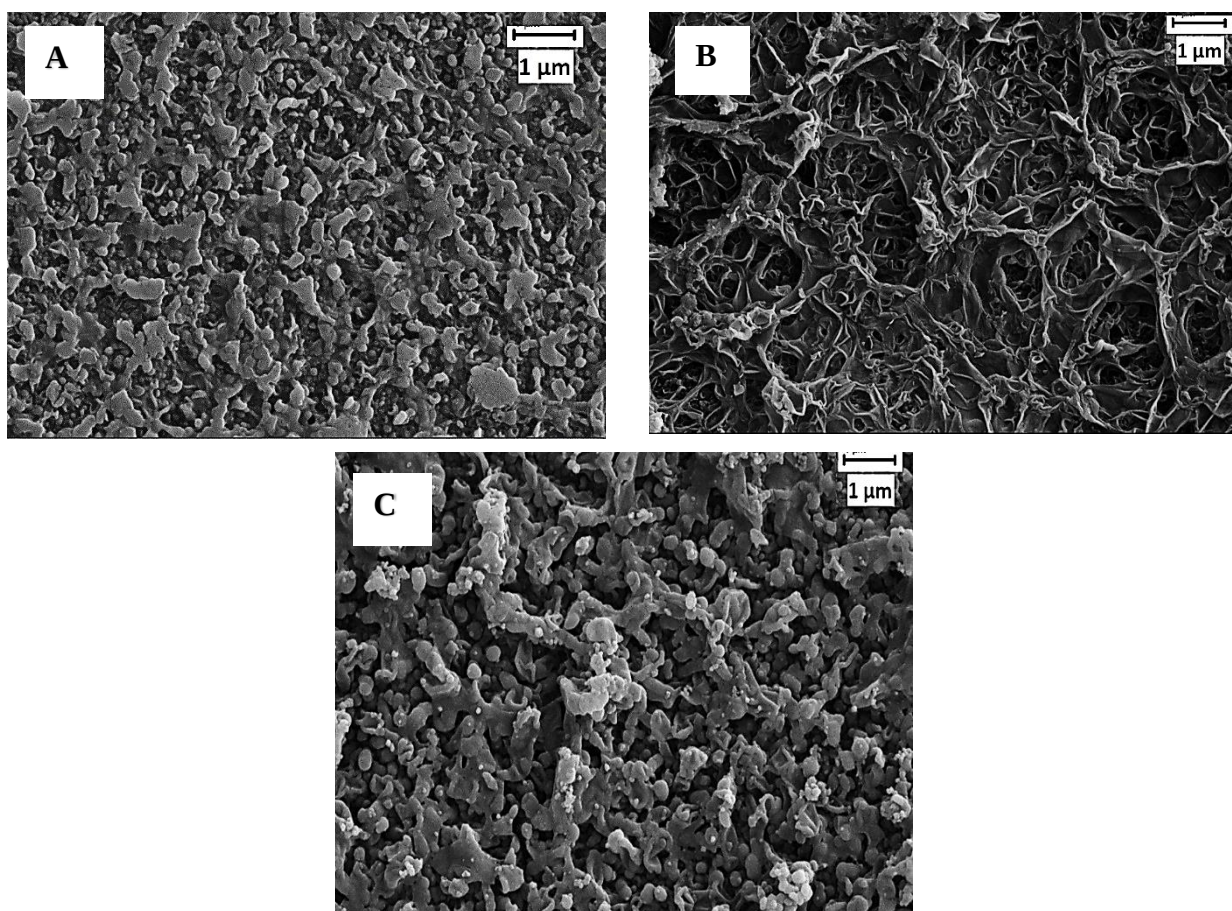


Figure 5.1: SEM-EDX of TFC (A), GO (B) and cysteine functionalised GO (C) TFN membranes

B. Elemental analysis

The elemental analysis of TFC, GO and rGO-SH TFN membranes was performed after the leaching studies and showed a decrease in the carbon and oxygen content compared to the thin film composite (TFC) membrane only (Table 5.1). The nitrogen content decreased when GO nanosheets were added, this is because GO particles disrupted the amide bond formation occurring during IP and interfered with the diffusion of MPD which forms the ridge part of the morphology. The additional percentage of carbon, hydrogen, nitrogen and sulphur for the rGO-SH TFN membrane is due to the *L*-cysteine used to functionalise GO. The increased sulphur content improved membrane performance by increasing the removal of Hg(II) ions, because sulphur is a chalcophile. The sulphur content on the TFC membrane is from the support polymer (polysulfone).

The elemental analysis only states the percentage of elements in a compound or material but not how they are bonded, hence FTIR characterisation to determine surface functional groups in the TFN membranes.

Table 5.1: CHNS results for the membrane with and without graphene oxide

Elements (%)					
Sample	C	H	N	S	O
TFC	75.4	3.02	2.70	5.98	12.9
GO TFN	71.1	5.83	1.87	5.84	15.4
rGO-SH TFN	73.2	7.03	4.07	9.61	6.11

C. Fourier Transform Infrared spectroscopy (FTIR)

Surface functional groups present in the TFN membranes were evaluated by the FTIR spectra in Figure 5.2. Peaks at 1650 cm^{-1} (amide I, C=O stretching vibrations of amide), 1547 cm^{-1} (amide II, in-plane N–H bending and C–N stretching vibrations), 1610 cm^{-1} (N–H stretching of amide), 1500 cm^{-1} (C=O stretching of acyl chloride) and $1350\text{--}1200\text{ cm}^{-1}$ (asymmetric SO_2) originated from the polyamide polymerization involving *m*-phenylene diamine and trimesoyl chloride and the support polymer (Figure 5.2C). The peaks are consistent with the existence of amide functional groups found in literature for the thin film composite membranes (He et al., 2015; Mahdavi and Rahimi, 2018; Wen et al., 2017; Yin et al., 2016). With amide peaks at for the in-plane bending C-N stretching at 1541 cm^{-1} , C=O stretching at 1660 cm^{-1} and the N-H vibration at 1609 cm^{-1} .

The amide peaks decrease in intensity (Figure 5.2B) because the amide bond of the polyamide layer is disrupted by adding GO but remains the same for rGO-SH (Figure 5.2A) because of the amide bond formed between GO and L-cysteine. The broad peak appearing at a wavenumber of 3200 cm^{-1} for (Figure 5.2B) could be assigned to the stretching vibrations of the O–H groups attached to the basal plane of GO. The functional groups improved membrane hydrophilicity and anti-fouling properties by increasing membrane uptake of water and repelling foulants from attaching to the surface.

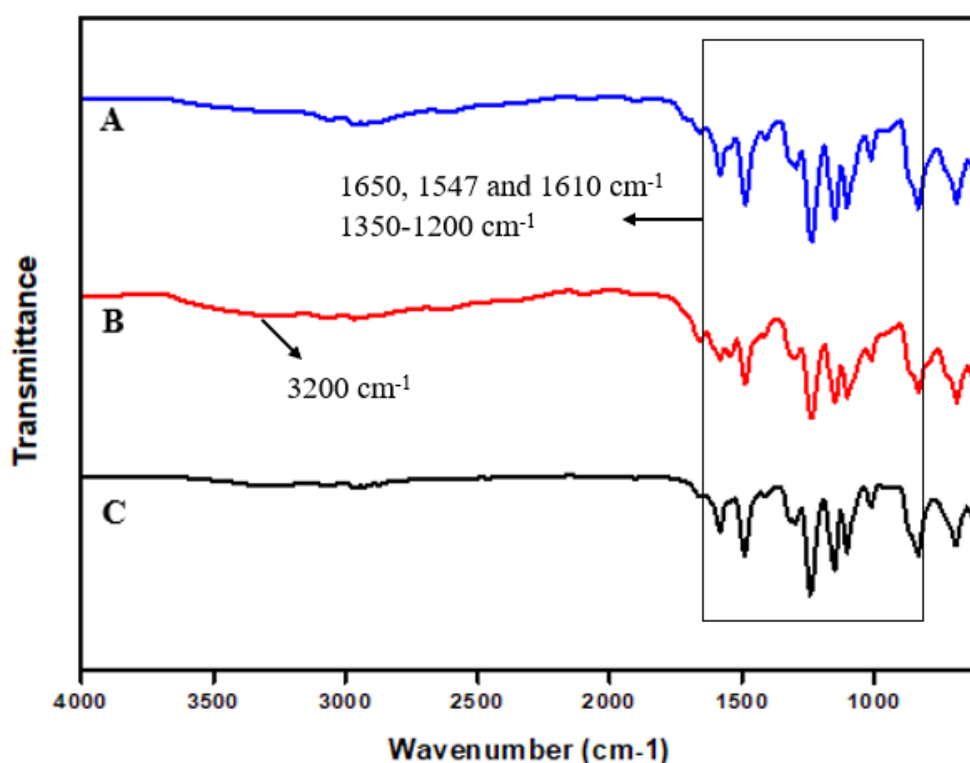


Figure 5.2: FTIR spectra of rGO-SH TFN (A), GO TFN (B), TFC (C) membranes

D. Atomic Force Microscopy (AFM)

The incorporation of GO nanosheets during the interfacial polymerization (IP) process had an impact on the membrane surface roughness and was evaluated using AFM (Figure 5.3 and Table 5.2). It was observed in (Figure 5.3) that after incorporating GO and rGO-SH nanosheets, the small ridges and valleys found in bare TFC membranes were substituted by the distinguished ridges and valleys in GO TFN and disappeared in rGO-SH TFN membranes. The morphology is consistent with what (Chae et al., 2015; Choi

et al., 2013; Mahdavi and Rahimi, 2018) found in their studies where GO and functionalised GO were incorporated.

When GO was added, it decreased the surface roughness of the TFN membrane from 232.9 nm (Table 5.2) to 177.2 nm for GO and TFC respectively. The observed results could be attributed to the interrupted diffusion of MPD into the organic layer by GO. Functionalisation of graphene oxide decreased the surface roughness further to 115.2 nm rGO-SH TFN, that could be attributed to the fact that dispersion of the functionalised GO sheets before the IP process was thorough, i.e. more sheets are present compared to only GO, and the configuration of the sheets show that they make the surface smoother and thus enhanced the membrane's anti-fouling properties. The smoother surface allowed for formation of a hydration layer that prevents hydrophobic foulants from attaching to the surface.

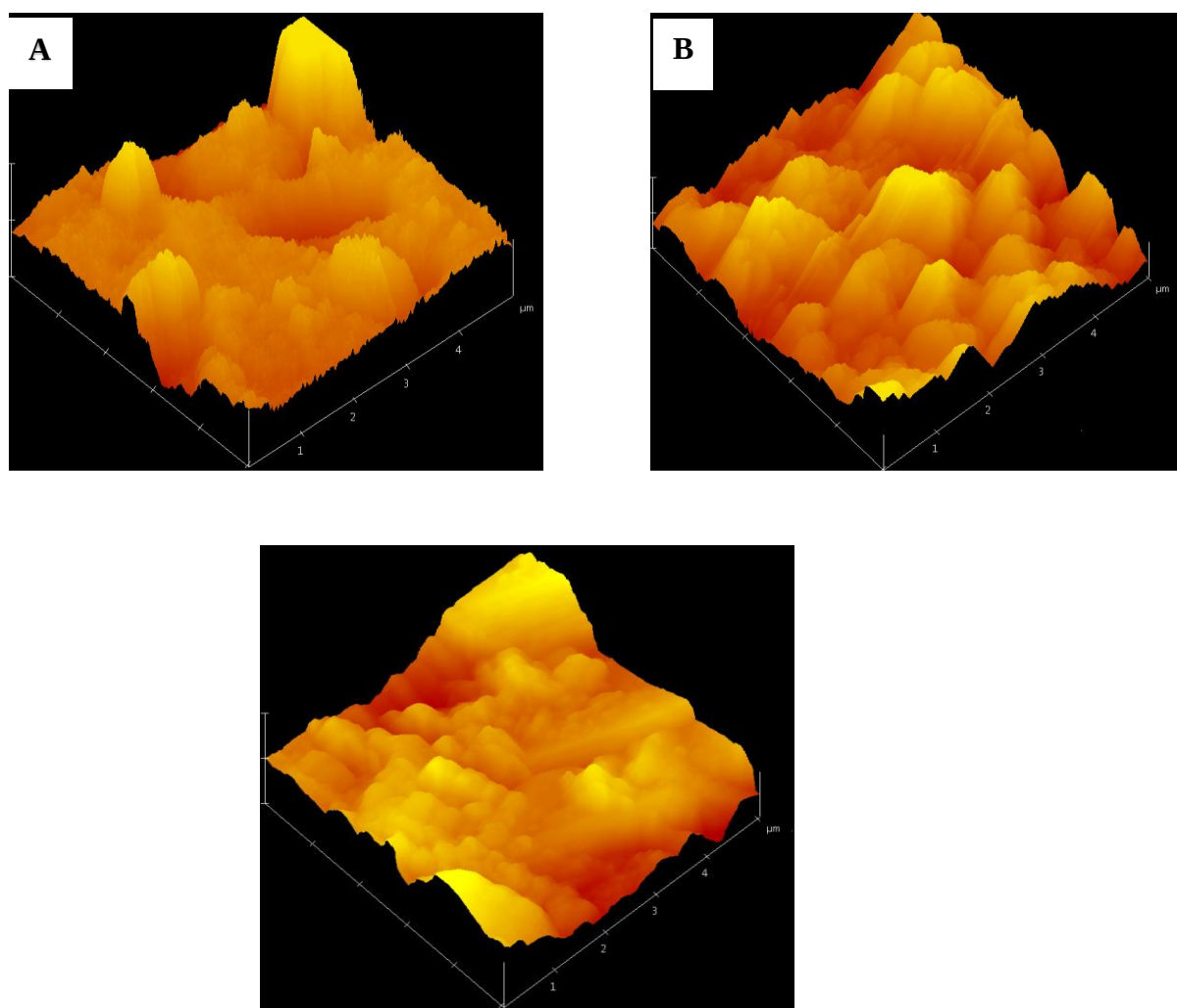


Figure 5.3: AFM image of TFC (A), GO TFN (B) and rGO-SH TFN (C) membranes showing the ridge and valley morphology

E. Contact angle

The water contact angle measurements in (Table 5.2) show a gradual decrease in angle with addition of graphene oxide and its functionalised derivatives. This means that membrane hydrophilicity is enhanced, which was proven by the permeate flux studies. The enhanced hydrophilicity is due to the hydroxylated groups found in GO and rGO-SH which provide less friction for faster flow of water molecules (He et al., 2015; Mahdavi and Rahimi, 2018; Xia et al., 2015; Yin et al., 2016).

Table 5.2: Surface roughness and water contact angle for the TFC, GO TFN and rGO-SH TFN membrane types

Membrane type	Surface roughness (nm)	Contact angle (°)
TFC	232.9	101.4 ± 5.9
GO TFN	177.2	87.8 ± 5.5
rGO-SH TFN	115.2	82.7 ± 2.3

5.2 Thin film nanocomposite membranes with GO and GO-PO₄

5.2.1 Characterisation

A. SEM

The morphology of the membrane's surface with graphene oxide (GO) and phosphate functionalized GO (GO-PO₄) is shown in Figure 4.4B and C. The membranes show an interruption of the ridge and valley surface morphology formed by the polymerisation of MPD and TMC monomers. The disruption is because of the addition of GO and GO-PO₄ nanosheets that prevent diffusion of the MPD into the organic layer. The changes are witnessed by the darkened areas on the membranes compared to the bare TFC membrane, Figure 4.4A (Xia et al., 2015; Yin et al., 2016). The GO-functionalised TFN membrane shows a leaf-like morphology formed when GO nanosheets reacted with the acyl chloride of TMC but GO-PO₄ functionalised membrane showed the nodular surface found in TFC with nanosheets embedded. Adding GO-PO₄ improved pure water flux of the membrane because the interlayer spacing of the GO-PO₄ nanosheets increased during synthesis and that provided less friction for water to flow through the membrane, i.e. more channels were created.

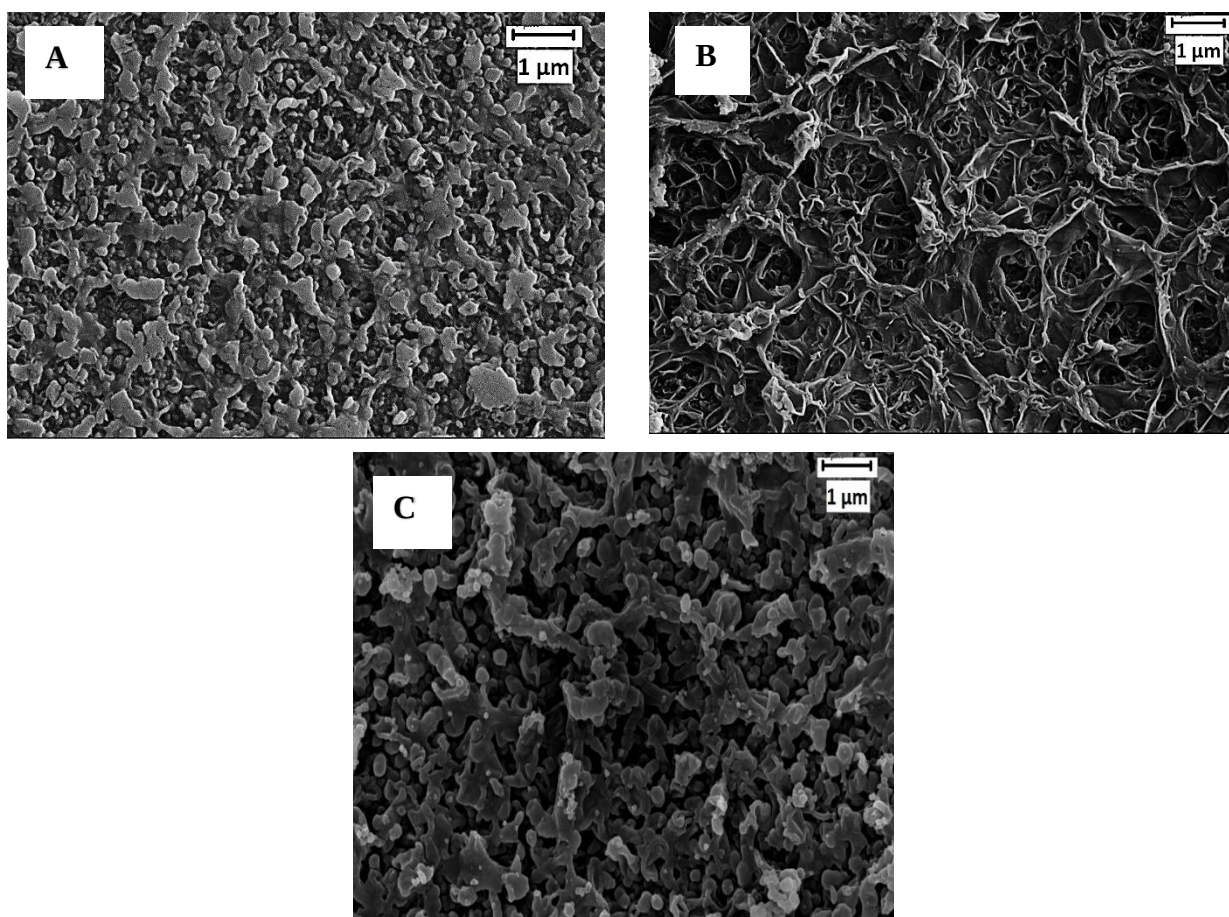


Figure 5.4: SEM-EDX of TFC (A), GO (B) and phosphate functionalised GO (C) TFN membranes

B. FTIR

Addition of GO and GO-PO₄ nanosheets on TFN membranes was confirmed by FTIR spectroscopy in Figure 5.5. Peaks at 1650 cm⁻¹ (amide I, C=O stretching vibrations of amide), 1547 cm⁻¹ (amide II, in-plane N-H bending and C-N stretching vibrations), 1610 cm⁻¹ (N-H stretching of amide) and 1500 cm⁻¹ (C=O stretching of acyl chloride) originated from the polyamide polymerization involving m-phenylene diamine and trimesoyl chloride (Figure 5.5C). The peaks are consistent with the existence of amide functional groups in a pristine thin film composite membranes (He et al., 2015; Mahdavi and Rahimi, 2018; Wen et al., 2017; Yin et al., 2016).

The amide peaks decrease in intensity (Figure 5.5A and B) because the amide bond of the polyamide layer is disrupted by adding GO and GO-PO₄. With functionalisation, the intensity of the peak at 3200 cm⁻¹ increased suggesting the number of O-H groups added has increased because of the phosphate groups. Phosphate moieties were also proven to

be incorporated in the membrane (Figure 5.5A) by showing a P-O vibration at 950 cm^{-1} and the C=O vibration that has decreased in intensity at 1450 cm^{-1} and a new peak emerged at 1750 cm^{-1} because of the phosphate groups (Ghafuri and Talebi, 2016; Liu et al., 2015; Nzihou and Sharrock, 2010). Literature reported that the C=O wavenumber shifts when phosphate groups are added and that P-O vibrations appear around 900 cm^{-1} . The hydrophilic groups that come with GO and GO-PO₄ increased permeate flux of the membranes by providing atoms for hydrogen bonding with water molecules and forming a hydration that allows water to flow through faster.

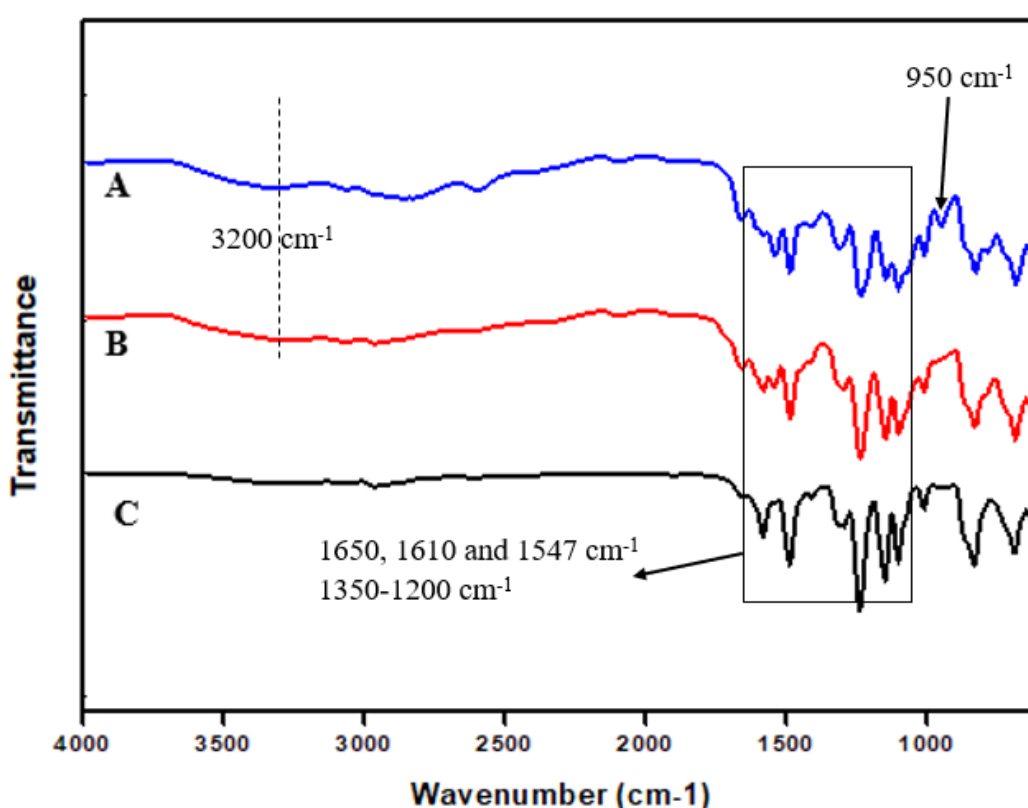


Figure 5.5: FTIR spectra of GO-PO₄ TFN (A), GO TFN (B), TFC (C) membranes

C. Atomic Force Microscopy (AFM)

The addition of GO on the TFC membrane had an impact on the membrane surface roughness, with a change when GO is functionalised. It was observed in (Figure 5.6) that after incorporating GO and GO-PO₄ nanosheets, the large ridges and valleys in bare TFC membrane (Figure 5.6A) were substituted by smaller ones. The morphology is consistent with what (Chae et al., 2015; Choi et al., 2013; Mahdavi and Rahimi, 2018) found in their studies where GO and functionalised GO were incorporated.

The incorporation of GO nanosheets decreased membrane surface roughness from 232.9 nm (Table 5.3) to 177.2 nm and 79.0 nm for GO TFN and GO-PO₄ TFN membranes respectively. Functionalisation of graphene oxide decreased the surface roughness further and that could be attributed to the fact that dispersion of the functionalised GO sheets before the IP process was thorough i.e. configuration of the nanosheets provided the decrease in roughness.

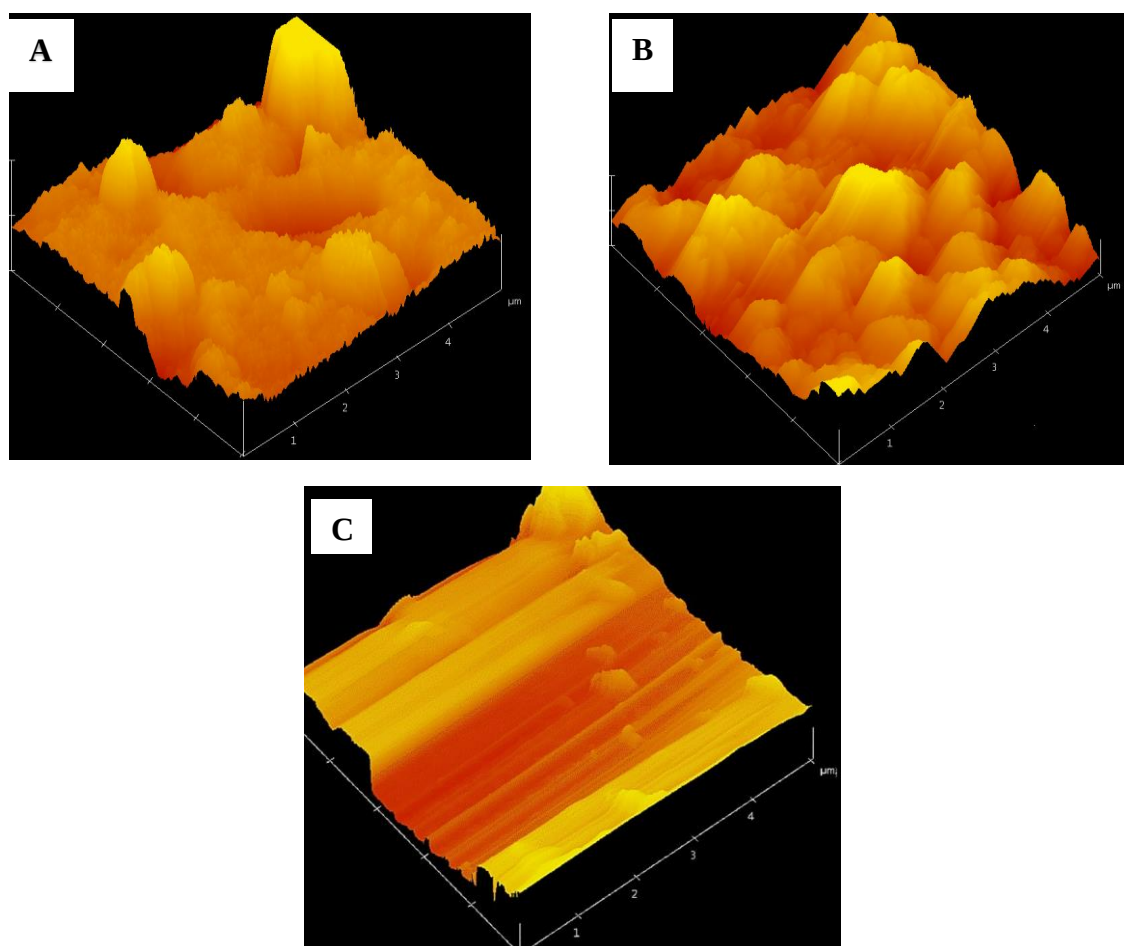


Figure 5.6: AFM image of TFC (A), GO TFN (B) and GO-PO₄ TFN (C) membranes showing the ridge and valley morphology

D. Contact angle

The water contact angle measurements in (Table 5.3) show a gradual decrease in angle with addition of graphene oxide and GO-PO₄. This means that membrane hydrophilicity is enhanced and proven by the permeate flux studies. The enhanced hydrophilicity is due to the hydroxylated and phosphate groups found in GO and GO-PO₄ which provide less friction for faster flow of water molecules (He et al., 2015; Mahdavi and Rahimi, 2018; Xia et al., 2015; Yin et al., 2016).

Table 5.3: Surface roughness and water contact angle for the TFC, GO TFN and GO-PO₄ TFN membrane types

Membrane type	Surface roughness (nm)	Contact angle (°)
TFC	232.9	101.4 ± 5.9
GO TFN	177.2	87.8 ± 5.5
GO-PO ₄ TFN	79.0	80.2 ± 3.9

5.3 Membrane performance

A. Permeate Flux

The impact of GO nanosheets on the membrane performance was evaluated by pure water permeate flux (Figure 5.7). At a constant 200 kPa ~ 15 psi feed pressure, the water flux was determined with 100 mL of deionised water that passed through the membrane and calculated the flux using (equation 14). Flux increased with functionalisation of the GO nanosheets because of the added hydrophilic functional groups. The functionalisation process in GO-PO₄ increased the lattice spacing between the sheets to provide accessible water channels and for water molecules to form a hydration layer. The flux is similar to what other studies have found in their membrane performance studies (Kim and Deng, 2011; Mahdavi and Rahimi, 2018) with an increase in water flux after nanoparticle functionalisation but decreased when nanoparticles loading was high. The significant increase in water flux for rGO-SH TFN and GO-PO₄ TFN is because of the increased hydrophilic functional groups (phosphates, thiols and amine groups), the increase in spacing between the nanosheets to provide water channels (GO-PO₄) and also functionalisation restricts GO aggregation and formation of voids between polyamide matrix and nanosheets (Mahdavi and Rahimi, 2018).

The pure water flux stability was tested after the initial flux studies to determine if the membrane continues to perform as the results suggest or the flux starts declining after 24 hours. The flux was observed to not be stable as it decreased. That can be attributed to the membrane being saturated i.e. the water molecules have saturated membrane pores or that the nanoparticles introduced in the polyamide layer are passing through and blocking membrane pores (Mahdavi and Rahimi, 2018; Yin et al., 2016, 2012).

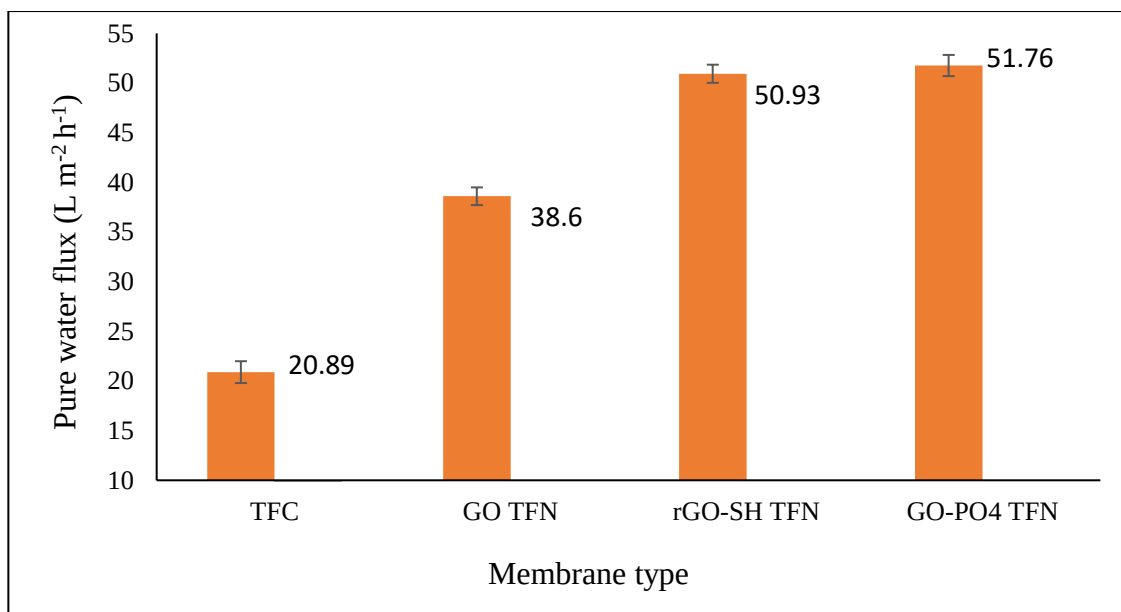


Figure 5.7: Permeate flux of TFC, GO TFN membrane and its functionalised derivatives

B. Membrane fouling

Fouling tests were conducted by using a decrease in membrane flux as an indicator over time. In (Figure 5.8), the initial flux values are lower than the pure water fluxes reported in (Figure 5.7) because of the effect of osmotic pressure difference across the membrane as feed solution is changed from deionized water to AMD-contaminated water. All the flux profiles showed to have decreased over time with the TFC membrane showing the highest reduction (from $19.35 \text{ L m}^{-2} \text{ h}^{-1}$ to $6.11 \text{ L m}^{-2} \text{ h}^{-1}$). The reason the membrane is fouling is because the bare TFC membrane has poor anti-fouling properties, i.e. no functional material introduced to prevent pore blockage and formation of a cake-layer (attachment of hydrophilic foulants), the phenomenon is also proven by the contact angle studies showing TFC membranes to have the highest water angle meaning the membrane is hydrophobic. The moderate flux reduction for GO, rGO-SH and GO-PO₄ modified TFN membranes shows that adding GO and its functionalised derivatives sufficiently suppressed the fouling process. The anti-fouling behaviour is mainly attributed to the increased hydrophilicity and smoother surface, which is provided by the hydrophilic groups from GO, rGO-SH and GO-PO₄ nanosheets. For a membrane with a hydrophilic surface, water molecules can easily adhere to the surface via hydrogen bonds, subsequently forming a thin water boundary between the membrane and bulk solution, which serves as a barrier to restrain undesirable adhesion of hydrophobic foulants on the

membrane surface (Xia et al., 2015). It can be seen that rGO-SH and GO-PO₄ modified TFN membranes have retained almost 95 % of the initial flux because the functionalised derivatives demonstrate a lesser amount of the deposited foulants but over time the flux decreased because of the concentration polarisation which forms a cake layer on the membrane surface and preventing water movement across the membrane (Machodi and Daramola, 2019)

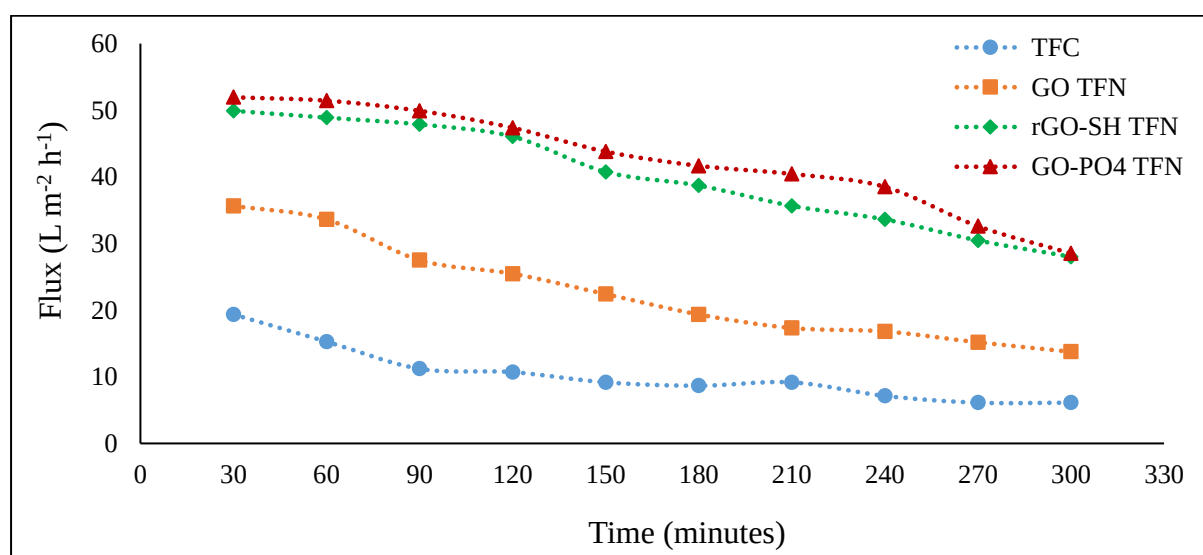


Figure 5.8: Fouling tests for TFC, GO TFN membranes and its functionalised derivatives

5.4 Removal of Hg(II) by TFN membranes with GO and rGO-SH

A. Effect of contact time

The effect of contact time on removal of mercury ions by TFC, GO and rGO-SH functionalized TFN membranes was investigated at pH 4 and reported in (Figure 5.9). The removal efficiency rapidly increased with increase in contact time from 0 to 20 minutes with removal efficiencies of (32, 91 and 95 % respectively) and reaches equilibrium (maximum) after 30 minutes in which there is no increase. The amount of Hg(II) adsorbed on TFC, GO and rGO-SH membranes is very rapid within first 20 minutes. In this case, the initial removal step makes mercury ions contact quickly with a lot of available active sites on the membrane. It can be noted that the adsorption behaviour of mercury on TFC, GO and rGO-SH modified membranes is similar but the efficiency for rGO-SH membrane is higher than GO TFN and bare TFC, this is due to the added S-H, amine and carboxyl functional groups on the surface of rGO-SH nanosheets than GO. The adsorption capacity for the membranes is two times or more of the particles and that can be attributed to the fact that when TFC membranes are functionalized with nanoparticles, more water channels are created and that facilitates the movement and permeability of ions through the membrane with improved interaction with the functional groups (Cui et al., 2014; Liu and Xu, 2016a; Yin et al., 2012). And, at the experimental pH, the surface of the membrane is negatively charged therefore electrostatic attraction between the cations and functional groups takes place.

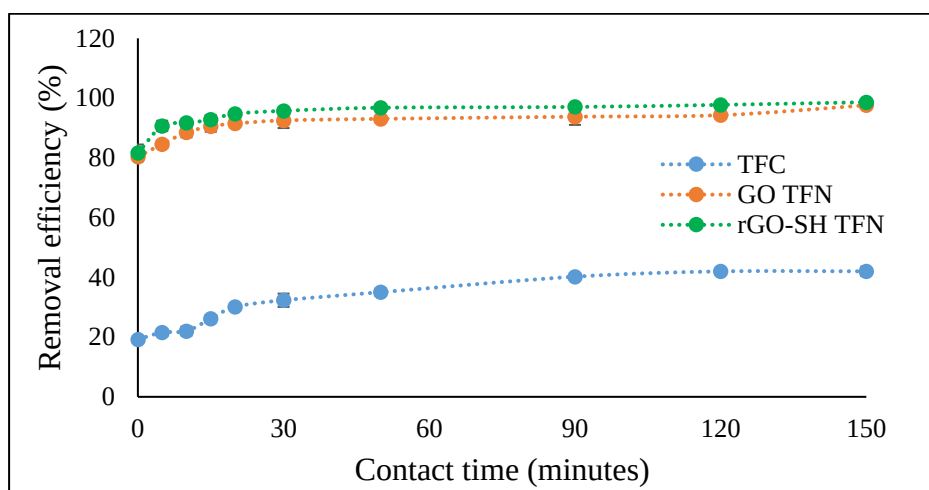


Figure 5.9: Effect of contact time on the adsorption of Hg(II) ions onto TFC, GO and rGO-SH functionalized TFN membrane

B. Effect of pH

The effect of pH on removal of Hg(II) ions by TFC, GO and rGO-SH functionalized thin film nanocomposite membranes is shown in (Figure 5.10). Mercury removal remained constant at ~100 for GO and rGO-SH functionalized thin film nanocomposite membranes than the TFC membrane from pH 2. The reason for the low removal at pH < 2 is because of the protonation of the functional groups present on the surface of the membrane hence they repel the dominant mercury species (Hg^{2+}) at this pH. The increase to ~100 % rejection at pH ≥ 2 is because of the electrostatic attraction between the Hg^{2+} ions and the negatively charged surface and from size exclusion of the hydroxide species i.e. HgOH^+ and $\text{Hg}(\text{OH})_2$. The continued increase in removal at pH > 6 can be attributed to adsorption and precipitation of the hydrolysed species, $\text{Hg}(\text{OH})_2$ (Chandra and Kim, 2011; Etale et al., 2014; Saad and Cukrowska, 2013).

The relatively low removal efficiency of Hg(II) ions by TFC membrane is because the membrane has no additional functional groups brought by nanoparticles to facilitate adsorption and the pore size of the membrane allows Hg(II) species to pass through.

There is no change in adsorption efficiency of Hg(II) ions at low pH values (Figure 5.10) for GO functionalised TFN membranes because the membrane is a nanofiltration-type membrane with pore size of 137 nm where it allows hydrogen ions, which are monovalent ions to pass through compared to Hg(II) ions, which are divalent and bigger in size, therefore no competition with the active binding sites (Azelee et al., 2017; Chen et al., 2017; Dong et al., 2016; Vieira et al., 2007).

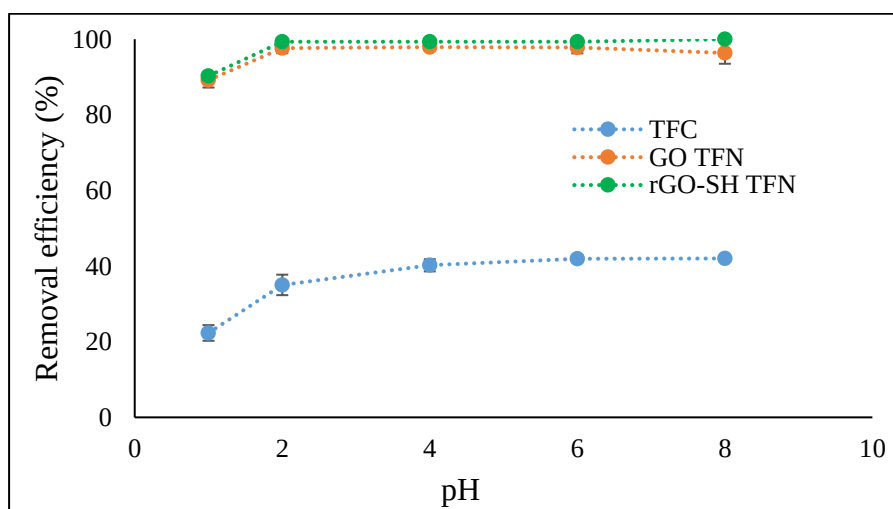


Figure 5.10: Change in pH on removal efficiency of Hg(II) ions onto TFC, GO and rGO-SH functionalized thin film nanocomposite membrane

C. Effect of initial concentration

Hg(II) solutions of varying concentrations from 2 to 100 $\mu\text{g L}^{-1}$ at pH 4 were subjected to TFC, GO and rGO-SH functionalized TFN membranes and the effect evaluated in (Figure 5.11). From the figure, the removal efficiency increased with increasing Hg(II) ion initial concentration, from 0.5-32, 5-84 and 73-97 % for TFC, GO and rGO-SH functionalized TFN membranes respectively. This is because the higher the initial Hg(II) ion concentration, the higher the driving force of the concentration gradient at solid-liquid interface which causes an increase in the amount of Hg(II) ions adsorbed on the functionalised membrane. With more Hg(II) ions present in solution, a larger fraction of the active sites is involved in the adsorption process. In addition to the fact that Hg(II) is sulphur-loving ion, Krishna Kumar et al, (2016) recently showed that binding of Hg(II) via surface complexation by GO occurs via electron pair sharing with oxygen moieties of oxygen-containing functional groups. Increasing the concentration of these groups such as thiols and amides found in rGO-SH and the polysulphone support polymer increases the chances of lone pair sharing with Hg(II).

The removal efficiency shows saturation at high concentrations because of the hydration layer formed between the membrane and bulk solution, thus increased rejection of Hg(II) ions (Vincenzo et al., 2017; Wan Azelee et al., 2017).

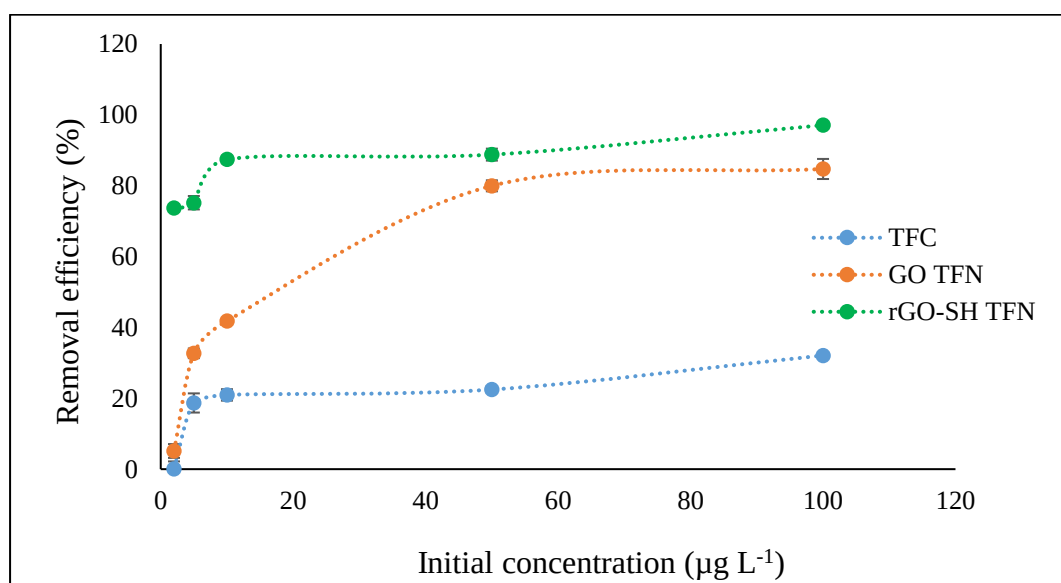


Figure 5.11: Removal efficiency of Hg(II) by TFC, GO and rGO-SH TFN membranes against concentration effect of Hg(II) ions.

5.5 Removal of U(VI) by TFN membranes with GO and GO-PO₄

A. Effect of contact time

The effect of contact time on the removal efficiency of U(VI) was observed and shown in (Figure 5.12). A rapid adsorption of U(VI) on bare TFC, GO and GO-PO₄ functionalized TFN membrane surface was observed and showed an increase from 16-63 % and 41-93 % for TFC and GO TFN membranes after 30 minutes, while for GO-PO₄ functionalized TFN membrane it was from 41-98 % after 5 minutes. The rapid increase in adsorption can be attributed to a high concentration gradient and more vacant active sites for adsorption. Prolonging the contact time to over 30 minutes showed no major improvement on the removal efficiency and hence chosen to be time at which U(VI) adsorption reached pseudo-equilibrium. The extremely fast reach in equilibrium for the GO-PO₄ functionalized TFN membrane compared to the other two membrane types is because of the phosphate groups present from the GO-PO₄ nanosheets in which U(VI) has a high affinity towards them (M. K. Sureshkumar et al., 2010)

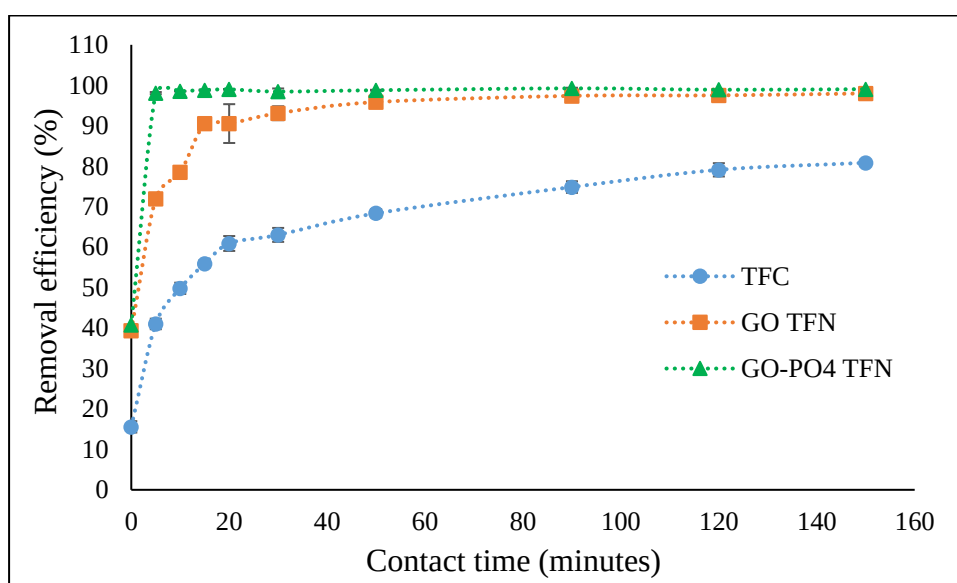


Figure 5.12: Effect of contact time on the removal of U(VI) ions by GO and GO-PO₄ functionalized TFN membranes

B. Effect of pH

The influence of solution pH on the adsorption of U(VI) by TFC, GO and GO-PO₄ functionalized thin film nanocomposite membranes is illustrated in (Figure 5.13). The removal efficiencies from pH 1 to pH 4 and then reached a plateau with efficiency of 51, 83 and 98 % for TFC, GO and GO-PO₄ membranes respectively. Solution pH affects the

adsorption mechanism of U(VI) through hydrolysis by varying the species of uranyl ions present. At lower pH values, uranium is present in solution as UO_2^{2+} ions, hence the low rejection. The reason is because at $\text{pH} < 2$, there is protonation of the functional groups on the surface of the membrane hence they repel the dominant uranyl species (UO_2^{2+}) at this pH. The increase to $\sim 100\%$ rejection at $\text{pH} \geq 2$ is because of the electrostatic attraction between the UO_2^{2+} ions and the negatively charged surface and from size exclusion of the hydroxide species i.e. $\text{UO}_2(\text{OH})^+$, $\text{UO}_2(\text{OH})_2^{2+}$. The continued increase in removal at $\text{pH} > 6$ can be attributed to the attraction of the positively charged species, precipitation of the hydrolysed species as schoepite ($\text{UO}_2(\text{OH})_2$) and repulsion of the polymerized hydrolysed uranyl species such as: $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2)_3(\text{OH})_7^-$ which are negatively charged and supposed to be repelled by the negatively charged surface of GO and GO- PO_4 membranes. The efficiencies were higher for GO- PO_4 membrane than the TFC and GO membranes due to the U(VI) ions binding strongly with phosphorus-related functional groups compared to carboxyl groups, this is due to the U–O–P complex formed (Liu et al., 2015)

The relatively low removal efficiency and adsorption efficiency of U(VI) ions by TFC membrane is because the membrane has no additional functional groups brought by nanoparticles to facilitate adsorption and the pore size of the membrane allows $\text{Hg}(\text{II})$ species to pass through.

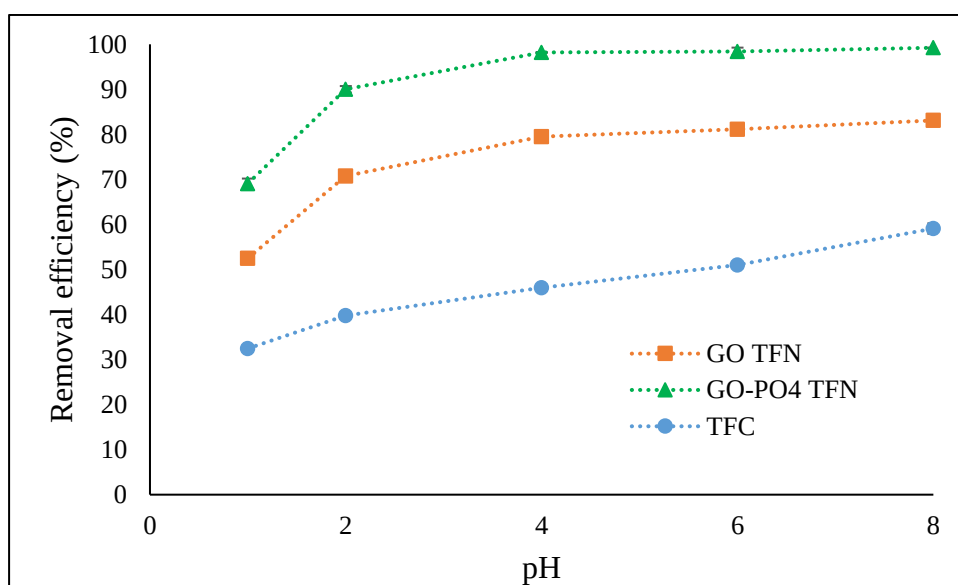


Figure 5.13: Effect of change in pH on removal of U (IV) ions by GO and GO- PO_4 functionalized thin film nanocomposite membranes

C. Effect of initial concentration

The varying removal efficiencies of U(VI) by TFC, GO and GO-PO₄ functionalized TFN membranes with change in initial U(VI) concentration is shown in (Figure 5.14). The results showed that functionalisation of the membrane with GO and GO-PO₄ nanosheets increased removal efficiency by ~85 % this could be attributed to fact that the membranes have more available active sites for interaction with U(VI) ions compared to the bare TFC membrane. This is attributed to the fact that GO and GO-PO₄ have electron rich groups such as COOH and PO₄, etc. that can donate their lone pairs to the vacant orbitals of the metal ions for metal coordination and also the double bonds present in GO and GO-PO₄ allow for cation- π interactions of the positively charged ions (Ai et al., 2018; Liu and Xu, 2016b).

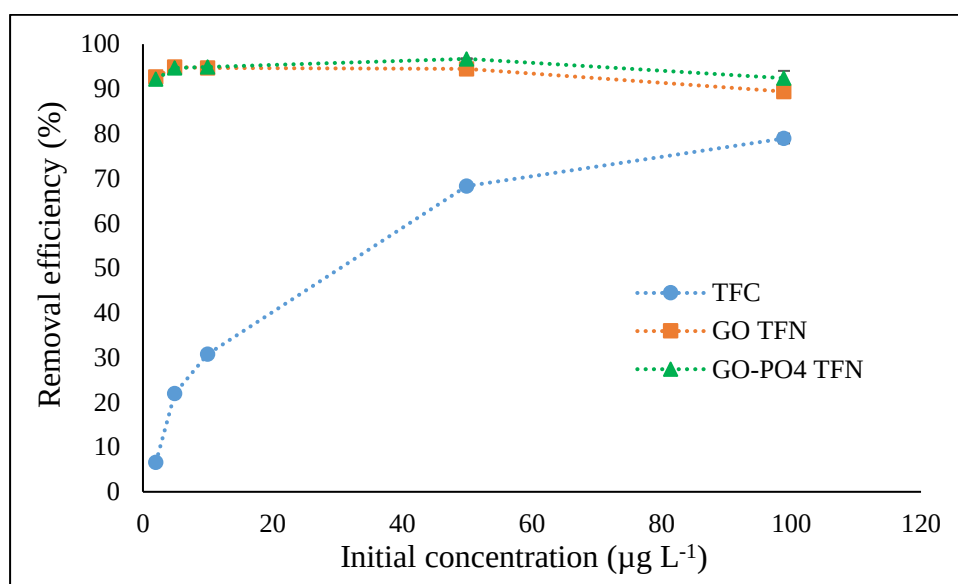


Figure 5.14: Removal efficiency of U(VI) onto GO and GO-PO₄ functionalized TFN membranes with change in initial concentration

5.6 Application studies

The ability of TFC, GO, rGO-SH and GO-PO₄ TFN membranes as adsorbents for removal of Hg (II) and U(VI) were tested on actual mine-drainage contaminated water, to evaluate their applicability in the treatment of real samples. As shown in Figure 5.15 below, almost all the metal ions were removed with high removal efficiencies except for Fe, Mg and Mn. The reason for the high rejection could be an electrostatic repulsion between the cations and the membrane surface, where at low pH values the functional groups present from graphene oxide and derivatives as NH, COOH, OH, SH are

protonated therefore the membrane surface becomes positively charged thus repels the cations in solution (Machodi and Daramola, 2019). Some metal ions in solution tend to exist as metal oxides e.g. UO_2^{2+} , so their ionic radii might be bigger than the membranes' pore sizes thus size exclusion can be the cause for the high rejection observed.

The other reason could be the interaction between ions and functional groups according to the Pearson's hard-soft acid-base (HSAB) theory. Where aluminium, chromium (III), arsenic (III), vanadium, magnesium and uranium, which are hard metals were better rejected by the rGO-SH and GO- PO_4 functionalized membranes. The removal efficiencies were ~100 % because rGO-SH and GO- PO_4 nanosheets are harder bases than GO. The softer metals like nickel and copper were better adsorbed by GO with removal efficiencies of 100 % and 92 % respectively.

And also, metal ion complexes are highly probably due to the functional groups present in the nanosheets embedded on the polyamide layer, which are electron rich, therefore electron pair sharing is likely to happen between the lone pairs on the functional groups and the vacant orbitals present in metal ions

All four adsorbents were able to remove U(VI) from AMD-contaminated water but the performance was the same for all functionalized membranes, with 100 % removal. We note, also, that for all four adsorbents, the q_e was higher in AMD than synthetic water e.g. 0.096 mg g^{-1} versus 0.406 mg g^{-1} for removal of U(VI) by GO, and 0.15 mg g^{-1} versus 1.91 mg g^{-1} for GO- PO_4 . This could be explained by the presence of phosphate groups forming U-O-P ligands. Hg(II) concentrations in the AMD-contaminated water were below the detection limit of the instrument.

The observed trend is not the same as for the particles adsorption and that might be because iron didn't form oxides with graphene oxide due to the limited number of available sites and because graphene oxide was immobilised on a support polymer.

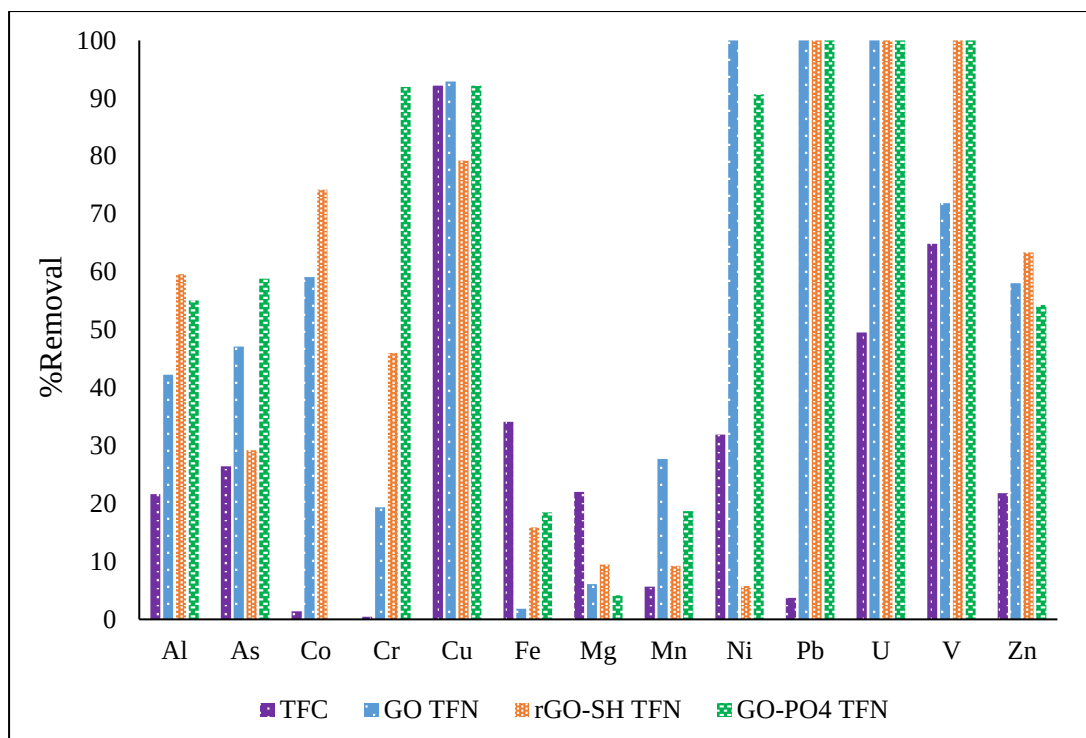


Figure 5.15: Removal of metal ions from AMD-contaminated water samples by functionalized graphene oxide thin film composite membranes.

5.7 Comparison on performance between the rGO-SH and GO-PO₄ thin film nanocomposite membranes

The functionalized thin film composite membranes were successfully synthesised and used for removal of Hg(II) and U(VI) ions in aqueous solutions.

The synthesised functionalised membranes showed a difference in the FTIR analysis the presence of P-O vibrations at 950 cm^{-1} for GO-PO₄ and an increase in intensity for the C-N bond and N-H bend at 1547 cm^{-1} and 1610 cm^{-1} respectively for rGO-SH TFN membranes. The surface hydrophilicity of the membranes showed to have increased when GO was functionalised with cysteine and phosphate groups, because the water contact angle increased from 87.8° for GO TFN to 82.7° and 80.2° for rGO-SH and GO-PO₄ TFN membranes respectively, these were proven by the increase in flux values reported.

Functionalisation of the nanosheets showed to improve membrane performance by decreasing the rate of membrane fouling. This is because of the decrease in contact angle and surface roughness i.e. smoother surface, this improved the hydrophilic character of the membranes by preventing attachment of foulants and that was due to the hydration

layer formed by hydrogen bonding between the water molecules and the hydrophilic groups from GO, rGO-SH and GO-PO₄.

The adsorption studies found that rGO-SH functionalised membranes removed Hg(II) better than GO and TFC membranes and not only because of the added functional groups such as thiol groups which prefer to complex with Hg(II) ions but also the increased electron density from the nitrogen groups in cysteine which can donate their lone pairs to the vacant orbitals of Hg for metal coordination and also the cation- π interaction played a role in the increased removal. The adsorption studies for U(VI) showed that GO-PO₄ membranes removed U(VI) ions better than GO and TFC membranes with ~100 % removal efficiency, this is because of GO-PO₄ TFN membranes are negatively charged on the surface at the experimental pH that attracts UO₂²⁺ ions. Size exclusion of the metal-oxide and hydroxides species in solution also played a role in the observed removal efficiency.

In conclusion, with the presence of other ions in solution like in AMD-contaminated water samples, the membranes reported an increase in removal efficiencies. For example, U, Cu, Ni, Pb and V ions were removed by the functionalised GO membranes with 100 % efficiency. This shows that several factors such as size exclusion for metal oxides, HSAB theory, electrostatic interaction and cation- π interactions are responsible for the high efficiency observed compared to nanosheets application studies.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

This chapter summarizes the findings reported in chapter 5 and 6, re

6 Conclusions and Future work

This chapter summarizes the findings made in this research with respect to the objectives of the study.

6.1 The effect of nanosheets functionalization on removal efficiency

The GO nanosheets were synthesized and characterized by TEM, CHNS, FTIR and XRD. The functionalization process of adding cysteine to GO with aid from a crosslinker, EDC, was successful and the characterization results showed the C-N and SH groups in FTIR and a decreased interlayer spacing with high 2θ because cysteine acted both for functionalization and reduction of GO. Phosphate groups were added and the P=O and C-O-P groups for the phosphate functionalized GO were present in FTIR spectra and the interlayer spacing increased with low 2θ value.

The potential for the synthesized nanosheets to remove Hg and U ions from AMD-contaminated water was examined. The effects of the investigated factors affecting metal adsorption by nanosheets at pH 4 can be summarized as:

Contact time: The metal ions investigated showed a rapid removal and reached equilibria within the first 30 minutes. The kinetics data were best fitted by the pseudo-second order model implying that adsorption of metal ions was via chemisorption. The results showed that removal efficiency is higher after functionalization because for Hg and U removal, the efficiency by GO nanosheets was ~75% and by functionalised GO nanosheets ~85%.

Metal concentrations: Metal ion uptake increased with increasing metal concentration from 2-100 $\mu\text{g L}^{-1}$ and reached equilibria at 50 $\mu\text{g L}^{-1}$ after which there was a decrease. The adsorption isotherms were best described by the Freundlich model implying that adsorption of Hg and U took place on a heterogeneous surface.

pH: Adsorption of Hg and U was also investigated at pH 1, 2, 6 and 8. Metal ions investigated reported an increase in removal of Hg at 40% for pH 1 to 75% and 77% at pH 4, 6 and 8 respectively for GO nanosheets. Functionalization with cysteine further increased the removal from 60% at pH 1 to 88%, 86% and 85% at pH 4, 6 and 8 respectively. For removal of U by GO nanosheets, the reported results showed an increase from 50% at pH 1 to 85%, 86% and 84% at pH 4, 6 and 8 respectively. After functionalization with phosphate groups, the removal efficiencies increased further from

70% at pH 1 to 97%, 98% and 99% at pH 4, 6 and 8 respectively. The reasons for the increase in both adsorbents are:

- i. Hydrolysis of the metal ions occurred at higher pH values
- ii. Functionalization of GO nanosheets provided more active sites for adsorption.

Application to field samples: The application of functionalised nanosheets to AMD-contaminated surface water samples followed the simulated wastewater trends with higher increase in removal i.e. 100% efficiency for U by GO-PO₄. The results showed greater removal for U because of Fe present in water, in which it can form iron oxides that attach themselves on the surface of nanosheets facilitating metal ion adsorption, hence increasing efficiency. The presence of other ions showed no difference to the removal efficiencies.

6.2 The effect of GO nanosheets on metal uptake by TFN membranes

Thin film nanocomposite membranes of this study were synthesized via the phase inversion method for the support polymer and interfacial polymerization for the thin film layer with addition of graphene oxide nanosheets and its functionalised derivatives. The characterization of the membranes was done by SEM, FTIR, AFM and Contact angle. Membrane performance was also evaluated by investigating permeate flux and fouling resistance.

The bound GO on the membranes was confirmed by FTIR by showing a broad peak of O-H from GO and a decrease in the amide peak intensity implying that adding GO and its functionalised derivatives disrupted the thin film layer formation. The nanosheets also affected the surface of the membranes by making the membrane smoother, which was confirmed by AFM.

A. Membrane performance

The impact of GO nanosheets on membrane performance showed that pure water flux increased when GO was introduced from 21 to 39 L m⁻² h⁻¹ and increased further to 51 L m⁻² h⁻¹ with the functionalised GO derivatives (rGO-SH and GO-PO₄). The reason for the spiked increase was because of the hydrophilic groups found in GO and its functionalised derivatives, that allowed for the formation of hydration layer, the increase in lattice spacing for GO and GO-PO₄ and that functionalization restricts GO

aggregation. Fouling tests were conducted and showed that adding GO nanosheets decreased the rate of fouling because of the hydrophilic surface that formed water boundaries between membrane and bulk solution, serving as a barrier to restrain foulants.

B. Application of membranes to field samples

The membranes showed >60% removal for many ions found in AMD-contaminated surface water samples. The effect showed that many ions exist as metal oxides, so their ionic radii might be bigger than the membranes' pore sizes thus size exclusion may be the main reason for the high removal experienced. The observed trend was not the same as for particles adsorption and that might be due to iron not forming oxides with the mobilized nanosheets.

From this study of thin film nanocomposite membranes for removal of Hg and U, concerns for the stability of the bound nanoparticles led to leaching studies which showed that GO nanosheets leach out to a certain degree. This might lead to investigating strategies that will strengthen the bond between nanoparticles and membranes, which will be impervious to changes in pH. Another strategy will be to look at the optimum concentration of nanoparticles to optimize stability, which might be the cause for the leaching.

6.3 Conclusions

The aim of the study for removal of Hg and U ions from synthetic and real water samples by using (i) graphene oxide nanosheets and its derivatives and (ii) thin film nanocomposite membranes functionalized with graphene oxide and derivatives was achieved because the synthesized nanosheets and the fabricated thin film membranes were successfully characterized.

One of the research questions about the stability of GO nanosheets in the polymer matrix of the TFN membranes was answered by the leaching studies, where GO leached out initially but decreased in concentration as volume of permeate increased.

The adsorption studies showed that functionalization increased removal of Hg(II) and U(VI) ions in solution with ~100 % efficiency for both particles and membrane adsorbents but statistically, there was no difference in removal between GO and functionalized GO nanosheets and membranes, however the adsorption capacities were higher for the membranes compared to the nanosheets for adsorption of Hg(II) and U(VI).

Both adsorbents performed exceptionally well in the presence of other ions in solution like in real AMD-contaminated water samples for removal of U(VI) with other metal ions, however the removal of other metal ions with same efficiency as U(VI) proves that the nanosheets and TFN membranes are not selective towards target metals.

It is clear from this work that optimization of the adsorption process depends on pH of solution but also more importantly functionalization of the nanosheets. A higher increase in removal efficiency was reported for the cysteine and phosphate functionalised GO nanosheets, the latter showed almost 100% removal. The functionalization strategy for GO by cysteine needs improvement by increasing the number of cysteine moieties bound to GO, therefore additional research is required on ways to reduce GO without compromising the number of cysteine moieties bound. As nanoparticles and membranes are still relatively expensive adsorbents, research to quantify their re-use is needed for the scale-up of the remediation process.

On the other hand, the toxicological effects of nanoparticles in aquatic environments needs to be investigated and that necessitates their immobilization.

.

7 References

- Abdi, G., Alizadeh, A., Zinadini, S., Moradi, G., 2018. Removal of dye and heavy metal ion using a novel synthetic polyethersulfone nanofiltration membrane modified by magnetic graphene oxide/metformin hybrid. *J. Memb. Sci.* 552, 326–335.
- Abdullah, N., Yusof, N., Lau, W.J., Jaafar, J., Ismail, A.F., 2019. Recent trends of heavy metal removal from water/wastewater by membrane technologies. *J. Ind. Eng. Chem.* 76, 17–38.
- Abhang, R.M., Wani, K.S., Patil, V.S., Pangarkar, B.L., Parjane, S.B., 2013. Nanofiltration for Recovery of Heavy Metal Ions from Waste Water - A Review. *Internaltional J. Res. Environ. Sci. Technol.* 3, 29–34.
- Ai, Y., Liu, Y., Lan, W., Jin, J., Xing, J., Zou, Y., Zhao, C., Wang, X., 2018. The effect of pH on the U(VI) sorption on graphene oxide (GO): A theoretical study. *Chem. Eng. J.* 343, 460–466.
- Akcil, A., Koldas, S., 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. *J. Clean. Prod.* 14, 1139–1145.
- Amini, M., Jahanshahi, M., Rahimpour, A., 2013. Synthesis of novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized multi-walled carbon nanotubes. *J. Memb. Sci.* 435, 233–241.
- Anirudhan, T.S., Suchithra, P.S., 2010. Heavy metals uptake from aqueous solutions and industrial wastewaters by humic acid-immobilized polymer/bentonite composite: Kinetics and equilibrium modeling. *Chem. Eng. J.* 156, 146–156.
- Anirudhan, T.S., Ramachandran, M., 2008. Synthesis and Characterization of Amidoximated Polyacrylonitrile/Organobentonite Composite for Cu(II), Zn(II), and Cd(II) Adsorption from Aqueous Solutions and Industry Wastewaters. *Ind. Eng. Chem. Res.* 47, 6175–6184.
- Aroua, M.K., Zuki, F.M., Sulaiman, N.M., 2007. Removal of chromium ions from aqueos solutions by polymer-enhanced ultrafiltration. *J. Hazard. Mater.* 147, 752–758.
- Awad, F.S., AbouZied, K.M., Abou El-Maaty, W.M., El-Wakil, A.M., Samy El-Shall, M., 2020. Effective removal of mercury(II) from aqueous solutions by chemically modified graphene oxide nanosheets. *Arab. J. Chem.* 13, 2659–2670.
- Azelee, I.W., Goh, P.S., Lau, W.J., Ismail, A.F., Wong, K.C., Subramaniam, M.N., 2017. Enhanced desalination of polyamide thin fi lm nanocomposite incorporated with acid treated multiwalled carbon nanotube-titania nanotube hybrid. *Desalination* 409, 163–170.
- Barakat, M. A., Schmidt, E., 2010. Polymer-enhanced ultrafiltration process for heavy metals

- removal from industrial wastewater. *Desalination* 256, 90–93.
- A.R.B.D. Mail, OpenStax CNX., 2014. Physical Methods in Chemistry and Nano Science. CNX available at http://cnx.org/contents/ba27839d-5042-4a40-afcf-c0e6e39fb454@19.1:41/Physical_Methods_in_Chemistry.
- Bashir, A., Malik, L.A., Ahad, S., Manzoor, T., Bhat, M.A., Dar, G.N., Pandith, A.H., 2018. Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods. *Environ. Chem. Lett.* 17, 729–754.
- Bassyouni, M., Abdel-Aziz, M.H., Zoromba, M.S., Abdel-Hamid, S.M.S., Drioli, E., 2019. A review of polymeric nanocomposite membranes for water purification. *J. Ind. Eng. Chem.* 73, 19-46.
- Bourlinos, A.B., Gournis, D., Petridis, D., 2003. Graphite Oxide : Chemical Reduction to Graphite and Surface Modification with Primary Aliphatic Amines and Amino Acids 6050–6055.
- Budak, T.B., 2013. Removal of heavy metals from wastewater using synthetic ion exchange resin. *Asian J. Chem.* 25, 4207–4210.
- Camarillo, R., Llanos, J., 2010. Treatment of copper (II) -loaded aqueous nitrate solutions by polymer enhanced ultrafiltration and electrodeposition. *Sep. Purif. Technol.* 70, 320–328.
- Chae, H.R., Lee, J., Lee, C.H., Kim, I.C., Park, P.K., 2015. Graphene oxide-embedded thin-film composite reverse osmosis membrane with high flux, anti-biofouling, and chlorine resistance. *J. Memb. Sci.* 483, 128–135.
- Chandra, V., Kim, K.S., 2011. ChemComm Highly selective adsorption of Hg 2 + by a polypyrrole – reduced graphene oxide composite w 3942–3944.
- Chen, G., Liu, R., Kyong, H., Wang, Y., Song, J., Li, X., He, T., 2017. Open porous hydrophilic supported thin- fi lm composite forward osmosis membrane via co-casting for treatment of high-salinity wastewater. *DES* 405, 76–84.
- Choi, J., Im, S., Jang, A., 2019. Chemosphere Application of volume retarded osmosis e Low pressure membrane hybrid process for recovery of heavy metals in acid mine drainage. *Chemosphere* 232, 264–272.
- Choi, W., Choi, J., Bang, J., Lee, J.-H., 2013. Layer-by-Layer Assembly of Graphene Oxide Nanosheets on Polyamide Membranes for Durable Reverse-Osmosis Applications. *ACS Appl. Mater. Interfaces.* 5, 12510-12519.
- Choi, W., Jeon, S., Kwon, S.J., Park, H., Park, Y.I., Nam, S.E., Lee, P.S., Lee, J.S., Choi, J., Hong, S., Chan, E.P., Lee, J.H., 2017. Thin film composite reverse osmosis membranes prepared via layered interfacial polymerization. *J. Memb. Sci.* 527, 121–128.

- Crock, C.A., Rogensues, A.R., Shan, W., Tarabara, V. V, 2013. Polymer nanocomposites with graphene-based hierarchical fillers as materials for multifunctional water treatment membranes. *Water Res.* 47, 3984–3996.
- Cui, Y., Ge, Q., Liu, X., Chung, T., 2014. Novel forward osmosis process to effectively remove heavy metal ions. *J. Memb. Sci.* 467, 188–194.
- Dąbrowski, A., Hubicki, Z., Podkościelny, P., Robens, E., 2004. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere* 56, 91–106.
- Dada, A.O., Olalekan, P.A., Olatunya, A.M., 2012. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn ²⁺ Unto Phosphoric Acid Modified Rice Husk. *IOSR J. Appl. Chem.* 3, 38–45.
- Department of Water affairs and forestry, 1996. Water quality guidelines: Domestic use.
- Dialynas, E., and Diamadopoulos, E., 2009. Integration of a membrane bioreactor coupled with reverse osmosis for advanced treatment of municipal wastewater. *Desalination* 238, 302–311.
- Dong, L., Huang, X., Wang, Z., Yang, Z., Wang, X., Tang, C.Y., 2016. A thin-film nanocomposite nanofiltration membrane prepared on a support with in situ embedded zeolite nanoparticles. *Sep. Purif. Technol.* 166, 230–239.
- Drahansky, M., Paridah, M., Moradbak, A., Mohamed, A., Owolabi, F. abdulwahab taiwo, Asniza, M., Abdul Khalid, S.H., 2016. We are IntechOpen , the world ’ s leading publisher of Open Access books Built by scientists , for scientists TOP 1 %. *Intech i*, 13.
- El Adraa, K., Georgelin, T., Lambert, J.F., Jaber, F., Tielens, F., Jaber, M., 2017. Cysteine-montmorillonite composites for heavy metal cation complexation: A combined experimental and theoretical study. *Chem. Eng. J.* 314, 406–417.
- Emadzadeh, D., Lau, W.J., Matsuura, T., Ismail, A.F., Rahbari-Sisakht, M., 2014. Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization. *J. Memb. Sci.* 449, 74–85.
- Enemu, N.D., 2018. CHARACTERIZATION AND LEACHING STUDIES OF COBALT AND NICKEL-POLYSULFONE NANOCOMPOSITE. University of Witwatersrand.
- Ennigrou, D.J., Gzara, L., Ramzi, M., Romdhane, B., Dhahbi, M., 2009. Cadmium removal from aqueous solutions by polyelectrolyte enhanced ultrafiltration. *Desalination* 246, 363–369.
- Ennigrou, D.J., Sik Ali, M. Ben, Dhahbi, M., Ferid, M., 2015. Removal of heavy metals from aqueous solution by polyacrylic acid enhanced ultrafiltration. *Desalin. Water Treat.* 56, 2682–2688.

- Etale, A., Tutu, H., Drake, D.C., 2016. Application of maghemite nanoparticles as sorbents for the removal of Cu(II), Mn(II) and U(VI) ions from aqueous solution in acid mine drainage conditions. *Appl. Water Sci.* 6, 187–197.
- Etale, A., Yalala, B., Tutu, H., Drake, D.C., Etale, A., Yalala, B., Tutu, H., Drake, D.C., 2014. Adsorptive removal of mercury from acid mine drainage : a comparison of silica and maghemite nanoparticles. *Toxicol. Environ. Chem.* 96, 542–554.
- Faria, A.F., Liu, C., Xie, M., Perreault, F., Nghiem, L.D., Ma, J., Elimelech, M., 2017. Thin-film composite forward osmosis membranes functionalized with graphene oxide–silver nanocomposites for biofouling control. *J. Memb. Sci.* 525, 146–156.
- Feini, L.I.U., Guoliang, Z., Qin, M., Hongzi, Z., 2008. Performance of Nanofiltration and Reverse Osmosis Membranes in. *Environ. Eng. Sci.* 16, 441–445.
- Figoli, A., Cassano, A., Criscuoli, A., Mozumder, M.S.I., Uddin, M.T., Islam, M.A., Drioli, E., 2010. Influence of operating parameters on the arsenic removal by nanofiltration. *Water Res.* 44, 97–104.
- Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* 92, 407–418.
- Gazea, B., Adam, K., Kontopoulos, A., 1996. A review of passive systems for the treatment of acid mine drainage. *Miner. Eng.* 9, 23–42.
- Ghaedi, M., Nasab, A.G., Khodadoust, S., Rajabi, M., Azizian, S., 2014. Application of activated carbon as adsorbents for efficient removal of methylene blue: Kinetics and equilibrium study. *J. Ind. Eng. Chem.* 20, 2317–2324.
- Ghafuri, H., Talebi, M., 2016. Water-Soluble Phosphated Graphene: Preparation, Characterization, Catalytic Reactivity, and Adsorption Property. *Ind. Eng. Chem. Res.* 55, 2970–2982.
- Gherasim, C.V., Cuhorka, J., Mikulasek, P., 2013. Analysis of lead(II) retention from single salt and binary aqueous solutions by a polyamide nanofiltration membrane: Experimental results and modelling. *J. Memb. Sci.* 436, 132–144.
- González, M.G., Cabanelas, J.C., Baselga, J., 2012. Applications of FTIR on epoxy resins—Identification, monitoring the curing process, phase separation and water uptake, in: Theophile, T. (Ed.), *Infrared Spectroscopy: Materials Science, Engineering and Technology*. InTech Open, pp. 261–284.
- Goods, J.B., Sydlík, S.A., Walish, J.J., Swager, T.M., 2014. Phosphate functionalized graphene with tunable mechanical properties. *Adv. Mater.* 26, 718–723.

- Goodwin, D.G., Adeleye, A.S., Sung, L., Ho, K.T., Burgess, R.M., Petersen, E.J., 2018. Detection and Quantification of Graphene-Family Nanomaterials in the Environment. *Environ. Sci. Technol.* 52, 4491–4513.
- Hadi, P., To, M.H., Hui, C.W., Lin, C.S.K., McKay, G., 2015. Aqueous mercury adsorption by activated carbons. *Water Res.* 37-55.
- He, L., Dumée, L.F., Feng, C., Velleman, L., Reis, R., She, F., Gao, W., Kong, L., 2015. Promoted water transport across graphene oxide-poly(amide) thin film composite membranes and their antibacterial activity. *Desalination* 365, 126–135.
- He, Y., Liu, J., Han, G., Chung, T., 2018. Novel thin-film composite nanofiltration membranes consisting of a zwitterionic co-polymer for selenium and arsenic removal. *J. Memb. Sci.* 555, 299–306.
- Hu, J., Chen, G., Lo, I.M.C., 2006. Selective Removal of Heavy Metals from Industrial Wastewater Using Maghemite Nanoparticle: Performance and Mechanisms. *J. Environ. Eng.* 132, 709–715.
- Huang, Y., Du, J., Zhang, Y., Lawless, D., Feng, X., 2016. Batch process of polymer-enhanced ultrafiltration to recover mercury (II) from wastewater. *J. Memb. Sci.* 514, 229–240.
- Huang, Y., Feng, X., 2019. Polymer-enhanced ultrafiltration: Fundamentals, applications and recent developments. *J. Memb. Sci.* 586, 53–83.
- Iijima, S., 1991. Helical microtubules of graphitic carbon. *Nature* 354, 56–58.
- Inglezakis, V.J., Stylianou, M.A., Gkantzou, D., Loizidou, M.D., 2007. Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents. *Desalination*. 210, 248-256.
- Jia, T., Lu, J., Cheng, X., Xia, Q., Cao, X., 2019. Surface enriched sulfonated polyarylene ether benzonitrile (SPEB) that enhances heavy metal removal from polyacrylonitrile (PAN) thin-film composite nanofiltration membranes. *J. Memb. Sci.* 580, 214–223.
- Kazemi, M., Jahanshahi, M., Peyravi, M., 2018. Hexavalent chromium removal by multilayer membrane assisted by photocatalytic couple nanoparticle from both permeate and retentate. *J. Hazard. Mater.* 344, 12–22.
- Kefeni, K.K., Msagati, T.A.M., Mamba, B.B., 2017. Acid mine drainage: Prevention, treatment options, and resource recovery: A review. *J. Clean. Prod.* 151, 475–493.
- Kim, E.S., Deng, B., 2011. Fabrication of polyamide thin-film nano-composite (PA-TFN) membrane with hydrophilized ordered mesoporous carbon (H-OMC) for water purifications. *J. Memb. Sci.* 375, 46–54.

- Kim, H., Baek, K., Kim, B., Yang, J., 2005. Humic substance-enhanced ultrafiltration for removal of cobalt. *J. Hazard. Mater.* 122, 31–36.
- Kowanga, K.D., Gatebe, E., Mauti, G.O., Mauti, E.M., 2016. Kinetic , sorption isotherms , pseudo-first-order model and pseudo-second-order model studies of Cu (II) and Pb (II) using defatted *Moringa oleifera* seed powder. *J. Phytopharm.* 5, 71–78.
- Koyuncu, I., Wiesner, M.R., 2007. Morphological Variations of Precipitated Salts on NF and RO Membranes. *Environ. Eng. Sci.* 24, 602–614.
- Krishna Kumar, A.S., Jiang, S.J., Tseng, W.L., 2016a. Facile synthesis and characterization of thiol-functionalized graphene oxide as effective adsorbent for Hg(II). *J. Environ. Chem. Eng.* 4, 2052–2065.
- Kütahyalı, C., Eral, M., 2004. Selective adsorption of uranium from aqueous solutions using activated carbon prepared from charcoal by chemical activation. *Sep. Purif. Technol.* 40, 109–114.
- Kuyucak, N., 2002. Role of Microorganisms in Mining: Generation of Acid Rock Drainage and its Mitigation and Treatment. *Eur. J. Miner. Process. Environ. Prot.* 2, 179–196.
- Largitte, L., Pasquier, R., 2016. A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chem. Eng. Res. Des.* 109, 495–504.
- Lau, W.J., Gray, S., Matsuura, T., Emadzadeh, D., Paul Chen, J., Ismail, A.F., 2015. A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches. *Water Res.*
- Leng, Y., 2008. *Materials Characterization: Introduction to Microscopic and Spectroscopic Methods*, Second edi. ed. Wiley-VCH, Hong Kong.
- Li, Y., Li, S., Zhang, K., 2017. Influence of hydrophilic carbon dots on polyamide thin film nanocomposite reverse osmosis membranes. *J. Memb. Sci.* 537, 42–53.
- Li, Y., Liu, F., Xia, B., Du, Q., Zhang, P., Wang, D., Wang, Z., Xia, Y., 2010. Removal of copper from aqueous solution by carbon nanotube/calcium alginate composites. *J. Hazard. Mater.* 177, 876–880.
- Liao, Y., Loh, C.-H., Tian, M., Wang, R., Fane, A.G., 2018. Progress in electrospun polymeric nanofibrous membranes for water treatment: Fabrication, modification and applications. *Prog. Polym. Sci.* 77, 69–94.
- Liu, C., Lei, X., Wang, L., Jia, J., Liang, X., Zhao, X., Zhu, H., 2017. Investigation on the removal performances of heavy metal ions with the layer-by-layer assembled forward osmosis membranes. *Chem. Eng. J.* 327, 60–70.

- Liu, M., Lü, Z., Chen, Z., Yu, S., Gao, C., 2011. Comparison of reverse osmosis and nanofiltration membranes in the treatment of biologically treated textile effluent for water reuse. *Desalination* 281, 372–378.
- Liu, Q., Xu, G.-R., 2016a. Graphene oxide (GO) as functional material in tailoring polyamide thin film composite (PA-TFC) reverse osmosis (RO) membranes. *Desalination* 394, 162–175.
- Liu, Q., Xu, G.R., 2016b. Graphene oxide (GO) as functional material in tailoring polyamide thin film composite (PA-TFC) reverse osmosis (RO) membranes. *Desalination* 394, 162–175.
- Liu, X., Li, J., Wang, Xiangxue, Chen, C., Wang, Xiangke, 2015. High performance of phosphate-functionalized graphene oxide for the selective adsorption of U(VI) from acidic solution. *J. Nucl. Mater.* 466, 56–64.
- Machodi, M.J., Daramola, M.O., 2019. Synthesis and performance evaluation of PES/chitosan membranes coated with polyamide for acid mine drainage treatment. *Sci. Rep.* 9, 1–14.
- Macingova, E., Luptakova, A., 2012. Recovery of metals from acid mine drainage. *Chem. Eng. Trans.* 28, 109–114.
- Mahdavi, H., Rahimi, A., 2018. Zwitterion functionalized graphene oxide/polyamide thin film nanocomposite membrane: Towards improved anti-fouling performance for reverse osmosis. *Desalination* 433, 94–107.
- Mahdavinia, G.R., Hasanpour S., Behrouzi, L., Sheyhloie, H., 2016. Study on adsorption of Cu(II) on magnetic -polyamidoxime/montmorillonite/Fe₃O₄ nanocomposites as novel chelating ligands. *J. Mater. Sci.* 68, 188–199.
- Malamis, S., Katsou, E., Takopoulos, K., Demetriou, P., Loizidou, M., 2012. Assessment of metal removal, biomass activity and RO concentrate treatment in an MBR-RO system. *J. Hazard. Mater.* 209–210, 1–8.
- Mccarthy, T.S., Africa, S., Africa, S., 2011. The impact of acid mine drainage in South Africa 107, 1–7.
- Mellah, A., Chegrouche, S., Barkat, M., 2006. The removal of uranium(VI) from aqueous solutions onto activated carbon: Kinetic and thermodynamic investigations. *J. Colloid Interface Sci.* 296, 434–441.
- Meyer, J.C., Geim, A.K., Katsnelson, M.I., Novoselov, K.S., Booth, T.J., Roth, S., 2007. The structure of suspended graphene sheets. *Nature* 446, 60–63.
- Mohan, D., Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents--A critical review. *J. Hazard. Mater.* 142, 1–53.

- Mohsen-Nia, M., Montazeri, P., Modarress, H., 2007. Removal of Cu^{2+} and Ni^{2+} from wastewater with a chelating agent and reverse osmosis processes. *Desalination* 217, 276–281.
- Molinari, R., Poerio, T., Argurio, P., 2008. Selective separation of copper (II) and nickel (II) from aqueous media using the complexation – ultrafiltration process. *Chemosphere* 70, 341–348.
- Msaasi, R., Ammar, S., Chehimi, M.M., Yagci, Y., 2017. Diazonium-based ion-imprinted polymer nanocomposite for the selective extraction of lead (II) ions in aqueous media. *Eur. Polym. J.* 89, 367–380.
- Muralikrishna, S., Sureshkumar, K., Varley, T.S., Nagaraju, D.H., Ramakrishnappa, T., 2014. In situ reduction and functionalization of graphene oxide with l-cysteine for simultaneous electrochemical determination of cadmium(ii), lead(ii), copper(ii), and mercury(ii) ions. *Anal. Methods* 6, 8698–8705.
- Murthy, Z.V.P., Chaudhari, L.B., 2008. Application of nanofiltration for the rejection of nickel ions from aqueous solutions and estimation of membrane transport parameters. *J. Hazard. Mater.* 160, 70–77.
- Naicker, K., Cukrowska, E., McCarthy, T.S., 2003. Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs. *Environ. Pollut.* 122, 29–40.
- Nasir, A., Masood, F., Yasin, T., Hameed, A., 2019. Progress in polymeric nanocomposite membranes for wastewater treatment: Preparation, properties and applications. *J. Ind. Eng. Chem.* 79, 29–40.
- Nayak, V., Jyothi, M.S., Balakrishna, R.G., Padaki, M., Deon, S., 2017. Novel modified poly vinyl chloride blend membranes for removal of heavy metals from mixed ion feed sample. *J. Hazard. Mater.* 331, 289–299.
- Nayak, V., Jyothi, S., Balakrishna, R.G., Padaki, M., 2015. Preparation and Characterization of Chitosan Thin Films on Mixed-Matrix Membranes for Complete Removal of Chromium. *ChemistryOpen*. 4, 278–287.
- Nedzarek, A., Drost, A., Harasimiuk, F.B., Torz, A., 2015. The influence of pH and BSA on the retention of selected heavy metals in the nanofiltration process using ceramic membrane. *Desalination* 369, 62–67.
- Nekhunguni, P.M., Tavengwa, N.T., Tutu, H., 2017a. Sorption of uranium(VI) onto hydrous ferric oxide-modified zeolite: Assessment of the effect of pH, contact time, temperature, selected cations and anions on sorbent interactions. *J. Environ. Manage.* 204, 571–582.
- Nekhunguni, P.M., Tavengwa, N.T., Tutu, H., 2017b. Investigation of As(V) removal from acid mine

- drainage by iron (hydr) oxide modified zeolite. *J. Environ. Manage.* 197, 550–558.
- Nethaji, S., Sivasamy, A., Mandal, A.B., 2013. Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from *Juglans regia* shell biomass. *Int. J. Environ. Sci. Technol.* 10, 231–242.
- Nzihou, A., Sharrock, P., 2010. Role of Phosphate in the Remediation and Reuse of Heavy Metal Polluted Wastes and Sites. *Waste Biomass Valor* 1, 163–174.
- Orth, E.S., Ferreira, J.G.L., Fonsaca, J.E.S., Blaskiewicz, S.F., Domingues, S.H., Dasgupta, A., Terrones, M., Zarbin, A.J.G., 2016. PKa determination of graphene-like materials: Validating chemical functionalization. *J. Colloid Interface Sci.* 467, 239–244.
- Ozaki, H., Sharma, K., and Saktaywin, W., 2002. Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: Effects of interference parameters. *Desalination* 144, 287–294.
- Park, S.H., Ko, Y.S., Park, S.J., Lee, J.S., Cho, J., Baek, K.Y., Kim, I.T., Woo, K., Lee, J.H., 2016. Immobilization of silver nanoparticle-decorated silica particles on polyamide thin film composite membranes for antibacterial properties. *J. Memb. Sci.* 499, 80–91.
- Pham, T.A., Kim, Jeong Sik, Kim, Jeong Su, Jeong, Y.T., 2011. One-step reduction of graphene oxide with l-glutathione. *Colloids Surfaces A Physicochem. Eng. Asp.* 384, 543–548.
- Philippus, J.M., 2006. Treatment of industrial effluents for neutralization and sulphate removal 129.
- Pillay, K., Cukrowska, E.M., Coville, N.J., 2009. Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution. *J. Hazard. Mater.* 166, 1067–1075.
- Pookrod, P., Haller, K.J., Scamehorn, 2010. Removal of Arsenic Anions from Water Using Polyelectrolyte - Enhanced Ultrafiltration. *Sep. Sci. Technol.* 39(4) 811-831.
- Pozo-Antonio, S., Puente-Luna, I., Lagüela-López, S., Veiga-Ríos, M., 2014. Techniques to correct and prevent acid mine drainage: A review. *Dyna* 81, 73.
- Qiu, M., He, C., 2019. Efficient removal of heavy metal ions by forward osmosis membrane with a polydopamine modified zeolitic imidazolate framework incorporated selective layer. *J. Hazard. Mater.* 367, 339–347.
- Rajaeian, B., Rahimpour, A., Tade, M.O., Liu, S., 2013. Fabrication and characterization of polyamide thin film nanocomposite (TFN) nanofiltration membrane impregnated with TiO₂ nanoparticles. *Desalination* 313, 176–188.

- Saad, D.M., Cukrowska, E.M., 2013. Selective removal of mercury from aqueous solutions using thiolated cross-linked polyethylenimine 527–534.
- Sadegh, H., Ali, G.A.M., Gupta, V.K., Makhoulf, A.S.H., Shahryari-ghoshekandi, R., Nadagouda, M.N., Sillanpää, M., Megiel, E., 2017. The role of nanomaterials as effective adsorbents and their applications in wastewater treatment. *J. Nanostructure Chem.* 7, 1–14.
- Sampaio, R.M.M., Timmers, R.A., Xu, Y., Keesman, K.J., Lens, P.N.L., 2009. Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor. *J. Hazard. Mater.* 165, 256–265.
- Sandino, A., Bruno, J., 1992. The solubility of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$ and the formation of U(VI) phosphate complexes: Their influence in uranium speciation in natural waters. *Geochim. Cosmochim. Acta* 56, 4135–4145.
- Savage, N., Diallo, M.S., 2005. Nanomaterials and water purification: Opportunities and challenges. *J. Nanoparticle Res.* 7, 331–342.
- Seenivasan, R., Chang, W.J., Gunasekaran, S., 2015. Highly Sensitive Detection and Removal of Lead Ions in Water Using Cysteine-Functionalized Graphene Oxide/Polypyrrole Nanocomposite Film Electrode. *ACS Appl. Mater. Interfaces* 7, 15935–15943.
- Shao, F., Dong, L., Dong, H., Zhang, Q., Zhao, M., Yu, L., Pang, B., Chen, Y., 2017. Graphene oxide modified polyamide reverse osmosis membranes with enhanced chlorine resistance. *J. Memb. Sci.* 525, 9–17.
- Shibuya, M., Yasukawa, M., Mishima, S., Tanaka, Y., Takahashi, T., Matsuyama, H., 2017. A thin-film composite-hollow fiber forward osmosis membrane with a polyketone hollow fiber membrane as a support. *Desalination* 402, 33–41.
- Simate, G.S., Ndlovu, S., 2014. Acid mine drainage: Challenges and opportunities. *J. Environ. Chem. Eng.* 2 (3), 1785-1803.
- Simsek, S., Ulusoy, U., 2012. Uranium and lead adsorption onto amidoxime functionalised bentonite and zeolite modified thin film nanocomposite membrane. *J. Radioanal. Nucl. Chem* 292, 41–51.
- Sirinupong, T., Youravong, W., Tirawat, D., Lau, W.J., Lai, G.S., Ismail, A.F., 2018. Synthesis and characterization of thin film composite membranes made of PSF-TiO₂/GO nanocomposite substrate for forward osmosis applications. *Arab. J. Chem.* 11, 1144–1153.
- Son, M., Park, H., Liu, L., Choi, Hyeongyu, Kim, J.H., Choi, Heechul, 2016. Thin-film nanocomposite membrane with CNT positioning in support layer for energy harvesting from saline water. *Chem. Eng. J.* 284, 68-77.

- Sureshkumar, M.K., Das, D., Mallia, M.B., Gupta, P.C., 2010. Adsorption of uranium from aqueous solution using chitosan-tripolyphosphate (CTPP) beads. *J. Hazard. Mater.* 184, 65–72.
- Sureshkumar, M. K., Das, D., Mallia, M.B., Gupta, P.C., 2010. Adsorption of uranium from aqueous solution using chitosan-tripolyphosphate (CTPP) beads. *J. Hazard. Mater.* 184, 65–72.
- Tang, J., Huang, Y., Gong, Y., Lyu, H., Wang, Q., Ma, J., 2016. Preparation of a novel graphene oxide/Fe-Mn composite and its application for aqueous Hg(II) removal. *J. Hazard. Mater.* 316, 151-158.
- Tang, L., Livi, K.J.T., Chen, K.L., 2015. Polysulfone membranes modified with bioinspired polydopamine and silver nanoparticles formed in situ to mitigate biofouling. *Environ. Sci. Technol. Lett.* 2, 59–65.
- Turhanen, P.A., Vepsäläinen, J.J., Peräniemi, S., 2015. Advanced material and approach for metal ions removal from aqueous solutions. *Sci. Rep.* 5, 1–8.
- Tutu, H., Cukrowska, E.M., McCarthy, T.S., Hart, R., Chimuka, L., 2009. Radioactive disequilibrium and geochemical modelling as evidence of uranium leaching from gold tailings dumps in the Witwatersrand basin. *Int. J. Environ. Anal. Chem.* 89, 687–703.
- Ulrich, K.-U., Rossberg, A., Foerstendorf, H., Zänker, H., Scheinost, A.C., 2006. Molecular characterization of uranium(VI) sorption complexes on iron(III)-rich acid mine water colloids. *Geochim. Cosmochim. Acta* 70, 5469–5487.
- Vatanpour, V., Safarpour, M., Khataee, A., Zarrabi, H., Yekavalangi, M.E., Kaviani, M., 2017. A thin film nanocomposite reverse osmosis membrane containing amine-functionalized carbon nanotubes. *Sep. Purif. Technol.* 184, 135–143.
- Vieira, R.S., Guibal, E., Silva, E.A., Beppu, M.M., Guibal, E., 2007. Adsorption and desorption of binary mixtures of copper and mercury ions on natural and crosslinked chitosan membranes. *Adsorption* 13, 603-611.
- Vincenzo, M. Di, Barboiu, M., Tiraferri, A., Legrand, Y.M., 2017. Polyol-functionalized thin-film composite membranes with improved transport properties and boron removal in reverse osmosis. *J. Memb. Sci.* 540, 71–77.
- Vorrada, L., Krit, T., Passakorn, E., Wanchai, B., Achanai, B., 2013. Preparation and Characterization of Reduced Graphene Oxide Sheets via Water-Based Exfoliation and Reduction Methods. *Adv. Mater. Sci. Eng.* 2013, 1–5.
- Wagner, J., 2001. Membrane filtration handbook, second ed., Osmonics. Osmonics, minnesota.
- Wan Azelee, I., Goh, P.S., Lau, W.J., Ismail, A.F., Rezaei-DashtArzhandi, M., Wong, K.C.,

- Subramaniam, M.N., 2017. Enhanced desalination of polyamide thin film nanocomposite incorporated with acid treated multiwalled carbon nanotube-titania nanotube hybrid. *Desalination* 409.
- Wang, X. Wang, A., 2010. Adsorption characteristics of chitosan modified thin film nanocomposite for Hg(II) ions from aqueous solution. *Sep. Sci. Technol.* 45, 2086–2094.
- Wang, L., Yang, Z., Gao, J., Xu, K., Gu, H., Zhang, B., Zhang, X., Xu, B., 2006. A Biocompatible Method of Decorporation: Bisphosphonate-Modified Magnetite Nanoparticles to Remove Uranyl Ions from Blood. *J. Am. Chem. Soc.* 128, 13358–13359.
- Wen, P., Chen, Y., Hu, X., Cheng, B., Liu, D., Zhang, Y., Nair, S., 2017. Polyamide thin film composite nanofiltration membrane modified with acyl chlorided graphene oxide. *J. Memb. Sci.* 535, 208–220.
- White, R.L., White, C.M., Turgut, H., Massoud, A., Tian, Z.R., 2018. Journal of the Taiwan Institute of Chemical Engineers Comparative studies on copper adsorption by graphene oxide and functionalized graphene oxide nanoparticles. *J. Taiwan Inst. Chem. Eng.* 85, 18–28.
- Wilkinson, J., 2016. Developing Graphene Oxide Membranes for the Purification of Water and Green Fuels. *AZO NANO* 1–10.
- Wingenfelder, U., Hansen, C., Furrer, G., Schulin, R., 2005. Removal of heavy metals from mine waters by natural zeolites. *Environ. Sci. Technol.* 39, 4606–4613.
- Wu, C., Mouri, H., Chen, S., Zhang, D., Koga, M., 2016. Journal of Water Process Engineering Removal of trace-amount mercury from wastewater by forward osmosis. *J. Water Process Eng.* 14, 108–116.
- Wu, F.-C., Tseng, R.-L., Juang, R.-S., 2005. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, *Wat. Res.* 287 (1), 25–34.
- Wu, H., Tang, B., Wu, P., 2013a. Optimizing polyamide thin film composite membrane covalently bonded with modified mesoporous silica nanoparticles. *J. Memb. Sci.* 428, 341–348.
- Wu, H., Tang, B., Wu, P., 2013b. Optimization, characterization and nanofiltration properties test of MWNTs/polyester thin film nanocomposite membrane. *J. Memb. Sci.* 428, 425–433.
- Xia, S., Yao, L., Zhao, Y., Li, N., Zheng, Y., 2015. Preparation of graphene oxide modified polyamide thin film composite membranes with improved hydrophilicity for natural organic matter removal. *Chem. Eng. J.* 280, 720–727.
- Xie, W., Geise, G.M., Freeman, B.D., Lee, H.-S., Byun, G., McGrath, J.E., 2012. Polyamide interfacial composite membranes prepared from m-phenylene diamine, trimesoyl chloride and

- a new disulfonated diamine. *J. Memb. Sci.* 403–404, 152–161.
- Xu, S., Li, F., Su, B., Hu, M.Z., Gao, X., Gao, C., 2018. Novel graphene quantum dots (GQDs) - incorporated thin fi lm composite (TFC) membranes for forward osmosis (FO) desalination. *Desalination*. 1–12.
- Yan, M., 2017. nanocomposite for the magnetic separation of proteins †. *RSC Adv.* 7, 30109–30117.
- Yin, J., Deng, B., 2015. Polymer-matrix nanocomposite membranes for water treatment. *J. Memb. Sci.* 479, 256–275.
- Yin, J., Kim, E.S., Yang, J., Deng, B., 2012. Fabrication of a novel thin-film nanocomposite (TFN) membrane containing MCM-41 silica nanoparticles (NPs) for water purification. *J. Memb. Sci.* 423–424, 238–246.
- Yin, J., Zhu, G., Deng, B., 2016. Graphene oxide (GO) enhanced polyamide (PA) thin-film nanocomposite (TFN) membrane for water purification. *Desalination* 379, 93–101.
- Ying, X., Fang, Z., 2006. Experimental research on heavy metal wastewater treatment with dipropyl dithiophosphate. *J. Hazard. Mater.* 137, 1636–1642.
- Yoon, Y., Kyu, W., Hwang, T., Ho, D., Seok, W., Kang, J., 2016. Comparative evaluation of magnetite – graphene oxide and magnetite-reduced graphene oxide composite for As (III) and As (V) removal. *J. Hazard. Mater.* 304, 196–204.
- You, S., Lu, J., Tang, C.Y., Wang, X., 2017. Rejection of heavy metals in acidic wastewater by a novel thin-film inorganic forward osmosis membrane. *Chem. Eng. J.* 320, 532–538.
- Z.C. Di, J. Ding, X.J. Peng, Y.H. Li, Z.K. Luan, J.L., 2015. Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles nanocomposite. *Chemosphere* 74, 861–865.
- Zhang, P., Gong, J.L., Zeng, G.M., Deng, C.H., Yang, H.C., Liu, H.Y., Huan, S.Y., 2017. Cross-linking to prepare composite graphene oxide-framework membranes with high-flux for dyes and heavy metal ions removal. *Chem. Eng. J.* 322, 657–666.
- Zhao, X., Li, J., Liu, C., 2017. A novel TFC-type FO membrane with inserted sublayer of carbon nanotube networks exhibiting the improved separation performance. *Desalination* 413, 176–183.
- Zheng, G., He, Y., Zhan, Y., Zhang, L., Pan, Y., Zhang, C., 2016. Novel polyvinylidene fluoride nanofiltration membrane blended with functionalized halloysite nanotubes for dye and heavy metal ions removal. *J. Environ. Manage.* 317, 60–72.
- Zhu, W.P., Gao, J., Sun, S.P., Chung, T.S., Zhang, S., 2015. Poly(amidoamine) dendrimer (PAMAM)

grafted on thin film composite (TFC) nanofiltration (NF) hollow fiber membranes for heavy metal removal. *J. Memb. Sci.* 487, 117–126.

Zhu, W.P., Gao, J., Sun, S.P., Chung, T.S., Zhang, S., 2014. Dual-layer polybenzimidazole/polyethersulfone (PBI/PES) nanofiltration (NF) hollow fiber membranes for heavy metals removal from wastewater. *J. Memb. Sci.* 456, 117–127.

8 Appendices

8.1 Copyright licenses for figures

Figure 2.1

04/2020

RightLink Private License

ELSEVIER LICENSE
TERMS AND CONDITIONS

Sep 04, 2020

This Agreement between Ms. Dineo Nhlane ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4902011449469
License date	Sep 04, 2020
Licensed Content Publisher	Elsevier
Licensed Content Publication	Desalination
Licensed Content Title	Graphene oxide (GO) as functional material in tailoring polyamide thin film composite (PA-TFC) reverse osmosis (RO) membranes
Licensed Content Author	Qian Liu,Guo-Rong Xu
Licensed Content Date	Sep 15, 2016
Licensed Content Volume	394
Licensed Content Issue	n/a
Licensed Content Pages	14
Start Page	162
End Page	175

<https://100.copyright.com/RightLinkDispatchServlet>

Figure 2.2

04/2020

RightLink Private License

ELSEVIER LICENSE
TERMS AND CONDITIONS

Sep 04, 2020

This Agreement between Ms. Dineo Nhlane ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4902030729774
License date	Sep 04, 2020
Licensed Content Publisher	Elsevier
Licensed Content Publication	Progress in Polymer Science
Licensed Content Title	Progress in electrospun polymeric nanofibrous membranes for water treatment: Fabrication, modification and applications
Licensed Content Author	Yuan Liao, Chun-Heng Loh, Miao Tian, Rong Wang, Anthony G. Fane
Licensed Content Date	Feb 1, 2018
Licensed Content Volume	77
Licensed Content Issue	n/a
Licensed Content Pages	26
Start Page	69
End Page	94

<https://s100.copyright.com/AppDispatchServlet>

Figure 2.3

9/7/2020

RightLink Private License

ELSEVIER LICENSE
TERMS AND CONDITIONS

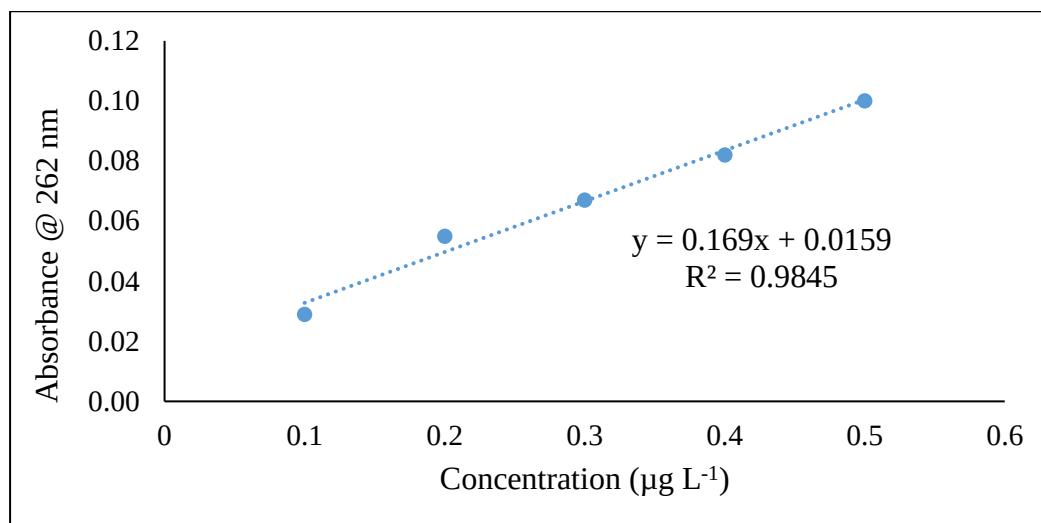
Sep 07, 2020

This Agreement between Ms. Dineo Nhlane ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

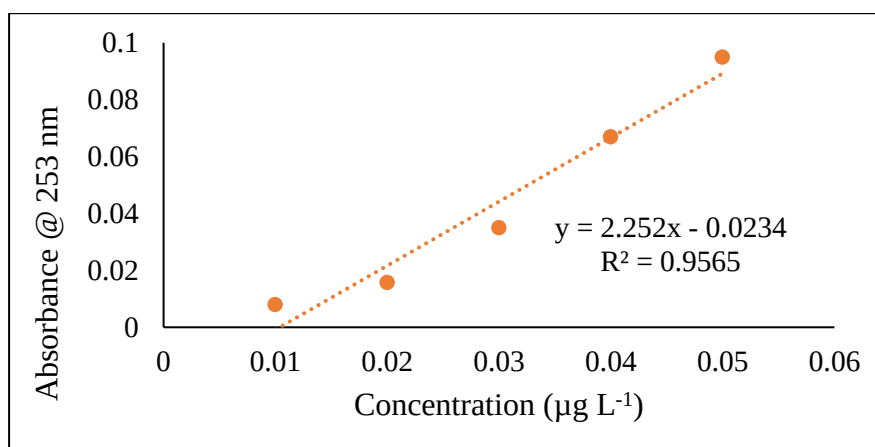
License Number	4903700053679
License date	Sep 07, 2020
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Membrane Science
Licensed Content Title	Polymer-matrix nanocomposite membranes for water treatment
Licensed Content Author	Jun Yin,Baolin Deng
Licensed Content Date	Apr 1, 2015
Licensed Content Volume	479
Licensed Content Issue	n/a
Licensed Content Pages	20
Start Page	256
End Page	275

<https://s100.copyright.com/AppDispatchServlet>

8.2 Calibration curves for GO and functionalised GO leaching



Appendix 1: Calibration curve of GO standard concentrations at 262 nm absorbance

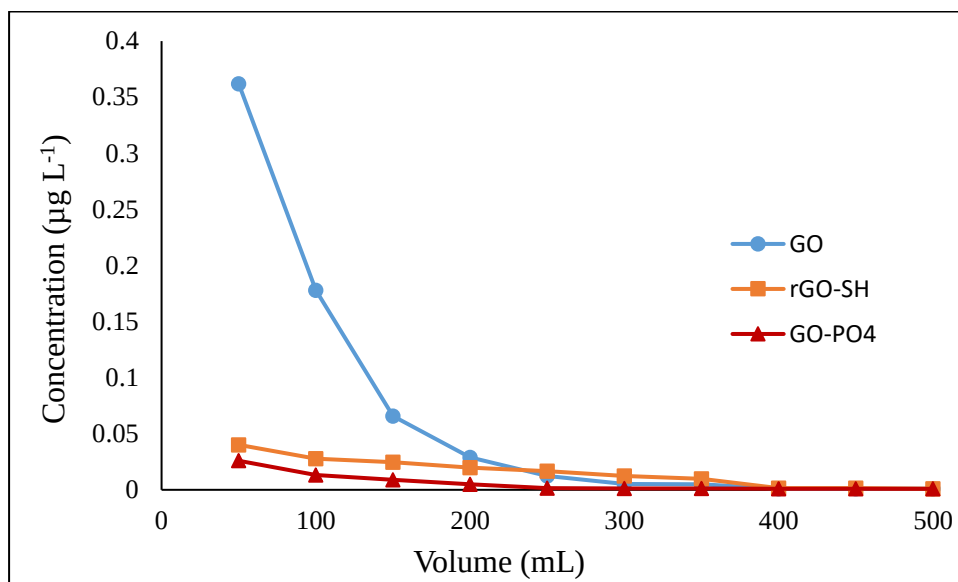


Appendix 2: Calibration curve of functionalised GO concentrations at 253 nm absorbance.

8.2 Leaching studies

Stability of nanomaterials bound to polymer matrix for water treatment is vital, from (Appendix 3) it shows that graphene oxide and its derivatives leach out as volume of permeate increases until it reaches equilibrium. The high initial concentration is due to the loose and unbound graphene oxide on the thin film layer (Goodwin et al., 2018). This proves that not all the GO and functionalized GO added during the interfacial polymerization process form a bond with TMC. This could mean that the concentration of GO is more than the number of available active sites to form a bond with the monomers of the polyamide layer. The leachate concentration of graphene oxide and its derivatives

decreased when volume of filtrate increased. There were studies done on the leaching of other nanomaterials from membrane matrix (Co and Ni nanoparticles) that gave similar behavior to this study (Enemuo, 2018). On the study the concentrations of Co and Ni leached out decreased with increase in volume of filtrate ($22-0$ and $400-0 \mu\text{g L}^{-1}$ for Ni and Co respectively).



Appendix 3: Leaching of graphene oxide and functionalized graphene oxide as volume of permeate increases.