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SILVER-COATED POLYETHENE TEREPHTHALATE MEMBRANE FOR DETECTION OF PHARMACEUTICALS USING SURFACE-ENHANCED RAMAN SPECTROSCOPY

By

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RESPICE PROSPICE
UNIVERSITY of the
WESTERN CAPE

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WESTERN CAPE

Abstract

Surface-enhanced Raman spectroscopy (SERS) has emerged as one of the analytical tools for detection of micro pollutants in the aquatic environment. The SERS technique is touted to have fingerprinting capability, specificity, ease of operation and single-molecule sensitivity. Therefore SERS can be used for detection of trace level organic pollutants in water. Trace level aquatic micro pollutants such as pharmaceuticals, have been detected in effluents from water treatment plants. Pharmaceuticals, due to the intended therapeutic use, may have adverse effects on living organisms, even in trace-level concentrations. Furthermore, the growing interest to reuse wastewater to augment conventional water supplies has resulted in a growing demand to explore sensitive and rapid analytical techniques such as SERS. In addition the use of track-etched polymer membranes in the filtration process has attracted considerable attention due to their flexibility in providing shape, durability and pore size control versatility. In this work, a silver-coated track-etched polyethene terephthalate (PET) membrane was developed as a platform to detect acetaminophen and had its surface-enhance Raman properties evaluated. The silver-coated track-etched PET membrane was fabricated by modifying the surface of the PET membrane with diethylenetriamine (DETA) via solid-liquid interface reaction known as aminolysis. The characterisation techniques used to ascertain the surface modification of track-etched PET membrane are Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS). Silver nanoparticles were immobilised on the amine-modified surface of track-etched polyethene terephthalate membrane by immersing an amine-modified track-etched PET membrane in a 102 mL mixture of 1 mM of silver nitrate and 1% trisodium citrate heated at 90 ^{o}C for 30 minutes. The immobilised silver nanoparticles were of varying sizes with an average size of 62 nm and mostly of spherical shape. The successful immobilisation of silver nanoparticles on modified track-etched PET membrane was further characterised by ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The silver-coated track-etched PET membrane was used as a

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RESPICE PROSPICE

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platform for detection of acetaminophen by SERS. The acetaminophen solutions were prepared in concentrations of 15.10 mg/L, 1.510 mg/L and 0.151 mg/L. Raman spectroscopy was used to qualify the detection of the acetaminophen on the surface of the silver-coated track-etched PET membrane. Raman spectroscopy was also used to qualify the suitability of a silver-coated track-etched PET membrane for the detection of acetaminophen. One of the achievements was the suppression of the Raman signal of the polyethene terephthalate monomer of the polymer membrane itself by a layer of silver nanoparticles. The immobilisation of silver nanoparticles on the surface of amine-modified track-etched PET membrane using diethylenetriamine, during reduction reaction of silver nitrate by trisodium citrate has not been reported anywhere in literature. The acetaminophen was detected using a 514 nm monochromatic excitation laser. The acetaminophen concentrations were 0.151 mg/L, 1.510 mg/mL and 15.10 mg/L. The use of track-etched membrane for pre-concentration was found not to be a useful pre-concentration filtration technique as envisaged in the proposal. The pores were too large to retain all acetaminophen molecules on the surface. Thus pre-concentration would require pores in low nanometre range, less than 100 nm. The acetaminophen was filtered through along with water molecules. As a result a drop and dry method was adopted as a way of preparing the samples of acetaminophen for detection on the surface of track-etched polymer membrane. The acetaminophen was identified when it was dropped and dried on the surface of silver-coated track-etched PET membrane. The unmodified track-etched PET membrane did not show any fingerprint peaks of acetaminophen spectrum; the only observable peaks were those of the polyethene terephthalate membrane itself. This confirmed that the detection of acetaminophen by Raman spectroscopy was as a result of Raman signal enhancement by silver nanoparticles that were immobilised on the surface of the amine-modified track-etched PET membrane.

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WESTERN CAPE

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Declaration

I declare that *Silver-coated polyethene terephthalate membrane for detection of pharmaceuticals using surface-enhanced Raman spectroscopy* is my own work, that has not been submitted for any other degree or examination in any other university and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

George Michael Ndilowe November 2017

Signed......................................

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WESTERN CAPE

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RESPICE PROSPICE
UNIVERSITY of the
WESTERN CAPE

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Contents

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WESTERN CAPE

http://etd.uwc.ac.za

UNIVERSITY of the WESTERN CAPE

http://etd.uwc.ac.za

UNIVERSITY of the WESTERN CAPE

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http://etd.uwc.ac.za

RESPICE PROSPICE
UNIVERSITY of the
WESTERN CAPE

http://etd.uwc.ac.za

List of Figures

http://etd.uwc.ac.za

UNIVERSITY of the
WESTERN CAPE

http://etd.uwc.ac.za

List of Tables

UNIVERSITY of the
WESTERN CAPE

http://etd.uwc.ac.za

Abbreviations

PET	Polyethene terephthalate
SERS	Surface-enhanced Raman spectroscopy
GC/MS	Gas chromatography/Mass spectrometry
TEM	Transmission Electron Microscope
UV-Vis	Ultra-Violet - Visible
SEM	Scanning electron microscopy
FTIR	Fourier transform infrared
XPS	X-ray photoelectron spectroscopy
TGA	Thermogravimetric analysis

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WESTERN CAPE

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CHAPTER ONE

Introduction

1 Introduction

This chapter outlines a brief background related to the main focus areas of the study. The chapter covers an overview of environmental pollution particularly in the aquatic environment and the existence of pharmaceuticals as persistent organic pollutants. The chapter also briefly mentions analytical techniques in detection of pharmaceuticals focusing on surface-enhanced Raman spectroscopy (SERS) as well as the synthesis and use of silver nanoparticles as SERS active materials (SERS substrates) and the application of polymer membrane technology in water purification. The chapter goes further to outline the problem statement, aim and objectives, research questions and approach, and the scope and delimitations. A brief thesis layout is also included at the end.

1.1 Background of the study

Anthropogenic water pollution has become an increasingly serious environmental problem (Li *et al.*, 2014a). This has arisen due to the exponential growth of the human population, thereby putting more stress on already scarce clean water sources (Mokhena *et al.*, 2015). South Africa is one of the countries with a high scarcity of fresh water systems arising from highly variable and spatially distributed rainfall (Adewumi *et al.*, 2010). However, there is a growing interest worldwide to reuse wastewater so as to address some of the challenges associated with clean water shortages (Mulamattathil *et al.*,2014). The reuse of wastewater could augment conventional water supplies through improving the quality of unconventional water sources (Qu *et al.*, 2013). Wastewater reuse affects the quality of water if proper treatment procedures are not followed. The use of recycled wastewater for consumption exposes users to high levels of persistent organic pollutants such as personal care products and pharmaceuticals

RESPICE PROSPICE UNIVERSITY of the WESTERN CAPE

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(Stackelberg *et al.*, 2004). Pharmaceuticals and personal care products have been detected at low concentrations in wastewater treatment plant effluent, surface water, drinking water and groundwater (Pavlović *et al.*, 2013; Ratola *et al.*, 2012). These persistent organic pollutants find their way into water systems from wastewater treatment plant effluents due to ineffective treatment protocols and due to improper disposal of pharmaceuticals and personal care products (Ratola *et al.*, 2012).

Pharmaceuticals are human and veterinary medicinal compounds that have a specific activity in the body (Klavarioti *et al.*, 2009). Pharmaceuticals are physically and chemically dynamic as they vary widely in molecular weight, structure, shape and their specific activities, which are influenced by functional groups (Nghiem *et al.*, 2005). They are polar molecules and their properties vary with solution pH and temperature in aqueous environments (Fatta-Kassinos *et al.*, 2011). Some pharmaceuticals are lipophilic and moderately soluble in water. Others can modify their chemical structure when subjected to metabolic reactions (Rivera-Utrilla *et al.*, 2013). Pharmaceuticals are discharged into the aquatic environment by the disposal of expired pharmaceuticals, inadequate treatment of wastewater treatment plants' effluents and leachate from pit latrines in developing countries (Wood *et al.*, 2015; Schaider *et al.*, 2014). These pharmaceuticals such as acetaminophen and sulfamethoxazole, have been detected in rivers, lakes and groundwater in European and Asian countries (Simazaki *et al.*, 2015), wastewater treatment plant effluents and drinking water, which means that they are not completely removed and mineralised by current treatment methods (Pinhancos *et al.*, 2011). For instance, ibuprofen and carbamazepine are stable during photo-degradation treatment (Simazaki *et al.*, 2015). Although recently, there are increased numbers of published reports on pharmaceuticals in the aquatic environment (Agunbiade *et al.*, 2014), very little research has been carried out in South Africa to detect and identify pharmaceuticals in water sources. Pharmaceuticals such as antiretroviral compounds used for HIV treatment and other varieties of pharmaceuticals have been detected in water sources across South Africa (Wood *et al.*, 2015;

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Agunbiade *et al.*, 2014). The pharmaceuticals may have potentially adverse effects on humans and the ecosystem (Schaider *et al.*, 2014; Nikolaou *et al.*, 2007). The various adverse effects include feminisation or masculinisation of aquatic organisms due to exposure to hormones as well as the development of microbial resistance to antibiotics (Agunbiade and Moodley, 2016). The challenge with the presence of many different pharmaceuticals that exist in very low concentrations in the aquatic environment is that they require extensive sample preparation to be detected and identified (Tijani *et. al.*, 2013), each compound requires a specific analytical process in order for the compound to be identified and quantified and also validate the results.

There are several conventional analytical techniques such as high-performance liquid chromatography (HPLC), gas chromatography and liquid chromatography coupled with mass spectrometry (GC-MS, LC-MS), electrochemical and spectrophotometry which are well established for analysis of water pollutants (Li *et al.*,2014a). These techniques require complex sample preparation processes and lack the sensitivity and recognition capacity for different persistent organic pollutants (Li *et al.*, 2014b). Although such pharmaceutical pollutants can be detected, it has been found to be difficult to identify or quantify them at low concentrations. These limitations have led to the exploration of novel detection technologies such as biosensors, fluorescence probes, surface-enhanced Raman spectroscopy (SERS), etc. with the aim of detecting the very low concentration of diverse pollutants (Pavlović *et al.*, 2013; Comerton *et al.*, 2009). Among the emerging techniques, SERS has attracted considerable attention in the detection of trace level analytes (Li *et al.*, 2014b; Smith, 2008) in chemical analysis and biochemistry (Botti *et al.*, 2014). SERS, an extension to Raman spectroscopy, is an analytical technique based on molecular vibrations (Sharma *et al.*, 2009). SERS relies on a combination of electromagnetic and chemical enhancement mechanisms that involve surface electron movement in the SERS-active material and a charge transfer between the SERS-active material and the analyte of interest (Banholzer *et al.*, 2008). Electromagnetic enhancements arise from the excitement of surface plasmon (oscillating electron wave) of the SERS-active

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material that has been induced by an incident laser, thereby creating an electromagnetic field (Halvorson *et al.*, 2010). The energy from the surface plasmon is then absorbed by a nearby or an adsorbed analyte molecule, which then transfers back the energy to the SERS-active material less the amount transferred to its nuclei (McNay *et al.*, 2011). SERS has several analytical advantages over other methods, including ultra-sensitivity and inherent molecular specificity (Huh *et al.*, 2009). The technique requires little or no sample preparation (Zhang *et al.*, 2015; Culha *et al.*, 2012) and, is a convenient and cost-effective process for development of miniaturised equipment (Ma *et al.*, 2015). Furthermore, it can be directly used for water sample analysis with negligible background noise (Li *et al.*, 2010). The performance of SERS is based on detection sensitivity, which depends on the surface property of SERS active materials (Botti *et al.*, 2014).

SERS active materials, usually metal nanoparticle assemblies or nanostructured metal surfaces, are required for measurement and their plasmonic activity defines the extent of SERS applications (Culha *et al.*, 2012). Noble metal nanoparticles (e.g. gold, silver and copper) are good SERS active materials when compared to other transition metals and silver nanostructures have commonly been used as SERS-active materials (Sharma *et al.*, 2013). These noble metal nanoparticles enhance the Raman signal when molecules of analytes are attached or in close proximity to them (Schmidt *et al.*, 2004). Effective adsorption of analytes on SERS active materials is critical when working with low concentrations of analytes (Smith, 2008) such as pharmaceuticals. Among the noble metals, silver has been the most commonly used metal nanoparticles. Silver nanoparticles have the highest surface plasmon resonance in an easily accessible spectral region i.e. in the visible or near infra-red region (Muehlethaler *et al.*, 2015). Immobilisation of SERS active materials on stable supports such as polymer membranes improves reproducibility of the surface-enhanced Raman spectroscopy (Taurozzi and Tarabara, 2007).

RESPICE PROSPICE
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Polymer membranes are organic membranes synthesised from chemically reactive monomers, which have desirable gaseous and aqueous separation capabilities (Adeniyi, 2015). Track-etched polymer membranes are thin polymer membranes that have been bombarded with heavy ions of inert gases such as krypton and xenon that result in latent tracks in the polymer which are further enlarged by physicochemical treatment such as etching to create pores (Fatiyants *et al.*, 2013). Membrane separation processes in the aquatic environment have been extensively utilised due to their benefits, which include the production of high water quality with ease of maintenance, inertness, flexibility and excellent separation efficiency (Lee *et al.*, 2016; Fatiyants *et al.*, 2013; Velleman *et al.*, 2012). Amongst high-performance polymer membranes such as polycarbonate (PC), polyimide (PI), etc, polyethene terephthalate (PET) has good mechanical strength, and thermal and chemical resistance (Korolkov *et al.*, 2015; Muthuvijayan *et al.*, 2009). PET is a linear, aromatic polyester type of organic polymer (Marchand-Brynaert *et al.*, 1995). PET, being an inert polymer, lacks the functional groups on the surface to sustainably support SERS active materials. As such it is required that PET membranes undergo surface modification (Muthuvijayan *et al.*, 2009), in order to chemically link metal nanoparticles to the polymer surfaces.

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WESTERN CAPE

There are several surface modification methods such as plasma treatment, corona discharge, UV irradiation, surface graft polymerisation and chemical treatment (Dauginet *et al.*, 2001; Marchand-Brynaert *et al.*, 1995). Chemical modification through wet chemistry methods have been studied before (Fan *et al.*, 2011; Muthuvijayan *et al.*, 2009). Chemical modifications such as aminolysis, hydrolysis, amidation and carboxylation have been used to introduce reactive functional groups on the surface of PET (Muthuvijayan *et al.*, 2009). This functionalisation is achieved through liquid-solid phase organic synthesis. The organic synthesis provides the most stable covalent bond (linkage) to immobilise active compounds such as biomolecules and nanoparticles to functionalised polymer surfaces (Goddard and Hotchkiss, 2007). The choice of the chemical linker, therefore, depends on the chemical properties of the compound to be

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immobilised (Sperling and Parak, 2010). For instance, thiols and amines have a high affinity for noble metal nanoparticles (Braun *et al.*, 2009).

1.2 Problem statement

Pharmaceuticals, which are some of the persistent organic pollutants and emerging endocrine disrupting compounds, have been detected in wastewater treatment plants' effluents and drinking water by electrochemical, chromatography and mass spectroscopy methods. These current analytical techniques are suitable where there is a significant concentration of only a few, known pollutants but fail to detect very low concentrations of diverse contaminants in water samples. The analytical methods in present use also have no simple pre-concentration means to improve the concentration of the pollutant before detection. In recycled water, the concentration of pollutants may be very low but very diverse contaminants may be present and therefore difficult to detect by present analytical methods. As such, there is a need to explore novel and reliable analytical techniques that can detect low concentrations of many different pharmaceuticals with ultra-sensitivity, rapid response and fingerprint capability at low process cost. To address the limitations on detection of low concentrations of pharmaceutical, the use of surface-enhanced Raman spectroscopy is considered as a suitable detection technique in this study. The use of track-etched polymer membrane as both a filter and support for SERS active materials would also be explored. Although SERS has the advantages outlined above, fabrication of SERS active materials that have an affinity for the analytes of interest has been a challenge. It has also been observed that SERS active materials tend to leach off the support due to the lack of a chemical bond between them and the polymer support. The environmental impact of releasing silver nanoparticles is known to be affecting living organisms.

1.3 Significance of study

The use of surface-enhanced Raman spectroscopy (SERS) for detection of low concentrations of diverse analytes is a promising technology that has distinct advantages of ultra-sensitivity, fingerprint capability, rapid responsiveness and

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low-cost process (McNay *et al.*, 2011). This study will explore the use of the track-etched polymer membrane for two purposes: (i) to support plasmonic nanoparticles for the surface-enhanced Raman spectroscopy and; (ii) to act as a platform to capture and pre-concentrate low concentrations of analytes for ease of detection. It is anticipated that this study will serve to provide the rapid identification of low concentrations of pharmaceuticals in wastewater treatment plant effluents and in drinking water.

1.4 Aim

The aim of this study is to fabricate a stable silver nanoparticle coated track-etched polyethene terephthalate (PET) membrane for detection of trace levels of pharmaceuticals in water samples using the surface-enhanced Raman spectroscopy (SERS) technique.

1.5 Objectives

The objectives of the research study are:

- To fabricate a SERS active membrane surface by immobilising silver nanoparticles via a chemical linker (diethylenetriamine) on the track-etched polyethene terephthalate membrane.
- To detect low concentrations of pharmaceutical pollutants in water samples by SERS using silver nanoparticles supported on modified track-etched PET membrane.

1.6 Research questions

The study aimed at providing answers to the following questions:

- Are the nano-silver SERS active materials deposited on a track-etched polyethene terephthalate membrane physically stable?
- Is the chemical linker suitable for immobilising silver nanoparticles on modified track-etched PET membrane surface?
- Is the silver-coated surface of PET membrane able to enhance the Raman signal in order to detect trace level analytes in water samples using SERS?
- Can track-etched polymer membrane be able to pre-concentrate pollutants during filtration?

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- Can the SERS technique quantify, in addition, to identify detected analytes (pharmaceuticals)?

1.7 Hypothesis

The above research questions would be answered by the following hypotheses according to literature review carried out in the thesis:-

- Stable immobilisation of silver nanoparticles on amine-modified track-etched polymer membrane which would not leach from the surface;
- Pollutants can be pre-concentrated using track-etched polymer membrane.
- SERS capability to detect a low concentration of analytes after pre-concentration of the analytes and can be achieved using silver nanoparticles immobilised by aminolysis on the track-etched polymer membrane.

1.8 Research approach/methodology

The following experimental protocol was used in order to realise the aim and objectives of the study:

1.8.1 Modification of track-etched polyethene terephthalate membrane

The as-received track-etched polythene terephthalate (PET) membrane was modified by wet chemistry that involved a solid-liquid interface reaction. The surface of PET membrane was modified with triamine reagent, having amine terminal groups. The amine molecules were coupled to the membrane surface via the carbonyl carbon of the ester of PET by a process known as aminolysis. The reason for using amine terminated molecules was that one of the two amine end groups would be coupled to the PET membrane surface whilst the other free amine group would be used to immobilise the silver nanoparticles via the nitrogen of the amine molecule.

1.8.2 Synthesis of silver nanoparticles

Silver nanoparticles were prepared by a modified method of Lee and Meisel (1982). The silver nanoparticles were synthesised by reducing silver salt precursor (silver nitrate) by a reducing and stabilising agent (trisodium citrate) in aqueous media at a chosen temperature.

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1.8.3 Immobilisation of silver nanoparticles

Silver nanoparticles were immobilised on modified track-etched PET membrane, using a modified method of Solov'ev *et al*, (2007). Amine-modified track-etched PET membrane was immersed in a solution in which silver nitrate was reduced by trisodium citrate. The silver nanoparticles were subsequently immobilised on the surface of the PET membrane during the silver nitrate reduction reaction. The parameters explored during the experimental, are concentration of the silver salt precursor and reducing agent, time and temperature of reaction.

1.8.4 Characterisation techniques

Each stage of modification was characterised by Fourier transform infrared (FTIR), scanning electron microscope (SEM), transmission electron microscope (TEM), ultraviolet-visible spectroscopy (UV-vis), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, zeta (ζ) potential, contact angle measurements and thermogravimetric analysis (TGA). Visual changes were recorded before and after each modification. All membranes obtained after each stage of modification including the initial track-etched membrane were then used to detect pharmaceuticals by surface-enhanced Raman spectroscopy (SERS) in order to verify the effectiveness of the modifications. Acetaminophen (analytical grade) was used as an analyte of interest to check the enhancement of Raman signal by the modified track-etched PET membrane compared to unmodified track-etched PET membrane surface. Acetaminophen is one of the commonly prescribed pharmaceuticals and can be obtained over the counter without a prescription.

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1.9 Scope and delimitations

This study seeks to address the limitations of analytical techniques in detecting very low concentrations of pharmaceuticals present in the water after treatment. The use of the surface-enhanced Raman spectroscopy (SERS) technique aims to incorporate the application of track-etched polyethene terephthalate polymer membrane technology as a support for SERS active materials that will enhance the Raman signal for ease of detection of pharmaceuticals. Acetaminophen will be used as a simulated pharmaceutical pollutant in water. The study has not addressed enhancement factor of the silver nanoparticles immobilised on the surface of track-etched polyethene terephthalate (PET) membrane. Also not investigated is the use of track-etched PET membranes with pore sizes lower than 100 nm for pre-concentration.

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1.10 Thesis layout

The section outlines the thesis chapters and overviews each chapter's main contents that constitute the thesis. The thesis is divided into seven chapters.

Chapter one: The chapter gives the overall concept of the study in addition to the general introduction of the research area. The chapter summarises the possibility of detecting pharmaceuticals in water using surface-enhanced Raman spectroscopy technique via a silver-coated track-etched polyethene terephthalate membrane.

Chapter two: This chapter outlines in detail the review of the literature that leads to the background of the study in the areas of water pollution, pharmaceuticals as persistent and emerging organic pollutants and the use of surface-enhanced Raman spectroscopy for detection of such compounds. The synthesis of silver nanoparticles and modification of polymer membranes are also reviewed. The chapter also presents a critical review of the challenges in the modification of a polymer membrane, immobilisation of silver nanoparticles on polymer surface and application of surface-enhanced Raman spectroscopy in the aquatic environment. A background appraisal of suitable characterisation techniques is also summarised in this chapter.

Chapter three: The chapter presents the modified and adopted experimental protocols used to achieve the objectives outlined in chapter one in order to fulfil the overall aim of the study. Also included in this chapter are the materials and chemical reagents used and the actual settings and conditions applied during characterisation of the samples.

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Chapter four: The observations and results of the study are discussed in this chapter with reference to objectives, hypothesis and research questions of the study as outlined in chapter one. The characterisation results attained are also compared to those results found in the literature review of similar research outcomes. Also discussed are the possible mechanisms of the reactions involved to achieve the method development of fabricating a silver-coated polymer membrane.

Chapter five: In this chapter, the outcomes of the application of the detection method developed are presented and discussed. The results and observations of the developed silver-coated track-etched PET membrane as a surface-enhanced Raman spectroscopy technique for detecting pharmaceuticals in water are also presented in this chapter.

Chapter six: This chapter concludes findings of the study and sets out the recommendations for further investigations and review.

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CHAPTER TWO

Literature Review

2 Introduction

This chapter outlines the background related to the main focus areas of the study. The background covers the overview of environmental pollution particularly in the aquatic environment; the existence of pharmaceuticals as emerging organic micro pollutants; the analytical techniques for detection of pharmaceuticals focusing on conventional techniques as well as surface-enhanced Raman spectroscopy (SERS); the synthesis of silver nanoparticles; and the application of polymer membrane technology in water filtration and as SERS-active material support for detecting micro pollutants.

2.1 Water pollution

Water pollution caused by human activities has become an increasingly serious environmental concern due to its adverse effects upon living organisms (Li *et al*., 2014a). This has arisen due to the exponential growth of the human population and industrialisation, putting more stress on already scarce water sources (Mokhena *et al*., 2015). South Africa is one of the countries with a high scarcity of fresh water systems arising from highly variable and spatially distributed rainfall (Adewumi *et al*., 2010). The available water has not been suitable for human consumption due to the presence of low quantities of organic micro pollutants that are harmful to living organisms (Mouele *et al*., 2015). However, there is a growing interest to reuse wastewater so as to address some of the challenges associated with clean water shortages (Mulamattathil *et al*., 2014). The wastewater reuse would augment conventional water supplies through the safe use of unconventional water sources (Qu *et al*., 2013). Wastewater is defined as a "combination of one or more of the following: domestic effluent consisting

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of black-water (excreta, urine) and greywater (bathing wastewater); effluent from commercial establishments and institutions including hospitals; industrial effluent, stormwater, and urban runoff; agricultural and aquaculture effluent, either dissolved or as suspended matter" (Corcoran *et al*., 2010). Wastewater reuse affects the quality of water if proper treatment procedures are not followed (de Jesus Gaffney *et al*., 2015). The direct or indirect reuse of recycled wastewater for consumption exposes users to high levels of organic micro pollutants such as personal care products and pharmaceuticals (Stackelberg *et al*., 2004).

2.2 Emerging organic micro pollutants

Emerging micro pollutants are chemical compounds that have inherent properties (Bu *et al*., 2016) to resist chemical, biological and photolytic degradation (Bantz *et al*., 2009). The degradation process of emerging organic micro pollutants depends highly on environmental conditions such as microorganism activity, temperature, chemical reactivity due to redox status, pH of solution and exposure to sunlight (Bu *et al*., 2016). The emerging organic micro pollutants have been considered as chemicals of environmental concern that can potentially have adverse effects on living organisms due to their persistence, long-range transportability and bio-accumulation (Xu *et al*., 2013), as well as causing microbial resistance and synergistic effects (Huerta-Fontela *et al*., 2011: Tijani *et al*., 2013). These micro pollutants include a wide range of different chemical compounds as well as metabolites such as pharmaceuticals and personal care products, pesticides, other industrial compounds and by-products (Lapworth *et al*., 2012). These emerging organic micro pollutants are released into the aquatic environment via wastewater treatment plant effluents or improper industrial and household disposal (Tijani *et al*., 2013).

2.3 Pharmaceuticals

Pharmaceuticals are synthetic or natural chemicals used as human and veterinary medicinal compounds that have a specific activity in the body (Klavarioti *et al*., 2009) and are designed to activate therapeutic actions at low concentrations

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(Altintas *et al*., 2016: de Jesus Gaffney *et al*., 2015). Pharmaceuticals are physically and chemically stable and diverse as they vary widely in molecular weight, structure, and shape. Further to such properties, their activities are influenced by functional groups that induce their pharmacological effect (Nghiem *et al*., 2005). The functional groups are either polar or nonpolar and their physicochemical properties vary with the pH of the aqueous solution and temperature of an aquatic environment. Some pharmaceuticals are designed to be more lipophilic (hydrophobic) and therefore, are only moderately soluble in water. Others modify their chemical structure when subjected to metabolic reactions or when exposed to acidic or alkaline environments (Rivera-Utrilla *et al*., 2013). Since pharmaceuticals are made to be stable and highly active even in very low concentrations, they are sometimes excreted in a partially metabolised form or not metabolised at all (Huerta-Fontela *et al*., 2011). In the review by Li, (2014a), the following classes were cited as the most commonly prescribed pharmaceuticals: analgesics/anti-inflammatory (acetaminophen, ibuprofen, etc.); antibiotics (amoxicillin, penicillin, etc.); anti-hypertensive (calcium channel blockers, thiazide diuretics, etc.); psychostimulants (caffeine, etc.); antiepileptics (carbamazepine, etc.) and; hormonal compounds (estradiol, estrone, etc.).

Pharmaceuticals are discharged into water sources through untreated or poorly treated sewerage, from the uncontrolled disposal of pharmaceuticals, from inadequately treated effluents from wastewater treatment plants and from leachate from pit latrines in developing countries (Wood *et al*., 2015). The major contributor of pharmaceuticals and their metabolites that enter the aquatic environment is sewage effluent. The use of pharmaceuticals has drastically increased globally with an increase in the population. This has resulted in their high discharge into the sewerage systems (Li, 2014b). Removal of pharmaceuticals from wastewater depends on the type of treatment technique and physicochemical properties of pharmaceuticals. Additionally, the removal rate of pharmaceuticals in wastewater treatments plants can be as low as 10% (Gaw *et al*., 2014). Pharmaceuticals in the aquatic environment are considered as emerging organic micro pollutants that are suspected to adversely affect living

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organisms (Li, 2014b). Pharmaceuticals may have potential long-term adverse effects on humans and the ecosystem (Altintas *et al.*, 2016: Nikolaou *et al*., 2007) as they are designed to induce therapeutic effects at low doses (de Jesus Gaffney *et al*., 2015). The observed adverse effects include, but are not limited to, feminisation or masculinisation of aquatic organisms due to exposure to hormones such as 17α-ethinylestradiol (Li, 2014b) and the development of microbial resistance to antibiotics (Agunbiade and Moodley, 2016). For instance, carbamazepine was cited by Yuan *et al*., (2013) to be potentially harmful to aquatic organisms at very low concentrations.

Various pharmaceuticals have been detected by chromatographic, electrochemical and mass spectrometry techniques in wastewater treatment plant effluents and drinking water. This is an indication that they are not completely removed by water treatment methods (Pinhancos *et al*., 2011). The occurrence and fate of pharmaceuticals in many water systems vary with consumption patterns, season, geographical location, and are also influenced by the presence of microorganisms for biodegradation. Such occurrence is in addition to continuous prescription and high release of pharmaceuticals into the environment (Bu *et al*., 2016). Although recently, there is an increased number of published reports on the occurrence of pharmaceuticals in aquatic environments, Agunbiade *et al*., (2014) noted that very little research has been carried out in South Africa to detect and identify pharmaceuticals in water sources. Of the few reports available, Wood *et al*., (2015) reported the detection of pharmaceuticals such as antiretroviral compounds used for HIV treatment in water sources across South Africa. Other varieties of pharmaceuticals such as antibiotics and antipyretics were also reported to have been detected and quantified in KwaZulu-Natal (Agunbiade *et al*., 2014). The challenge with the presence of many different pharmaceuticals in aquatic environments is that they exist in very low concentrations, which require extensive sample preparation (Tijani et. al., 2013) for them to be detected and quantified by current analytical techniques e.g. chromatography and mass spectrometry. Moreover, each of the myriads of

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pharmaceuticals requires specific protocols to be developed for separation and accurate identification and quantification.

2.4 Detection techniques

There are several conventional techniques such as high-performance liquid chromatography (HPLC), gas chromatography coupled with mass spectrometry (GC/MS) and liquid chromatography coupled with mass spectrometry (LC/MS), as well as electrochemical and spectrophotometry methods, which are well established for the analysis of water pollutants (Li *et al*., 2013a). These techniques require complex sample preparation processes and lack the sensitivity and recognition capacity for different persistent organic micro pollutants. Furthermore, quantification of low concentrations of pharmaceuticals is also a challenge as some recent studies have shown that most micro pollutants could not be quantified, although they were detected in treated drinking water (Luo *et al*., 2014). The study by Wood *et al*., (2015), on antiretroviral drugs' occurrence in surface water across South Africa, reported an average detection limit of 90 ng/L by using ultrahigh-pressure liquid chromatography tandem mass spectrometry (UHPLC/MS/MS). These limitations, therefore, encourage efforts to develop novel techniques that are able to detect micro pollutants to a single molecule limit. The World Health Organization report of 2012 on pharmaceuticals in drinking water indicated that "monitoring programs for pharmaceuticals in water face practical difficulties due to lack of standardised analytical protocols, high costs and limited availability of analytical instruments". The analytical techniques currently in use for detection of pharmaceuticals such as GC/MS and HPLC/MS are time-consuming, expensive to operate, and restricted to non-mobile operations, which makes them less attractive in emergencies and out of laboratory analysis (Li *et al*., 2013b). In a study conducted by Yuan *et al*., (2013), it was noted that although LC/MS/MS is versatile and selective, the technique is susceptible to matrix interferences that suppress analyte signals and generate inaccurate results. Validation of the results of recoveries is also time-consuming and recovery is prone to inaccuracy.

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These limitations have led to the exploration of novel detection technologies such as biosensors, fluorescence probes, surface-enhanced Raman spectroscopy (SERS), etc. with the aim of detecting trace micro pollutants (Comerton *et al*., 2009; Pavlović *et al*., 2013). Among the emerging techniques, SERS has attracted considerable attention in the detection of trace level analytes in chemical analysis (Smith, 2008) and biotechnology (Botti *et al*., 2014). Therefore, portable SERS equipment could be used as a technique for on-site detection as opposed to chromatography and mass spectrometry that are laboratory based techniques. In addition to portability, SERS has been reported to have ultra-high sensitivity, selectivity, fingerprinting capability and rapid detection (Botti *et al*., 2014). As noted by Li *et al*., (2014a), in the case of an emergency where the demand to identify pollutants in remote areas is a necessity, there is a need to develop convenient analytical techniques for identification and quantification without the need for recovery protocols.

2.5 Surface-enhanced Raman spectroscopy

Surface-enhanced Raman spectroscopy (SERS) is a combination of vibrational spectroscopy and surface chemistry techniques, where the Raman scattering signal enhancement is provided by localised surface plasmon resonance in metallic nanostructures (Le Ru and Etchegoin, 2008). SERS is, therefore, an advanced extension of Raman spectroscopy (Lamsal *et al*., 2012). SERS application can be done where ordinary Raman spectroscopy is short of an identifiable signal from a chosen analyte. Although the SERS application has extensively been studied in the life sciences sector, it is also finding its way into the chemical and materials sciences (Schlücker, Sebastian 2014).

2.5.1 Raman spectroscopy

Raman spectroscopy, as an analytical technique, is based on the interaction between molecules and photons that result in scattering of radiation (McMahon, 2008). This kind of spectroscopy is based on the detection of vibrations arising from changes in polarisability of bonds in an excited molecule due to the Raman effect. The phenomenon that occurs when the inelastic monochromatic light is scattered by molecules at a different wavelength to that of the incident light is

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known as the Raman effect (Lombardi and Birke, 2009). This Raman effect occurs when a molecule is struck by electromagnetic radiation resulting in a shift of the wavelength of the inelastically scattered radiation. When the Raman shift is towards the longer wavelength, it is called Stokes scattering and when shifted towards the shorter wavelength, it is termed Anti-Stokes scattering (Meyers, 2000). Rayleigh scattering is when the overall Raman shift is zero i.e. there is no energy increase or decrease related to vibrational energy levels in the ground electronic state of the molecule (Meheretu, et al., 2014). The Raman shift occurrence can be illustrated in the energy diagram in Figure 2.1. Raman scattering occurs when a laser in the visible or near infrared strikes a molecule and interacts with the electron clouds of that molecule.

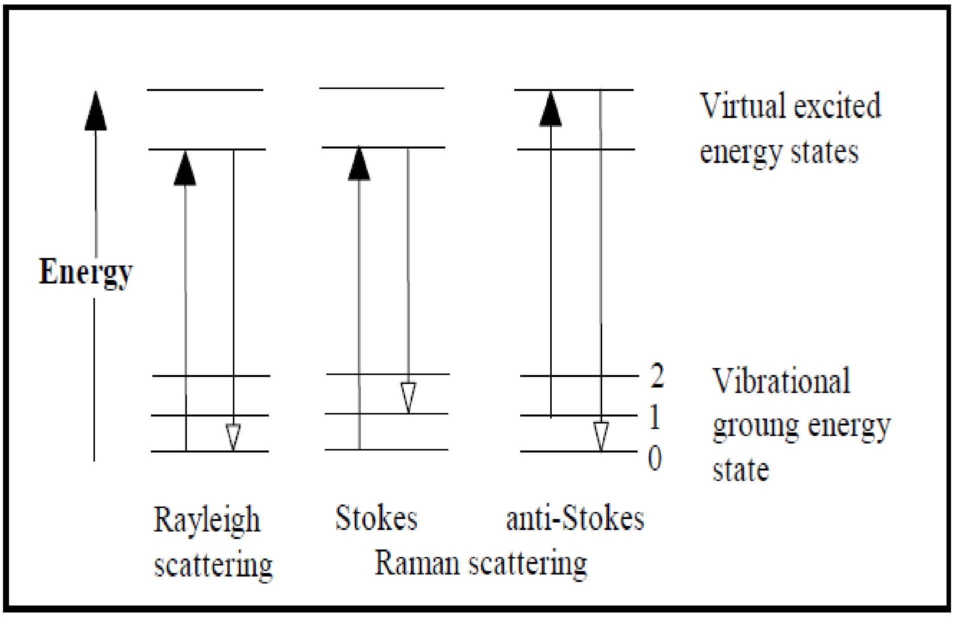

Figure 2.1: Energy level diagram showing the states involved in Raman spectrum and the elastic and inelastic Raman scatterings (Rayleigh, Stokes and Anti-Stokes).

Raman scattering also depends on the polarisability of molecules (Ferraro *et al.*, 2003). The incident photon energy in the laser can excite vibrational modes of the molecules to yield scattered light with diminished energy (Reichenbächer and Popp, 2012). Raman signals are relatively weak when compared to infrared

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signals and they are easily obscured by fluorescence (Boujday *et al.*, 2015). The advantage of Raman over infrared is that it can be used in the aqueous environment since water causes a negligible Raman effect (McMahon, 2008; Matousek *et al.*, 2006). Raman spectroscopy has not been extensively used due to its weak signals. For this reason, much interest has been focused on surface-enhanced Raman scattering through which the Raman signal is enhanced by metal nanostructures (Le Ru and Etchegoin, 2008).

2.5.2 Origins of Surface-enhanced Raman spectroscopy

Surface-enhanced Raman spectroscopy (SERS) relies on electromagnetic and chemical interactions acting on an analyte that has been adsorbed on the surface of a SERS-active material, which has been irradiated by laser light (McNay *et al.*, 2011). In SERS, the Raman scattering signal is amplified by the excitation of localised surface plasmons on a roughened metal which generates amplified electromagnetic fields (Sharma *et al.*, 2013) and charge transfer occurring in the analyte metal complex (Halvorson and Vikesland, 2010). SERS is Raman scattering that enhances vibrational absorbance of analytes adsorbed on or in close proximity (Lamsal *et al.*, 2012) to metal nanoparticles or roughened surfaces (Boujday *et al.*, 2015; Craig *et al.*, 2013). Plasmonic metallic nanostructures increase the signal intensities of Raman scattering, which enables detection of single molecules (Gühlke *et al.*, 2016).

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SERS was first observed in 1974 (Boujday *et al.*, 2015) during the study of pyridine on a roughened silver electrode but was not recognised as an enhanced surface Raman scattering phenomenon until it was later reported in 1977 (Sharma *et al.*, 2013). Later, other authors in their studies claimed to have detected a single molecule of analytes of interest (Kleinman *et al.*, 2013). Over the years the explanation about the occurrence of the SERS signal enhancement has been debated and is resolved to be caused by contributions from the electromagnetic effect, a chemical mechanism, and molecular resonance enhancement (Muehlethaler *et al.*, 2015). The electromagnetic effect arises from the interaction of the excitation laser with an oscillating electron wave on the metal surface (Halvorson and Vikesland, 2010). Electromagnetic enhancement is the most prominent (Péron *et al.*, 2009) of all three contributions as it neither requires the molecules of an analyte under study to be attached to the SERS active materials nor the absorption wavelength of the analyte to be equal or near that of exciting laser (Boujday *et al.*, 2015). The chemical mechanism enhancement occurs when the excitation radiation wavelength is resonant with the analyte-metal complex's charge transfer electronic states (McNay *et al.*, 2011). Molecular resonance enhancement exists when an absorption wavelength of the analyte occurs near the exciting laser wavelength (Muehlethaler *et al*., 2015; Pieczonka *et al.*, 2008). Thus, the molecular resonance enhancement is rarely cited by earlier authors (Lombardi and Birke, 2009).

Surface plasmon resonance (SPR) is the ensemble movement of surface electrons of the random or ordered metal nanostructures (Banholzer *et al*., 2008). Upon excitation of the metal in the charge transfer complex by the incident laser, an electron-hole is created through which energy is transferred to the analyte and Raman scattering occurs (McNay *et al*., 2011). The energy from the surface plasmon is then absorbed by an analyte nearby or adsorbed on the metallic SERS-active material, which then transfers the energy back to the SERS-active material less the amount it transferred to its nucleus (McNay *et al*., 2011). The magnitude of the enhancement mechanism depends on the morphology of the metal nanoparticles, the localisation of a molecule, the excitation wavelength and light polarisation (Craig *et al*., 2013; Lombardi & Birke, 2009). The dominating effects of spectral enhancement characteristics of the analyte caused by surface roughness are the surface plasmon resonance of the metallic surfaces and their corresponding variations (Craig *et al*., 2013; Pieczonka *et al*., 2008). The collective excitation of surface electrons (surface plasmon resonance) is affected by the distance between metal nanoparticles, the shape of nanoparticles and their dielectric functions (Rodrigues *et al*., 2013). The plasmonic metal nanostructures cause resonance Raman scattering that results in enhancement of both incident light and the inelastic light scattered by the adsorbed analyte (Craig *et al*., 2013).

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2.5.3 Surface-enhanced Raman spectroscopy active materials

The surface-enhanced Raman spectroscopy (SERS) active materials are metallic nanostructures, whose localised surface plasmons upon excitation enhance the Raman scattering signals of proximate or adsorbed analyte molecules (Wang *et al*., 2015). Noble metal nanoparticles (gold, silver, and copper) provide good SERS active materials when compared to other transition metals (Sharma *et al*., 2013; Wang *et al*., 2015). The surface plasmon resonance of these noble metals is easily obtained within the visible and near infrared region compared to other metals whose plasmonic effects lie outside the visible region (Álvarez-Puebla, 2012). SERS sensitivity of dilute solutions is improved by metallic nanostructures that increase the signal intensity of the Raman scattering by several factors (Gühlke *et al*., 2016). There are a number of optimisation factors that enhance the effectiveness of the active materials in terms of sensitivity and reproducibility. The controlled factors are the morphology of the metallic nanostructures (Muehlethaler *et al*., 2015: Kruszewski *et al.*, 2011). Further to morphology of nanostructures and orientation, the close spacing of nanostructures on the surface of an anchor material is beneficial for the production of strong localised electric field enhancements (Schlücker, 2014). The active materials are classified into groups based on how they are fabricated and used such as colloidal suspension, immobilisation on solid supports and template synthesis or lithography. When synthesising SERS active materials, the shape and size of nanoparticles are determined by the intended application and environments of use (Culha *et al*., 2012). For example, colloidal suspensions are mostly used in liquid environments (Fan *et al*., 2011). The uses of plasmonic nanostructures as SERS active materials provide a large surface area, which is one of the fundamental properties of nanotechnology. Most commonly used SERS active materials are colloidal metallic nanoparticles that are produced via simple and efficient bottom-up methods, by adding reducing agents to aqueous solutions of noble metal salts (Cialla *et al*., 2012). Although there are other efficient methods of preparing SERS surfaces such as vapour deposition and ion beam sputtering, such techniques require sophisticated equipment, and therefore are not cost effective (Ma *et al*., 2013). The colloidal SERS active materials self-

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assemble on planar supports via heteroatom molecules, usually thiols and amines (Caro *et al.*, 2008), which serve as anchors on which they are arranged in large arrays for SERS application (Cialla *et al*., 2012). Immobilisation of SERS active materials on stable supports such as modified membranes improves reproducibility of active materials and flexibility of their application in various fields (Taurozzi and Tarabara, 2007).

These noble metal nanoparticles enhance the Raman signal when molecules of analytes are attached or are in close proximity to them (Schmidt *et al*., 2004). The analytes with thiol and amine functional groups have an inherent affinity towards the SERS-active materials, which are made of silver, gold and copper, where localised surface plasmon resonances are created (Du *et al*., 2011). Effective adsorption of analytes on active materials is critical mainly when working with low concentrations of analytes (Lamsal *et al.*, 2012; Smith, 2008) which could be achieved by creating an environment that enhances the high affinity of analyte towards the SERS-active material (Bantz *et al*., 2009). In a report by Gühlke *et al*., (2016), it is noted that less water soluble organic compounds such as nonpolar carotenoids have a poor affinity for the silver nanoparticle surface. In order to improve enhanced SERS spectra of organic compounds with a low affinity towards silver nanoparticles, the nanoparticles were functionalised with an organic layer that created a hydrophobic environment (Gühlke *et al*., 2016). Such hydrophobic environments could be prepared by chemisorbing thiol or amine terminated organic molecules on silver or gold nanoparticles. Thiol and amine terminated organic compounds form covalent bonds between silver (and gold) and nitrogen (or sulphur) atoms. Straight chain alkanethiols such as pentanethiol and hexanethiol (Li *et al*., 2014a), have previously been employed to create hydrophobic environments that allow interactions of hydrophobic analytes with the functionalised nanoparticles (Bantz *et al*., 2009). In a study to detect polycyclic aromatic hydrocarbons (PAHs) using SERS, Costa *et al*., (2006) reported successful functionalisation of alkanethiol on gold nanoparticles used as SERS active materials and showed improved selectivity of hydrophobic polycyclic aromatic hydrocarbons (PAHs) and enhanced concentration of PAHs

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close to SERS active materials. Luo *et al*., (2014) reported that the alkanethiol-coated gold active materials immobilised on quartz, gave strong Raman signals (high sensitivity) and are reproducible. It has been noted that selectivity of analytes on SERS active materials could be intensified by intermolecular attractions such as electrostatic, van der Waals forces, hydrogen bonding between the analyte and metal nanostructure SERS-active material (Schlücker, 2014). The stability of SERS active materials can be enhanced by functionalising the SERS-active material with analyte specific molecules such as thiol-terminated molecules which form self-assembled monolayers on metal nanoparticles. Additionally, such functionalised molecules interact selectively with molecules of the analyte of interest, thereby attracting the analyte to the surface of the SERS-active material (Schlücker, 2014). Silver nanoparticles have the highest surface plasmon resonance in an easily accessible spectral region that is visible or near infra-red region (Muehlethaler *et al*., 2015). In this study silver nanoparticles serving as SERS active materials are immobilised on the surface of amine-modified track-etched PET membrane via a chemical bond with the nitrogen.

2.5.4 Silver nanoparticles

Nanoparticles are clusters of atoms that have formed nanoscale structures, in the size range of 1 to 100 nanometres (Sharma *et al*., 2009). These nanostructured materials exhibit physical, biological, electrical and chemical properties that differ substantially from bulk materials (Abou-el-Nour *et al*., 2010; Khodashenas *et al*., 2015). The exhibited properties of nanoparticles are dependent on size, shape and distribution. The nanoparticles have been of interest in the areas of catalysis, photography (Abou-El-Nour *et al*., 2010; Sharma *et al*., 2009; Smyth *et al*., 2013), biotechnology, sensing, optics and surface-enhanced Raman spectroscopy (Khan *et al*., 2011; Patil *et al*., 2012). Nanoparticles exhibit enhanced properties compared to bulk properties due to their high surface-to-volume ratio (Abou-El-Nour *et al*., 2010).

Nobel metal nanoparticles have many applications in nanotechnology due to their versatility, for instance, silver nanoparticles have anti-bacterial activity and

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exhibit narrowly localised surface plasmon resonance within the visible and near infrared region (Meng *et al*., 2010). Silver nanoparticles have attracted the attention of researchers due to their good conductivity, chemical stability, anti-bacterial activity, unique electrical and optical qualities (Khodashenas *et al*., 2015). Due to surface plasmon resonance qualities, silver nanoparticles have been studied as surface-enhanced Raman spectroscopy (SERS) active materials in the fields of biotechnology, biomedical, sensing and environmental monitoring (Natsuki *et al*., 2015; Reddy, 2015).

Synthesis of silver nanoparticles is done by two approaches: the chemical approach, which is bottom-up (use of silver salts as precursors) and the physical approach, which is mainly top-down, e.g. lithography (Biswas *et al*., 2012). All other routes of synthesis of silver nanoparticles except the physical route involve reduction of silver salts by chemical reducing agents, microorganisms, ultrasonic radiation, laser irradiation, ultraviolet-visible light, etc. (Ramírez-Meneses *et al*., 2015). The physical approaches of synthesising silver nanoparticles are carried out by processes such as evaporation-condensation and mechanical processes and require designated equipment to control fabrication parameters such as temperature and pressure (Abou-El-Nour *et al*., 2010; Tolaymat *et al*., 2010). This approach requires a great deal of energy in order to synthesise stable nanoparticles since it is based on external parameters (Biswas *et al*., 2012). The physical synthesis approach has an edge over the wet chemical approach due to the possible large-scale production of silver nanoparticles that have a very narrow size distribution. However, the approach utilises external physical energy that requires expensive equipment rendering the whole process costly (Tran *et al*., 2013). Synthetic methods falling under chemical reduction approaches are wet chemistry, radiation, electrochemical, photochemical, sonochemical and biological routes (Tan *et al*., 2013). The choice of synthesis method relates to the particular field of the application based on cost, stability, shape and size of nanoparticles and applicable properties (Natsuki *et al*., 2015; Niu *et al*., 2016; Reddy, 2015). Among the existing synthesis routes, the wet chemistry reduction method has been widely used due to cost effectiveness (Khan et al., 2011).

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Colloidal silver nanoparticles have been preferentially used as SERS active materials due to cost effectiveness and stability compared to gold nanoparticles and copper nanoparticles respectively (Natsuki *et al*., 2015). Parameters that are employed to synthesise silver nanoparticles of particular size, shape and dispersion are: controlled pH of solution; molar ratio of stabilising agents to that of silver salt precursors; temperature (Khodashenas *et al*., 2015); time of reaction or exposure; and power of photo-irradiation (Kshirsagar *et al*., 2011). Careful control of reaction parameters such as temperature, pH and concentrations of the silver salts and reducing agents lead to systematic nucleation and subsequent growth of initial silver nuclei (Tran *et al*., 2013). The most commonly used silver salt precursor is silver nitrate and water is the most common solvent. Sodium borohydride and sodium citrate have been used as reducing agents in most studies regarding the synthesis of silver nanoparticles (Tolaymat *et al*., 2010). In a study by Patil *et al*., (2012), it was noted that varying the concentration of silver salt precursor (silver chloride) or stabilising agent (polyvinyl alcohol) or time of reaction did affect the size of silver nanoparticles synthesised at fixed alkaline pH. Similarly, Khan *et al*., (2011), noted that changing the concentration of the reducing agent (aniline) had a significant effect on the size, shape and size distribution of synthesised silver nanoparticles. Following a study to synthesise silver nanoparticles by photo-reduction of silver nitrate, Kshirsagar *et al*., (2011), concluded that the rate of synthesis of silver nanoparticles varied with the power of the source for photoirradiation. Silver nanoparticles were synthesised at a faster rate when high-powered sources of photo irradiation were used compared to low powered sources (Kshirsagar *et al*., 2011). Strong reducing agents such as silver borohydride, of silver salt precursors, resulted in smaller spherical nanoparticles due to the spontaneous reaction that induces rapid nucleation process which is controlled by using dilute solutions (Qin *et al*., 2010). Weak reducing agents such as ascorbic acid become more effective at elevated temperatures than at room temperature but their effectiveness could be enhanced by the use of a catalyst (Singha *et al*., 2014). In a review by Tan *et al*., (2013), it was noted that the size and shape of the synthesised silver nanoparticles depended on the pH of the reaction solution. For instance, medium alkaline pH

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values (between 9 and 11) gave smaller sized nanoparticles as compared to weakly alkaline and slightly acidic reagents (Qin *et al*., 2010). In a report by Xu *et al*., (2008) it was stated that increasing the molar ratio in favour of the reducing and stabilising agent resulted in a faster rate of silver nanoparticle formation at the same UV irradiation time and alkaline pH. This was ascribed to the generation of more photoelectrons by a higher concentration of reducing and stabilising agent, resulting in a subsequent reduction of silver salts to metallic nanoparticles.

The green chemistry principles have attracted the interest of researchers due to increasing environmental concerns. This has led to the synthesis of silver nanoparticles using approaches that mitigate environmental degradation (Sharma *et al*., 2009). Important principles to consider in green chemistry synthesis of silver nanoparticles are the utilisation of environmentally benign solvents, environmental friendly reducing and stabilising agents, and non-toxic silver salt precursors (Raveendran *et al*., 2003). Most of the benign reducing and stabilising agents such as citrate ions have a weak binding interaction with metal nanoparticles (Schlücker, 2014) and so are easily displaced by strong binding ligands such as thiols or amines during ligand exchange reactions (Caragheorgheopol *et al*., 2008; Raveendran *et al*., 2003). In this study citrate ions, from reducing agent trisodium citrate, which are used to stabilise silver nanoparticles, would be displaced by amines or thiols during ligand exchange reactions (Sperling and Parak, 2010). The ligand exchange would occur during immobilisation of silver nanoparticles on amine-modified track-etched polyethene terephthalates membrane. Citrate ions chemisorb to noble metal nanoparticles via carboxylate groups, which have weak binding energy compared to thiols and amines (Schlücker, 2014).

2.5.5 Applications of surface-enhanced Raman spectroscopy

There is a wide range of applications of surface-enhanced Raman spectroscopy (SERS) as an analytical technique in the fields of biotechnology (Boujday *et al.*, 2015), food industry, warfare anti-terrorism, drug abuse (Craig *et al*., 2013) and

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environmental applications (Halvorson and Vikesland 2010), electrochemistry, surface and material science (Hering *et al*., 2008). The SERS technique has attracted many researchers in environmental pollutant analysis, with the main focus on detecting, identifying and quantifying very low concentrations of pollutants found either in air or water sources (Le Ru and Etchegion, 2008). The driving force behind research and development of SERS is the trace level analysis capability of the technique and cost effectiveness (Lucotti *et al.*, 2007). The technique also offers good practical utility (Li *et al*., 2014a). SERS has several analytical advantages over other methods including ultra-sensitivity, selectivity and inherent molecular specificity (Boujday *et al.*, 2015; Huh *et al.*, 2009). Chemical analysis by SERS requires little or no sample preparation (Zhang *et al*., 2015), is convenient and cost effective for development of miniaturised equipment (Ma *et al*., 2015; Lucotti *et al*., 2007). SERS has an edge over infrared spectroscopy, as it can be directly applied in the aquatic environment with negligible background noise due to low polarizability index of water (Li *et al*., 2014a). Although similar techniques such as fluorescence are already well established, the emerging SERS has attractive properties such that it can be used both in the near-infrared and the visible spectral region and does not require labelling the analyte of interest as is practised in the fluorescence technique (Cialla *et al*., 2012). The performance of SERS is based on its sensitivity, which depends on the surface property of SERS active materials (Botti *et al*., 2014) that can be tailored to suit the intended application (Péron *et al*., 2009; Costa *et al*., 2006). It is envisioned that SERS could be used to simultaneously identify multiple pollutants in a sample reliably, rapidly and at lower cost (Halvorson and Vikesland, 2010). The SERS technique is flexible such that it can be applied in sequence with other separation techniques, such as nano filtration polymer membrane technology and chromatography (Muehlethaler *et al*., 2015) scanning probe microscopy and microfluidics (Cialla *et al*., 2012).

2.6 Polymer membranes

Membranes are thin physical interfaces that regulate the movement of certain species, depending on physicochemical properties and interaction of the

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membrane surface and the species (Lee *et al*., 2016). Polymeric membranes are organic membranes synthesised from chemically reactive monomers, which have desirable gaseous and liquid separation capabilities. Polymer membrane materials have various applications in fields such as filtration, biotechnology, microelectronics, coating, thin-film technology, etc, which rely on their bulk properties and surface chemistry (Nady *et al*., 2011). Filtration technologies employ polymeric membranes due to their flexibility, stability and ease in processing compared to inorganic membranes (Ahmad *et al*., 2013). Amongst high-performance polymer membranes such as polycarbonate (PC), polyimide (PI), etc, polyethene terephthalate (PET) has good mechanical strength as well as thermal and chemical resistance (Korolkov *et al*., 2015; Muthuvijayan *et al*., 2009). PET is a linear, aromatic polyester type of organic polymer; its monomer is shown in Figure 2.2 (Marchand-Brynaert *et al*., 1995).

Figure 2.2: Monomer structure of polyethene terephthalate polymer

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Polymer membranes that have undergone bulk modification such as track-etching can be used as permeable supports for the surface-enhanced Raman spectroscopy SERS-active materials (Taurozzi and Tarabara, 2007).

2.6.1 Track-etched polymer membrane

The track-etched polymer membranes are porous polymer films/membranes that have been bombarded with energetic ions of inert (e.g. argon) or reactive (e.g. nitrogen) gases followed by physicochemical treatment with an alkali solution (Fatiyants *et al*., 2013). Track-etched polymer membranes that are micro porous, are generally used in microfiltration to separate solutes based on the size of particulate matter and the size of pores of the membrane (Lee *et al*., 2016). Polycarbonate and polyethene terephthalate are the most commonly used track-etched polymer membranes in the polymer industry (Apel, 2001) due to their mechanical properties and stability when exposed to acids and organic solvents (Lalia *et al*., 2013). Track-etched membranes have an edge over nonporous membranes as their pore structures can be controlled in terms of size, shape and density of pores to suit the intended application such as ultra filtration (Apel, 2001). The pore sizes and shape are determined through a process known as chemical etching; where etchants such as sodium hydroxide are used to control or increase the sizes of pores (Lalia *et al*., 2013). The track-etched membranes are prepared by bombarding polymer membranes with heavy ions that lead to the formation of latent tracks in the membrane. The membrane is then exposed to chemical etchants such as sodium hydroxide to reveal randomly distributed but uniform pores of a specific diameter, in a process called chemical etching (Apel *et al*., 2015). The pore density on the surface and the size of pores are controlled by the density of heavy ions and the concentration and type of etching reagents used to create tracks in the membrane (Dauginet *et al*., 2001).

2.6.2 Separation and filtration process

Membrane technology has been extensively used in water quality assurance due to its good performance and flexibility (Lee *et al*., 2016). Membrane separation processes in the aquatic environment have been extensively applied due to their benefits, which include the production of high water quality with ease of maintenance, inertness, flexibility and excellent separation efficiency (Fatiyants *et al*., 2013; Lee *et al*., 2016; Velleman *et al*., 2012). Although microporous membranes have pores with sizes much larger than the molecular sizes of organic micro pollutants, surface modification of the polymer has been used to enhance adsorption via hydrophobic interaction (Luo *et al*., 2014). The hydrophobic polymer membrane surfaces were used to retain hydrophobic pharmaceuticals such as estradiol due to higher octanol-water (K_{ow}) partitioning coefficient (Luo *et al*., 2014). Such chemistry of separation could be used to retain hydrophobic

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organic molecules of pharmaceuticals on track-etched PET membrane that has been modified accordingly.

2.6.3 Modification of polymer membrane surface

Several techniques have been reported in the literature for the surface modification of polymer membranes such as physical, chemical and bulk modification (Goddard and Hotchkiss, 2007). The techniques include: surface coating e.g. sputtering; chemical treatment e.g. cross linking and functionalising with reactive species; and annealing with heat treatment for bulk modification (Zhao *et al*., 2013). There are a number of factors to be considered during the surface modification processes such as uniformity, reproducibility, stability, process control and cost effectiveness (Nady *et al*., 2011). Control of reaction conditions limits degradation of the surface of the polymer membrane. This is a result of the wet chemical modification, which results in chain scission of the polymer that activates reactive moieties e.g. carboxyl and hydroxyl on the polyethene terephthalate (PET) membrane surface (Noel *et al*., 2013). Polymer membrane surfaces are modified in principle by two methods: the chemical methods that involve treatment with reagents, and the physicochemical methods that use external factors to induce chemical transformations (Fatiyants *et al*., 2013) and are further described in the following subsections.

2.6.4 Physicochemical methods of polymer membrane modification

Techniques that alter polymer membrane surface properties (surface chemistry) have attracted the attention of researchers in polymer membrane science with the aim of functionalising and immobilising compounds of interest on the surfaces for various applications (Talbert *et al*., 2012). Polymer membranes are inert and therefore lack reactive functional groups on which chemical linkers, metal nanoparticles and biomolecules could be attached sustainably (Goddard and Hotchkiss, 2007). The inert nature of most polymer surfaces limits their use in applications, hence surface modification is required to achieve the desired

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properties while maintaining the bulk polymer properties (Reznickova *et al*., 2014).

The most widely used physicochemical surface modification methods are plasma treatment, corona discharge, ultraviolet (UV) irradiation, and surface graft polymerisation (Dauginet *et al*., 2001; Marchand-Brynaert *et al*., 1995). Physicochemical modification methods such as plasma treatment lead to cleavage of chemical bonds, ablation of polymer surface layers, the creation of free radicals and conjugation of double bonds (Švorčík *et al*., 2011). Plasma treatment is also used to impart reactive species such as amines if nitrogen gas is used as plasma treatment medium or to introduce hydroxyl moieties when water is used in the treatment. Inert gases are applied in plasma treatment if no specific functional groups are to be introduced apart from the radicals resulting from chain scission of the polymer membrane (Drobota *et al*., 2013). Among the physicochemical modification methods, the plasma process is preferred since it results in the introduction of specific reactive species needed for the intended application (Long *et al*., 2006).

2.6.5 Chemical modification of polymer membrane surface

Chemical modification techniques are cost effective and make the control of both the functionalisation of molecules and immobilisation of nanoparticles easy (Xue *et al*., 2013). Physicochemical methods are considered as precursors to chemical modification. For instance, plasma activation could be followed by aminolysis or silanisation (Goddard and Hotchkiss, 2007). The most effective way of modifying the surface of a polymer membrane is using wet chemical treatment when all conditions have been optimised to give best results (Ozcam *et al*., 2009).

The surfaces of polyethene terephthalate membranes have been modified using wet chemical treatment by hydrolysis, reduction, aminolysis, carboxylation and glycolysis (Muthuvijayan *et al*., 2009; Ozcam *et al*., 2009). The intended application that demands modification of the surface of the polymer membrane determines the method of polymer surface modification (Fávaro *et al*., 2007).

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Velleman *et al*., (2012), observed that polymer surface modifications have definitive purposes based on the functional groups of molecules and nanoparticles to be immobilised for that intended application (Deldime *et al*., 1995). A careful choice of conditions for surface modification should be made to limit degradation of the desirable mechanical and chemical properties of the bulk polymer (Fatiyants *et al*., 2013). The wet chemistry parameters including temperature and time of treatment as well as solvent type and concentration must be accurately controlled to maintain consistent surface modification (Drobota *et al*., 2013; Xue *et al*., 2013). Irena *et al*., (2009) in a study on PET surface modification observed that aminolysis depended on the choice of amine and the varied treatment parameters which were temperature, time and amine solution concentration. It was reported that the number of reactive amine functionalities on PET surface increased with an increase in amine concentration until it reached an optimum point but decreased with a further increase in the amine concentration (Irena *et al*., 2009). In an aminolysis reaction, amine nitrogen through its lone pair attacks an electron deficient carbonyl carbon of the ester link of PET to form an amide bond (Drobota *et al*., 2013) as shown in Figure 2.3.

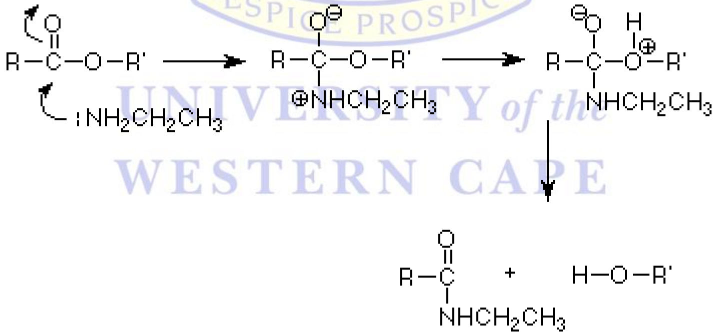

Figure 2.3: The aminolysis reaction scheme

In a review paper by Goddard and Hotchkiss, (2007), it is noted that covalent bond immobilisations provide the most stable bond between the functionalised polymer surface and the adsorbed compounds (biomolecules or nanoparticles). In the study by Xue *et al*., (2013), a comparison of suitable solvents for amine reagents was undertaken and it was observed that amines in ethanol and dimethyl

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sulphoxide introduced more reactive amine functionalities on PET surface than when water was used as a solvent.

2.6.6 Chemical linkers for polymer surfaces

The choice of the chemical linker depends on the chemical properties of the compound to be immobilised (Sperling and Parak, 2010). For instance, thiols and amines have a high affinity for noble metal nanoparticles (Braun *et al*., 2009). Additionally, the linker molecules functionalised on the modified membrane surface serve to modify the chemical properties of the surface. For instance, aliphatic and aromatic linkers provide a hydrophobic environment (Kubackova *et al*., 2014). The functionalised molecules are usually bifunctional so that one terminal group is chemisorbed to the metal nanoparticle or biomolecule and the other functional group is coupled to the modified polymer surface (Goddard and Hotchkiss, 2007). The number of immobilised metal nanoparticles or biomolecules on the functionalised membrane surface is determined by the available affinity functional groups such as thiols and amines (Caragheorgheopol *et al*., 2008). Noble metal nanoparticles chemisorb on thiols and amino terminal groups and form covalent bonds (Sperling and Parak, 2010). Molecules with polyfunctional groups have been coupled to modified polymer surfaces in order to increase the reactive sites on the polymer surface for immobilisation of metal nanoparticles and biomolecules (Goddard and Hotchkiss, 2007).

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Taurozzi and Tarabara (2007) reported successful functionalisation of aminopropyltrimethoxysilane (APTMS) via amide bond formation on the surface of a polycarbonate membrane and the immobilisation of colloidal silver nanoparticles via an amine-silver bond. Immobilised silver nanoparticles sustained hydraulic conditions applied during the experiment although the nanoparticles were scratched off under mechanical stress (Taurozzi and Tarabara, 2007). This is the advantage of a covalently bonded nanoparticle to polymer surface as there is no leaching into the environment. Andrade *et al.,* (2010) immobilised silver nanoparticles on the surface of modified glass via APTMS, which was coupled via siloxy linkages and the materials were used to detect congo red dyes by SERS. The siloxy linkages functionalised on a modified glass surface used by Andrade *et al*., (2010) were unstable when exposed to some solvent conditions. The siloxy linkage undergoes hydrolysis upon exposure to alkaline and high-temperature environments (Goddard and Hotchkiss, 2007). Švorčík *et al*., (2011) reported immobilising gold nanoparticles on modified track-etched polyethene and PET membranes via biphenyl-4, 4'-dithiol. The presence of the phenyl moiety eliminates any possibility of having both thiol terminals functionalised to the polymer surface.

The use of cross-linking agents results in a complete reaction that improves the number of tethered amines to carboxyl reactive moieties on the membrane surface. Mauter *et al*., (2011), indicated that when the coupling agent, 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride (EDC), was used to facilitate the formation of amide bonds between carboxyl and amine moieties, a higher concentration of immobilised silver nanoparticles is obtained. EDC reacts with carboxyl functionalities to form an amine-reactive intermediate, O-acylisourea, which then reacts with an amine to form an amide bond (Vashist, 2012). The O-acylisourea intermediate easily hydrolyses making it unstable in an aqueous environment. In order to increase the efficiency of EDC-mediated coupling reactions, N-hydroxysulfosuccinimide (NHS) is employed to react with the amine-reactive intermediate, thereby hindering susceptibility of O-acylisourea to hydrolysis (Liu *et al*., 2013). The combination of EDC and NHS, converts the carboxyl group to succinimide ester, an amine-reactive intermediate, thus making it susceptible to nucleophilic attack from a lone pair of electrons on the nitrogen of amine to form an amide bond (Chow *et al*., 2005). Alternatively EDC/NHS chemistry could be used to functionalise chemical linkers at room temperature rather than at elevated temperatures and under aqueous conditions. This would, therefore, limit exposure of the polymer membrane to heat and strong organic reagents/solvents. EDC/NHS chemistry has not been extensively used in coupling amine terminated molecules to reactive carboxyl moieties on track-etched polyethene terephthalate membranes (Mauter *et al*., 2011). The EDC-mediated

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coupling reaction involves many reaction steps to achieve the amide bond formation and therefore is not specific, and synthetically challenging.

2.6.7 Immobilisation of metal nanoparticles

The improvements of the adhesion properties of metal nanoparticles on solid supports help to maintain the integrity and performance of surface-enhanced Raman spectroscopy (SERS) active materials' stability over time (Park *et al*., 2013). Immobilisation of metal nanoparticles via electrostatic interactions is unstable in aqueous environments due to weak binding forces (Caro *et al*., 2008). The use of silver-coated membranes in an aqueous environment demands stable immobilisation of nanoparticles in order to reduce the risk of releasing a high load of nanoparticles into the aquatic environment (Yin *et al*., 2013). In the filtration, the unstable, immobilised metal nanoparticles on modified track-etched membranes could easily leach through the membrane resulting in deterioration and loss of application (Park *et al*., 2013). In a report by Reznickova *et al*., (2014), silver nanoparticles were immobilised on plasma treated polyethene terephthalate (PET) membrane via a biphenyl-4,4'-dithiol. One thiol terminal end was used to form the silver-sulphur bond and the other terminal thiol formed a bond with reactive species on the modified track-etched PET membrane surface. Yin *et al*., (2013) reported the successful immobilisation of silver nanoparticles on polyamide thin film composite membranes via cysteamine as a chemical linker, where the amine was coupled to carboxyl and thiol was covalently bonded to the silver nanoparticle.

It has been noted in literature that most of the polymer membrane modifications are applied in biotechnology, where proteins (amino acids), such as deoxyribonucleic acid (DNA) are anchored to the polymer surface via bi-functional molecules (Li *et al*., 2014a). As observed in some literature, hydrophobic interactions between the polymer surface and organic compounds have been the reason for polymer fouling during water filtration (Kochkodan & Hilal, 2015). The fouling mechanism could be applied in creating a hydrophobic environment on the surfaces of the SERS active materials in order to improve

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hydrophobic attraction between lipophilic organic micro pollutants (for example trace level pharmaceuticals) and the modified polymer surface (Nghiem *et al*., 2005).

In this study aminolysis of the PET membrane surface was carried out using mild reactant, diethylenetriamine that would not degrade the track-etched PET membrane surface in order to preserve its bulk properties such as the mechanical strength. Other factors to be considered would be the use of functionalising reagents whose reaction times are shorter than long chains and high molecular weight chemical linkers, in order to modify the surface of track-etched PET membrane. The study also involved direct immobilisation of silver nanoparticles on the surface of aminolysed track-etched PET membrane during reduction of silver salt precursor (silver nitrate) by a reducing and stabilising agent (trisodium citrate). The direct immobilisation methods saves energy and time as the other immobilisation methods require long hours of immobilisation under delicate conditions. The fabricated platform of silver-coated track-etched PET membrane would act as surface-enhanced Raman spectroscopy platform for detection of acetaminophen.

2.7 Characterisation techniques

Different characterisation techniques are used to investigate processes involving functionalisation of chemical linkers and immobilisation of silver nanoparticles on the modified polymer membrane, and also the synthesis of silver nanoparticles. In addition to the characterisation of the materials, Raman spectroscopy is used to detect acetaminophen as a chosen pharmaceutical which would be dropped and dried on the silver-coated track-etched polyethene terephthalate (PET) membrane.

The techniques usually employed for characterisation are scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet-visible spectroscopy (UV-Vis.), Fourier transform infrared spectroscopy (FTIR), contact angle measurements, Raman spectroscopy, thermogravimetric analysis (TGA), zeta (ζ) potential and X-ray photoelectron spectroscopy (XPS). This section gives

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a brief description of each characterisation technique that will be used to analyse silver nanoparticles, as well as modified and unmodified track-etched PET membranes.

2.7.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is an analytical technique that is widely used in membrane technology to characterise the surface morphology (size, shape and arrangement of particles), porosity, pore size and topography (surface features and texture) of sample materials (Lin *et al.*, 2016).

The electron scanning microscope generates an image of a sample's topography, morphology and also gives the chemical composition and relative ratios of elements and compounds constituting a sample when coupled with electron dispersive spectroscopy (McMahon, 2008). When a sample is scanned with a focused beam of electrons, various signals are produced due to electrons interacting with atoms in the sample. The images are created from detected secondary electrons that have been reflected from the sample's surface as a result of excitation by the primary electron beam (McMahon, 2008).

In this study, SEM is used to characterise and confirm the modification and functionalisation of triamine as a chemical linker on track-etched polyethene terephthalate (PET) membrane surfaces. The technique is also used to characterise immobilisation of silver nanoparticles on the chemical linker attached to the modified membrane.

2.7.2 Transmission electron microscopy

The transmission electron microscopy (TEM) is another electron microscopy technique, in which a beam of electrons passes through the sample as opposed to reflected electrons used in the scanning electron microscopy technique. As the beam of electrons passes through the sample, it interacts with atoms in the sample and in the process is attenuated and finally collected from below the sample through a camera or phosphorescent screen (McMahon, 2008). TEM has been

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used in environmental studies to identify and quantify colloidal nanoparticles in samples (Khan *et al.*, 2011).

TEM is used to characterise the synthesised silver nanoparticles in order to qualitatively determine structural information (shape, size) and particle size distribution (whether mono- or poly-dispersed). This technique complements results obtained from ultraviolet-visible spectroscopy characterisation.

2.7.3 Ultraviolet - visible spectroscopy

Ultraviolet (UV) light with a range of 190-350 nm and visible (Vis) light with a range of 350-800 nm radiations are absorbed by many molecules, upon excitation of the outer electrons in the molecule (McMahon, 2008). When radiation with a specific intensity is passed through a liquid sample, it loses some of its energy resulting in a reduction in intensity, due to reflection off the sample holder (cuvette), scattering and absorption by the sample itself (McMahon, 2008). In order to obtain the intensity attenuation due to absorption only, a control is used as a reference solution which has no analyte. The absorbance of radiation by the sample is shown by the absorption spectrum which is normally continuous and is a plot of absorbance versus wavelength in nanometres (McMahon, 2008).

The technique is used to confirm the formation of silver nanoparticles and information regarding size and shape of colloidal nanoparticles in the sample (Khan *et al.*, 2011, Xu *et al.*, 2008). Therefore, ultraviolet-visible spectroscopy (UV-Vis) would be used to characterise how successfully the silver nanoparticles have been synthesised in terms of size and shape).

2.7.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a nondestructive technique, in which absorption bands expressed in wavenumbers (cm^{-1}), are used to investigate deformations, bending and ring vibrations in a molecule (Schmitt et al., 1998). This technique is mostly used to study the chemical nature of polymer membranes, focusing on the chemical functionalities on the surface (Lin *et al.*, 2016). The technique gives fingerprint information that is specific to frequencies

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of vibrations of the bonds present in a sample material. This provides a convenient way to determine composition of a polymer through analysis of absorption bands and peaks of functional groups in polymer membranes (Lin *et al.*, 2016; McMahon, 2008).

The FTIR technique is used to investigate compositional changes of the modified compared to unmodified membrane.

2.7.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a characterisation technique that is used to determine the thermal profile of a material for comparison purposes when such material has been subjected to applied temperature. It is a technique used to measure the mass of the material as a function of time over temperature in order to determine the degradation, glass transition point of polymers and the melting point (McMahon, 2008).

The technique can be used to investigate the thermal profile of the unmodified, modified and silver-coated track-etched polyethene terephthalate (PET) membranes in terms of their mass loss as a function of temperature. This is for purposes of monitoring if the thermal properties of the PET membrane change with exposure to the modification conditions.

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2.7.6 Contact angle measurement

Contact angle measurement is a widely used method for determination of hydrophobic and hydrophilic behaviour of polymer membranes (Korolkov *et al.*, 2015). An attraction between two interfaces is indicated by the contact angle, whereas if the contact angle is more than 90^{o}, then there is less attraction, indicating hydrophobicity.

There are three options for measuring contact angle: (1) the static contact angle which is measured between a liquid and solid without a change from outside during the measurement, (2) the dynamic contact angle (advancing angle) that is measured in the course of wetting of the solid interface and is not affected by time and (3) receding angle which is also dynamic contact angle, but is measured

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during the de-wetting process and is usually smaller than the advancing angle. The static contact angle option is typically used to determine the contact angles.

The technique is used to confirm surface changes in terms of hydrophobicity and hydrophilicity between unmodified track-etched polyethene terephthalate (PET), amine-modified track-etched PET and silver-coated track-etched PET surface. The presence of amines on the PET surface would result in increased hydrophilic behaviour (Korolkov *et al*., 2015).

2.7.7 Raman spectroscopy

Raman spectroscopy is a characterisation technique hinged on the spectroscopic concept of light scattering by the sample rather than light absorption (McMahon, 2008; Meyers, 2000). Raman spectroscopy is based on the Raman effect which provides structural information in terms of functional groups in a molecule, based on the energy vibrational bands (O'Connor *et al.*, 2013). Raman spectroscopy, just like other spectroscopic methods, is widely used in testing laboratories as it offers data that has chemical specificity (Matousek *et al.*, 2006)

This technique is used in this study in two aspects: (i) as a characterisation technique and, (ii) as an applied analytical technique for detecting molecules on the surface of silver-coated track-etched polyethene terephthalate membrane. As a characterisation technique, it is used to complement other surface chemistry analytical techniques such as X-ray photoelectron spectroscopy (XPS). The technique is also used as a pollutant detecting method under the concept of surface-enhanced Raman spectroscopy.

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2.7.8 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is an analytical technique widely used to characterise surface chemistry of thin films such as polymer membranes (Duwez, 2004). The technique is therefore used to characterise elemental composition by electron spectroscopic means on the surface of the polymer membranes (Finklea *et al.*, 2000; Meyers, 2000). The XPS spectral data gives the binding energies of the atoms on the surface and their chemical environments and complements

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Fourier transform infrared (FTIR) spectra. The binding energy of emitted electrons from an atom is specific and characteristic of that atom and therefore gives fingerprint information (O'Connor *et al.*, 2013).

In this study, XPS is used to investigate the composition of the unmodified and modified track-etched polyethene terephthalate (PET) membrane in order to monitor surface changes resulting from the solid-liquid interface reactions between the amine and PET membrane. The XPS technique was further used to investigate the immobilisation of silver nanoparticles on the surface of modified track-etched PET membrane via a nitrogen atom.

2.7.9 Zeta potential

Zeta (ζ) potential is a technique that is used to determine the stability of the colloidal nanoparticles. The electric charges on the nanoparticles play a role in their stability as the charge hinders agglomeration of the nanoparticles by charge repulsion. The criterion is based on charges of nanoparticles that would repel so as to prevent the nanoparticles from forming clusters. Zeta potential values in either positive or negative direction of more than 20 mV are considered good for stability.

In the study zeta potential was carried to determine the physical stability of the colloidal silver nanoparticles synthesised by reduction of silver nitrate by trisodium citrate under aqueous media.

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2.8 Summary of the chapter

The literature review that was consulted in the present work has provided an important background with regard to limitations of the existing micro pollutants detecting techniques, outstanding properties of surface-enhanced Raman spectroscopy (SERS) in environmental monitoring as well its applications. Various methods were reviewed to fabricate a platform for detection of analytes using SERS, which involved the synthesis of active materials (metal nanostructures) and preparation of SERS-active material supports. An in-depth knowledge of the principles concerning the theory behind surface-enhanced Raman spectroscopy has been gained. The major focus of the literature review was on modification of the surface of polyethene terephthalate membranes, which serve as a SERS-active material support and as membrane for filtration. The review of the present surface modification methods of the SERS-active material membrane supports was undertaken to find ways of improving the stability and reproducibility of the fabricated SERS platform for detection of trace micro pollutants. It has been deduced that the chemically bonded metal nanostructures on the active materials' supports should be stable and reproducible. The chemical bonds should limit the probability of losing the nanoparticles by leaching through the nanopores of the track-etched membrane, thereby releasing them to the environment. In the review, it has been noted that the chemical modification of polyethene terephthalate (PET) membrane and immobilisation of silver nanoparticles should be done in such a way as to chemically bond the silver nanoparticles to the PET membrane surface as opposed to physical deposition of the nanoparticles.

This chapter also highlighted recent developments in the surface modification methods of polymer membrane where chemical methods were successfully applied, mainly in the biotechnology field. Other surface modification methods were reviewed and helped to elucidate an informed surface modification route for the study. The common methods of polymer surface modification are the physicochemical ones, which are expensive. Some modification methods are prone to poor reusability due to loss of SERS active materials that were

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physically adsorbed on the membrane surface. It was noted that wet chemistry modification is preferred due to the formation of strong covalent bonds between the chemical linker and the SERS active materials. The stability of the modified active materials improves reproducibility and good repeatability of SERS results. Although a number of the reviewed publications reported successful functionalisation of the amino-terminated molecules on the surface of membrane via siloxy linkage, the linkage is reported to be susceptible to hydrolysis in alkaline environments resulting in the breaking of the covalent bonds. As such the review looked at the formation of amide bond that would resist similar adverse conditions that weaken the siloxy linkage. The chapter also highlighted the experimental parameters for modification and synthesis of silver nanoparticles such as the temperature of reaction, the concentration of chemical linkers, reaction times, the concentration of silver salt precursors, stabilising and reducing agents. The chosen synthetic route should be based on the use of the chemical reagent that served as a reducing and stabilising agent. In the review, the ease of substitution of the stabilising agent by a chemical linker was considered, where nitrogen of the amine group displaces oxygen of citrate ions, which act as stabilising agents of silver nanoparticles.

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The other part of the literature review focused on the characterisation techniques applied for surface modification of polymer membrane and synthesis of silver nanoparticles. Different publications showed in detail the operating principles of the instrumentation as well as data that can be deduced from analyses. The characterisation techniques can provided analytical information to be used to determine how the surface of polymer membrane has been modified and immobilised with silver nanoparticles. Similarly, in the synthesis of silver nanoparticles, the analysis of data is required for the determination of the size and shape of silver nanoparticles synthesised. The techniques that have been reviewed were scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), ultraviolet-visible spectroscopy (UV-Vis), Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), contact angle measurement, zeta potential and Raman spectroscopy. The

Raman spectrometer is used in the study as a surface chemistry characterising technique complementing FTIR and XPS and also to detect samples of pharmaceuticals by using silver nanoparticles as SERS active materials to enhance the Raman signals.

Therefore, based on the literature reviewed on SERS, silver nanoparticles and track-etched polymer membranes, it would be interesting to investigate the possibility of combining the functions of the track-etched polyethene terephthalate membranes as SERS-active material supports as well as filtration membranes, for the pre-concentration and detection of trace pharmaceuticals found in wastewater treatment plant effluents. The wet chemistry modification of the surface of PET membrane for such purposes has not been investigated and the present work aims to study fabrication of stable SERS active materials that have been covalently bonded to the surface of PET membrane in order to have reproducible SERS signals. This type modification is relatively cheap as it does not require complex equipment. The nanoparticles serving as SERS active materials would not leach through the track-etched membrane to the environment as the nanoparticles are chemically attached to the surface of the track-etched PET membrane.

The chapter to follow describes the experimental procedures of modifying polyethene terephthalate membrane with diethylenetriamine and the process of immobilising silver nanoparticles on the surface. The chapter also outlines the execution of characterisation techniques.

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CHAPTER THREE

Experimental

3 Introduction

This chapter outlines detailed information on methodology as well as parameters investigated in the modification process of track-etched polyethene terephthalate (PET) membrane and synthesis of nanoparticles. The chapter also gives a description of chemicals and materials used to achieve the goals of the research. Also described in this chapter are the characterisation techniques and their sample preparation procedures used to investigate the PET membrane and silver nanoparticles. The chapter has four main sections dedicated to the experimental protocol of the study. The sections are (i) chemicals and materials; (ii) surface modification of the PET membrane; (iii) synthesis of silver nanoparticles; and (iv) characterisation techniques used in the study. The schematic experimental design is also provided in this chapter.

The methods applied in this study were the direct immobilisation of silver nanoparticles on amine treated, track-etched polyethene terephthalate membrane. The modification of the track-etched PET membrane was via wet chemistry methods which have been applied in biotechnology studies where proteins or enzymes are immobilised on the modified membranes (Irena *et al.*, 2009; Ozcam *et al.*, 2009). All amine modifications of the membrane were conducted at ambient conditions unless otherwise stated.

3.1 Chemicals and materials

The section presents the material and chemical reagents used in this study. The material specifications and sources are presented in Table 3.1. The chemical reagents specifications and suppliers are shown in Table 3.2.

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Table 3.1: Track-etched polymer membrane

Name	Polyethene terephthalate
Supplier	Joint Institute for Nuclear Research (JINR), Dubna, Russia
Thickness	23 μm
Pore density	1 x 10^9 cm^{-2}
Pore size	0.100 μm

In brief, the track-etched polyethene terephthalate (PET) membrane used in the study was prepared by bombarding the PET membrane with 147 MeV krypton ions. The latent track PET membrane was then radiated with ultraviolet (UV) light of wavelength 310 nm in order to improve the shape of latent tracks caused by krypton ions. The PET membrane was then etched using 6 M of sodium hydroxide in a thermo-bath between 70 ^{o}C and 90 ^{o}C. Whilst the track-etched membrane was still wet with etching agent (sodium hydroxide), it underwent neutralisation in diluted acetic acid. Thereafter the track-etched membrane was washed with distilled water and dried in hot air using hot air vents.

Table 3.2: Quartz:- Silver- coated glass

Name	Silver-coated glass (Quartz)
Supplier	Joint Institute for Nuclear Research (JINR), Dubna, Russia

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In brief quartz surface was prepared by modifying the silicon oxide solid substrate with silver nanoparticles via thermo vacuum and reactive magnetron sputtering. The sputtered silver nanoparticles were of size 30 nm. The silver-coated quartz was used as received and is herein code-named Quartz throughout the chapters.

Table 3.3: Chemical Reagents

Name of chemical reagent	**Supplier**	**Purity**
Diethylenetriamine (DETA)	Alfa Aesar, Germany	98%
Absolute ethanol (EtOH)	Sigma-Aldrich, South Africa	99.9%
Silver nitrate ($AgNO_3$)	Alfa Aesar, Germany	99+%
Trisodium citrate ($Na_3C_6H_5O_7$)	Alfa Aesar, Germany	98%
Acetaminophen	Sigma-Aldrich, South Africa	Analytical standard

The purchased chemical reagents were used as received. The PET membrane was thoroughly cleaned in a mixture of absolute ethanol and distilled water (1:1 v/v), dried in air under ambient conditions and used without further treatment. All aqueous solutions were prepared using distilled water.

3.2 Modification of the surface of polymer membrane

The surface modification of polyethene terephthalate track-etched membranes involved the following experimental steps: functionalisation (aminolysis) of the PET membrane surface with diethylenetriamine (DETA) via an amide bond; immobilisation of silver nanoparticles on the surface via the silver-nitrogen bond. The schematic experimental protocol in Figure 3.1 shows the surface modification and immobilisation of silver nanoparticles on track-etched PET membrane.

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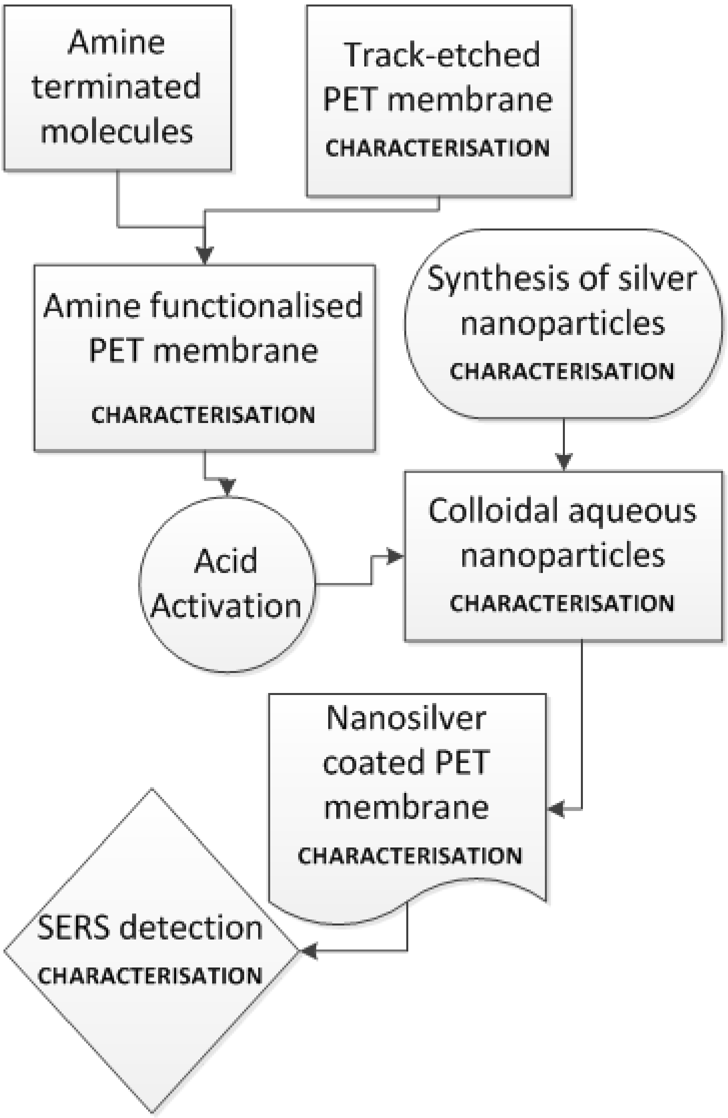

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Figure 3.1: Schematic experimental protocol for surface modification of PET membrane.

3.2.1 Aminolysis of the polyethene terephthalate membrane

The surface of polyethene terephthalate (PET) membrane was modified by immersing a 2 x 2 cm piece of track-etched PET membrane in a 50 mL aqueous solution of diethylenetriamine (DETA). The aqueous DETA concentrations of 45%, 60%, and 75% (v/v) were used for samples 45A-PET, 60A-PET and 75A-PET respectively. The sample codes are described in Table 3.3. One 2 x 2 cm piece of PET membrane was immersed in each of the concentrations of the aqueous DETA solution. The size of the PET membrane pieces were kept the

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same so that any changes to the surface were solely due to external effect not size and area of the membrane. The exposure of PET membranes to the amine solution was carried out at ambient temperature (approximately 23 ^{o}C) for 12 hours, 18 hours and 24 hours. The samples are code named as per Table 3.4.

The aminolysis reaction at the solid-liquid interface was left to run under agitation for a given times of 12 hours, 18 hours or 24 hours for samples 12-APET, 18-APET or 24-APET respectively. After subjecting the PET membranes to an aqueous solution of 75% (also for 60% and 45%) DETA, the membrane was double washed with distilled water and absolute ethanol (1:1 v/v) to remove physically adhered DETA from the surface of PET membrane. The modified track-etched PET membrane was then activated in 1 mM hydrochloric acid for 1 hour under agitation at ambient conditions. The rinsed PET membrane was air-dried at room temperature for 24 hours.

The modified and unmodified track-etched PET membranes were characterised by Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS) to confirm the formation of the amide bond and the presence of amine groups on the surface. The results are presented in Section 4.2.1 for FTIR and in Section 4.2.2 for XPS.

3.2.2 Synthesis of silver nanoparticles

The silver nanoparticles were synthesised using a modified wet chemical method by Lee and Meisel (1982). Silver nitrate was used as a silver salt precursor and trisodium citrate served both as a reducing and stabilising agent. The silver nanoparticles were synthesised by bringing a 100 mL volume of 1 mM of aqueous silver nitrate ($AgNO_3$) to 90 ^{o}C, 75 ^{o}C or 60 ^{o}C for samples coded 75C-PET, 75C-PET or 60C-PET respectively. Aliquots of 1 mL, 2 mL, and 3 mL solution of trisodium citrate (1 g/100 mL) representing samples 1-TriNa, 2-TriNa and 3-TriNa respectively were slowly added dropwise to the solution of silver nitrate upon reaching the determined temperature. Then the mixture was left to react for 10 minutes, 20 minutes or 30 minutes for sample coded 10-AgNP, 20-AgNP or 30-AgNP respectively. The sample codes for optimisation studies are

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described in Table 3.4 of Chapter 3 and Table 4.4 of Chapter 4. Thereafter, the solution was cooled to ambient temperature (23^{o}C). The three parameters (temperature, time and volume) in the synthesis of silver nanoparticles were separately optimised for the best conditions which were applied during direct immobilisation of silver nanoparticles on the PET membrane as described in section 3.3. The optimisation study results are presented in Section 4.3.1 of Chapter 4.

The synthesis of silver nanoparticles was confirmed by ultraviolet-visible (UV-Vis) spectroscopy of the silver nanoparticles solution after reduction of silver nitrate. The shape and sizes of silver nanoparticles were characterised by transmission electron microscopy (TEM). The results are presented in Section 4.3.1.1 for UV-Vis.

3.3 Silver nanoparticles immobilisation

Silver nanoparticles were immobilised on the surface of the amine-modified surface of the track-etched PET membrane by immersing the amine-modified membranes in the preheated silver nitrate solution to which trisodium citrate had been added. The immobilisation of silver nanoparticles on the surface was simultaneously carried out as the synthesis of silver nanoparticles occurred via reduction of silver nitrate by trisodium citrate. A volume of 100 mL solution of silver nitrate (1 mM) was heated to a temperature of 90 ^{o}C. Thereafter, a volume of 2 mL of an aqueous solution of trisodium citrate (1 g/100 mL) was added to the preheated silver nitrate solution followed by immersion of the amine-modified track-etched PET membrane. The reduction of silver nitrate was carried out for 10 minutes, 15 minutes, 20 minutes or 30 minutes for samples 10-AgPET, 15-AgPET, 20-AgPET, 25-AgPET or 30AgPET respectively. The silver nanoparticle-coated track-etched PET membrane was rinsed twice with distilled water to remove physically adsorbed nanoparticles on the surface membrane. Then the silver-coated track-etched PET membrane was air-dried at room temperature for 24 hours. The sample code descriptions are presented in Table 3.4 and experimental parameters in Table 4.4

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The surface morphology of silver-coated track-etched PET membrane was characterised by scanning electron microscopy (SEM) and the chemisorption of silver nanoparticles on the modified track-etched PET membrane was characterised by X-ray photoelectron spectroscopy (XPS). The percentage of silver nanoparticles immobilised on the modified surface of modified track-etched PET membrane is shown by XPS. The SEM and XPS results are presented in Section 4.3.2 of Chapter 4.

3.4 Detection using silver-coated track-etched polyethene terephthalate membrane by surface-enhanced Raman spectroscopy

The Raman spectroscopy technique was used to detect the presence of acetaminophen on the surface of unmodified and silver-coated track-etched polyethene terephthalate membranes. In the study, it is expected that the silver nanoparticles on the surface would enhance the Raman signal, and therefore generate a more visible and readable spectrum of acetaminophen. For concentration studies, three concentrations with sample codes in brackets, of 15.1 mg/L (Aceta-100), 1.51 mg/L (Aceta-010) and 0.151 mg/L (Aceta-001) were prepared in 20 μL aliquots. A 20 μL of acetaminophen was dropped on the surface of a 1x 1 cm piece of the membrane, which were cut from 2 x 2 cm piece that was prepared as described in Section 3.2.1 and was left to dry under ambient conditions for 24 hours since without drying,, it was not possible to detect. When the acetaminophen solution was dried, it was then placed on a platform of the Raman spectrometer for detection. The sample codes are described in Table 3.4. The results are presented in Sections 5.2 and 5.3.

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Table 3.4: Experimental parameters and sample codes for modification of polyethene terephthalate membrane, immobilisation of silver nanoparticles and surface-enhanced Raman spectroscopy (SERS) application.

Aminolysis of polyethene terephthalate (PET) membrane

Parameters	Time/Hours	Concentration%	Sample code
Time of reaction	12 hours	DETA 75%	12-APET
	18 hours	DETA 75%	18-APET
	24 hours	DETA 75%	24-APET
Concentration of DETA	24 hours	DETA 75%	75A-PET
	24 hours	DETA 60%	60A-PET
	24 hours	DETA 45%	45A-PET
	0 hours	DETA 0%	Co-APET

Synthesis of silver nanoparticles (optimisation)

Parameters	Volume	Time	Temperature	Sample Code
Volume of trisodium citrate	1 mL	20 min	75 ^{o}C	1-TriNa
	2 mL	20 min	75 ^{o}C	2-TriNa
	3 mL	20 min	75 ^{o}C	3-TriNa
Time of reduction reaction	2 mL	10 min	75 ^{o}C	10-AgNP
	2 mL	20 min	75 ^{o}C	20-AgNP
	2 mL	30 min	75 ^{o}C	30-AgNP
Temperature of reduction reaction	2 mL	20 min	90 ^{o}C	90C-Ag
	2 mL	20 min	75 ^{o}C	75C-Ag
	2 mL	20 min	60 ^{o}C	60C-Ag

Immobilisation of silver nanoparticles on modified track-etched PET membrane

Parameters	Volume	Time	Temperature	Sample code
Time of immobilisation	2 mL	10 min	90 ^{o}C	10-AgPET
	2 mL	15 min	90 ^{o}C	15-AgPET
	2 mL	20 min	90 ^{o}C	20-AgPET
	2 mL	25 min	90 ^{o}C	25-AgPET
	2 mL	30 min	90 ^{o}C	30-AgPET
			Control	Co-AgPET

Detection of acetaminophen using 30-AgPET sample (concentration)

	Volume	Time	Concentration	Sample code
Concentration of acetaminophen	20 µL	24 Hrs	15.10 mg/L	Aceta-100
	20 µL	24 Hrs	1.510 mg/L	Aceta-010
	20 µL	24 Hrs	0.151 mg/L	Aceta-001

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3.5 Characterisation techniques

This section describes the actual steps and conditions used to analyse the polymer samples and silver nanoparticles investigated under variable parameters. The main characterisation techniques used to achieve the goals of the research included: Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), UV-Vis spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Raman spectroscopy, contact angle measurement and zeta (ζ) potential. This section also outlines procedures for sample preparation for specific characterisation techniques.

3.5.1 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) was conducted to determine changes in functional groups on the polyethene terephthalate (PET) membrane surface. The analytical technique is based on transmitting infrared energy through the sample that gives out the spectra of vibrations of bonds or a collection of bonds. The spectra are then analysed to investigate the existing bonds and their associated functional groups. The modified and unmodified track-etched PET membranes were characterised by FTIR to confirm the formation of an amide bond and presence of amine moieties following the scission of the ester bond on the surface of the track-etched PET membrane. The FTIR spectra of the modified and unmodified track-etched PET membrane samples were obtained using Perkin Elmer model Spectrum Two^{TM} spectrometer. The spectra of the samples were obtained within the wavenumber range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and the scan rate was set at 20 scans per second. The samples were characterised as obtained after modification, no further sample preparation was carried out. The results complement those of X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

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3.5.2 X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) was used to characterise the surface chemistry of the polyethene terephthalate (PET) membranes for elemental analysis and binding energies. The technique complements the Fourier transform infrared (FTIR) and Raman spectroscopy results regarding the introduction of amine and amide functional group on the surface of the PET membrane. The technique was also used to confirm the presence of silver on the surface of the modified track-etched PET membrane after immobilising silver nanoparticles. The XPS measurement was performed using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer. The X-ray source type was a monochromated, micro-focused Al K-Alpha

3.5.3 Ultraviolet-visible spectroscopy

The ultraviolet-visible (UV-Vis) spectroscopy was carried out using Thermo Fisher Evolution 200 spectrometer to determine plasmonic peaks for the confirmation of synthesis of silver nanoparticles. The colloidal silver nanoparticles solutions (approximately 1.5 mL) was placed in a 1 cm path length cuvette. Distilled water was used as a blank to give the baseline spectrum. The spectral characterisation was performed in a 200 - 600 nm range at room temperature.

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3.5.4 Transmission electron microscopy

The morphology (size and shape) of the silver nanoparticles was analysed by characterising the colloidal silver nanoparticles samples using Tecnai G2F20 X-Twin MAT 200 kV field emission gun transmission electron microscope. The samples were prepared by drop-coating one drop of specimen solution onto a holey carbon coated nickel grid. This was then dried under a Xenon lamp for about 10 minutes, where after the sample coated grids were analyzed under the microscope. Transmission electron micrograms were collected using an FEI Tecnai G2 20 field-emission gun (FEG) TEM, operated in bright field mode at an accelerating voltage of 200 kV. Energy dispersive x-ray spectra were collected using an EDAX liquid nitrogen cooled Lithium doped Silicon detector.

3.5.5 Scanning electron microscopy

The scanning electron microscopy (SEM) was used to study the changes of the surface morphology of track-etched polyethene terephthalate (PET) polymer membrane samples after being exposed to silver nanoparticle solutions. The morphological features were investigated at different magnifications to view the effects of experimental parameters on each sample. The surface morphology was characterised using the Hitachi SU8020 scanning electron microscope. The samples were mounted on carbon coated aluminium stubs and were coated by sputtering with carbon using Quorum T15OT for 5 minutes prior to characterisation. The sputter coating was done to provide a conductive surface on the non-conductive PET polymer membrane. The working distance of the scanning probe was set at 5.6 mm and at magnifications of x40, 000, x50, 000 and x100, 000.

3.5.6 Thermogravimetric analysis

The thermal analysis of the unmodified, modified and silver-coated track-etched polyethene terephthalate (PET) membranes with respect to weight loss due to degradation as a function of temperature was characterised by thermogravimetric analysis (TGA). The thermal profile arising from the continuous degradation of the polymers through weight loss with increasing temperature was used to compare the PET membrane samples (unmodified track-etched PET, Amine-modified track-etched PET and silver-coated amine PET). The TGA was conducted using a Perkin Elmer TGA 4000. The PET membrane sample of at least 1.2 g was put in a platinum heating pan (that was cleaned by exposing the pan to the hottest part of the Bunsen burner flame for 5 minutes). The applied heating rate during the thermal analysis was 10 ^{o}C/min starting from an initial temperature setting of 30 ^{o}C to a maximum of 600 ^{o}C in a nitrogen inert

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atmosphere. The flow of nitrogen gas was maintained at 20 mL per minute and at a pressure of 3.8 bars.

3.5.7 Raman spectroscopy

Raman spectroscopy was carried out using a portable version of Enspectr R532 Raman spectrometer to study the surface chemistry of unmodified and modified track-etched polyethene terephthalate (PET) membrane samples. The spectrometer was also used for the surface-enhance Raman spectroscopy (SERS) application to detect analytes on the surface of unmodified and modified track-etched PET membranes besides the surface chemistry of silver-coated track-etched PET membrane. The Raman spectrometer is equipped with an internal laser of excitation wavelength 532 nm. The spectrometer is supplied with the objective lens, Olympus CX22 LED of magnification x10 and x40. The output power used was 20 mW. The exposure time was set at 600 ms with 20 frames. A manual locator was used to find the spot where to place the sample on the sample holder. Manual adjustments were properly made to get the right focus in order to get a focused spectrum.

The sample preparation for SERS application was done by drop and dry method. An analyte solution was dropped on the surface PET membrane and left to dry at room temperature before characterising with the spectrometer.

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3.5.8 Contact angle measurements

The contact angle measurements were done to characterise the variations in hydrophobicity and hydrophilicity of the track-etched membrane before and after modification. The contact angle measurements were carried out using a Kruss DSA 100, which is a drop shape analyser. Distilled water was used for measurement at ambient conditions.

3.5.9 Zeta (ζ) potential

The measurements of zeta potential were carried out in order to study the stability of the colloidal silver nanoparticles. Surface zeta potentials were measured using the zeta analyser, a Malvern Zetasizer Nano Z model. The colloidal silver

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nanoparticles solution samples (5 mL) were diluted with double distilled water (10 mL) and the pH was then adjusted to the required value of pH 6.5. The samples were shaken for 10 minutes. After shaking, the zeta potential of the metallic particles was measured. The sample was placed in a folded capillary cell with a minimum volume of 1.5 mL. The zeta potential values were read from the screen of the computer connected to the Zeta sizer. The characterisation was carried at ambient conditions.

3.6 Summary of the chapter

The description of materials, experimental scheme and protocols including characterisation techniques have been furnished in this chapter. The description in the chapter was specifically on how the experiments were conducted in the laboratory and how samples were prepared for each characterisation technique. The next chapter presents results and discussions regarding the modification of polyethene terephthalate (PET) membrane by diethylenetriamine and also immobilisation of silver nanoparticles. The chapter discusses how the modification of the PET membrane was verified and also the immobilisation of silver nanoparticles on the amine-modified track-etched PET membrane.

The characterisation and discussion include those for the synthesis of silver nanoparticles and characterisation techniques specifically for the monitoring of the property changes of PET membrane and stability of the nanoparticles.

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CHAPTER FOUR

Results and Discussions

4 Introduction

This chapter presents detailed results of the characterisation of unmodified and modified track-etched polyethene terephthalate (PET) membrane, synthesis of silver nanoparticles and immobilisation of silver nanoparticles on the surface of amine-modified track-etched PET membrane. The chapter also outlays a discussion of the outcomes to achieving a silver-coated track-etched PET membrane which is to be used for detection of acetaminophen as an example of a pharmaceutical pollutant in water using surface-enhanced Raman spectroscopy (SERS).

The main characterisation techniques used to determine the outcomes of the fabrication of a silver-coated track-etched PET membrane were the following: Fourier transformation infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible spectroscopy (UV-Vis), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Raman spectroscopy. In addition to these primary characterisation techniques listed above, the following techniques were also applied, namely thermogravimetric analysis (TGA), contact angle measurements and Zeta (ζ) potential. Thermogravimetric analysis was used to investigate the thermal effect arising from solid/liquid interface organic reaction of surface of track-etched PET membranes and diethylenetriamine solution and due to immobilisation of silver nanoparticles on the surface of amine-modified track-etched PET membrane. The contact angle measurements were made to study the water attraction behaviour of the surface of the modified and unmodified track-etched PET membranes as described in Table 3.3 in Chapter 3. The Zeta potential technique was used for

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determining the stability of colloidal silver nanoparticles. ImageJ software was used to calculate the size of the silver nanoparticles from the TEM and SEM images.

4.1 Chemical modification of track-etched polyethene terephthalate membrane

Aminolysis of the track-etched polyethene terephthalate (PET) membrane surface is one of the wet chemistry techniques used to introduce amines on the surface of the polymer membrane via an amide bond. The wet chemistry technique was employed in this research to modify the surface of the track-etched PET membrane. The solid/liquid interface organic reaction involving polyethene terephthalate on the surface of track-etched PET membrane and diethylenetriamine solution results in scission of the ester bond and formation of amide bond. The experimental set up is described in Sections 3.2 and 3.3 of Chapter 3. In brief the optimised experimental set up indicated in Figure 4.2 involved immersion of a 2x2 cm track-etched PET membrane in aqueous solution of diethylenetriamine of concentrations and for the durations defined in Section 3.2.1. Thereafter the track-etched PET membrane was washed with copious amounts of water/ethanol mixture (1:1 v/v). The rinsed membranes were immersed in 1 mM of hydrochloric acid for 1 hour at ambient conditions. The hydrochloric acid activated track-etched PET membrane was then immersed in a mixture of 1% trisodium citrate and 1 mM silver nitrate solution at temperature and time defined in Sections 4.2 and 4.3. The variable parameters in the solid/liquid interface organic reaction were the concentration of diethylenetriamine (75%, 60% and 45%) and the reaction times (24 hours, 18 hours and 12 hours). The parameters that were varied in the synthesis and immobilisation of silver nanoparticles on amine-modified track-etched PET membrane were the volume of 1% trisodium citrate, the temperature and time of reduction reaction of silver nitrate. The generalised reaction equation is shown in Figure 4.1 (Irena *et al.*, 2009).

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$$R-\overset{O}{\overset{\|}{C}}-O-R' + NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + R'OH$$

Figure 4.1: A generalised aminolysis reaction equation

The schematic mechanism of the wet chemistry surface modification of PET membrane with diethylenetriamine (DETA) and immobilisation of silver nanoparticles on the surface of modified track-etched PET membrane is presented in Figure 4.2.

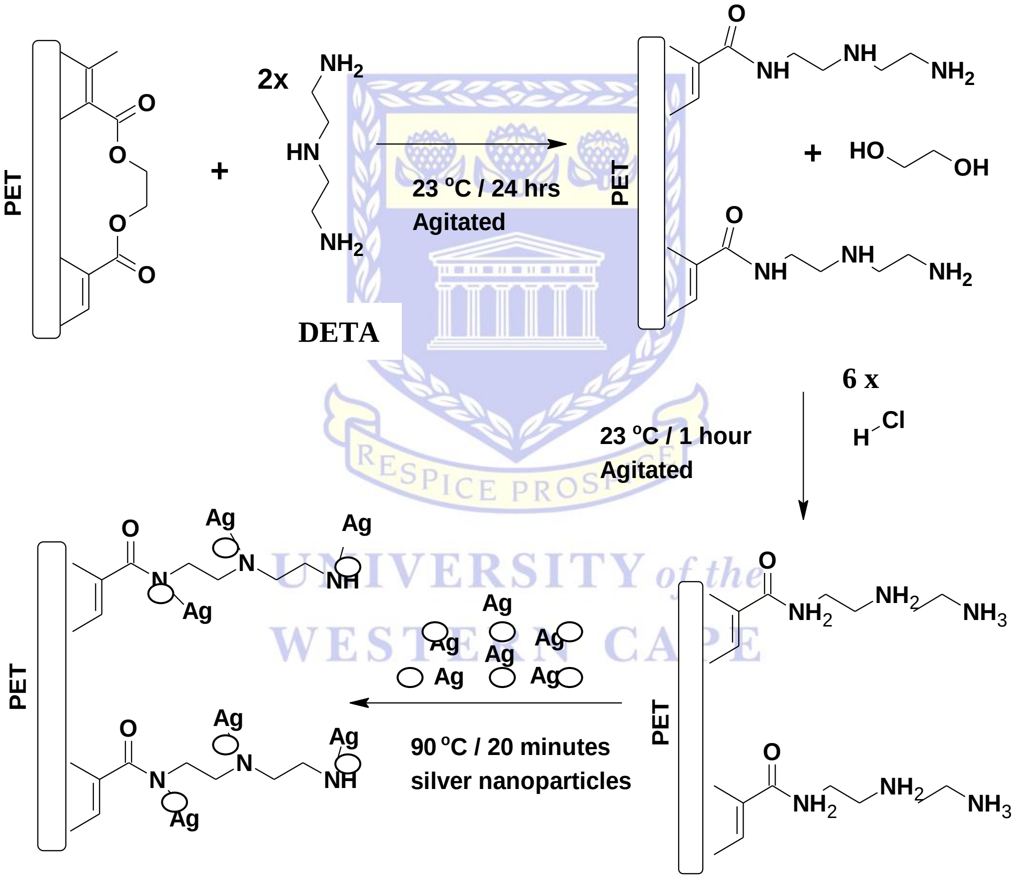

Figure 4.2: Proposed mechanism of modification of PET membrane with DETA and immobilisation of silver nanoparticles on the modified surface

Figure 4.2 shows the aminolysis reaction at the solid/liquid interface, a lone pair of electrons on the nitrogen of diethylenetriamine attack the partially positive carbon of carbonyl ester. The aminolysis brings about cleavage of the ester bond

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and formation of the amide bond losing the glycol moiety from the surface of the PET membrane. The activation of the surface of the amine-modified track-etched PET membrane with hydrochloric acid caused nitrogen in the amine to be protonated. Silver nanoparticles were then immobilised on the surface of amine-modified track-etched PET membrane via the protonated nitrogen.

The analysis of the results and discussion thereof are outlined in the following sections and subsections in reference to the proposed mechanism in Figure 4.2 and experimental steps presented in Figure 3.1 in Chapter 3.

4.2 Aminolysis of track-etched polyethene terephthalate membrane

The experimental results in this section and related subsections are for the wet chemistry modification of the track-etched polyethene terephthalate (PET) membrane with diethylenetriamine (DETA). The experimental procedure for the wet chemistry modification of PET membrane using DETA is described in Section 3.2.1 of Chapter 3. The fixed and variable parameters outlined in Table 4.1 were chosen in order not to cause serious degradation to the bulk of the track-etched PET membranes. All reactions were carried out at ambient conditions.

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Table 4.1: Sample codes for Fourier transform infrared and X-ray photoelectron spectroscopy with fixed and variable parameters (time of reaction and concentration of diethylenetriamine).

Sample code	Fixed condition	Variable condition
75A-PET	Time of reaction - 24 hrs	Concentration of DETA (75%)
60A-PET	Time of reaction - 24 hrs	Concentration of DETA (60%)
45A-PET	Time of reaction - 24 hrs	Concentration of DETA (45%)
24-APET	Concentration 75%	Time of reaction (24 hours)
18-APET	Concentration 75%	Time of reaction (18 hours)
12-APET	Concentration 75%	Time of reaction (12 hours)

The results of Fourier transform infrared and X-ray photoelectron are presented in Subsections 4.2.1 and 4.2.2 respectively

4.2.1 Fourier transformation infrared

Fourier transform infrared (FTIR) was used to compare various wet chemistry modifications of polyethene terephthalate (PET) membrane using diethylenetriamine (DETA) as described in Section 4.2 above. The results are presented in two series. One set of FTIR results is based on time of reaction studies and the other set of results are based on diethylenetriamine concentration studies. The following section presents reaction times studies results and discussion for FTIR.

4.2.1.1 Reaction times studies for surface modification

The reaction times studies were carried out as described in Section 3.2.1 of Chapter 3. The concentration of aqueous diethylenetriamine was kept constant at 75%. The reaction was carried out at ambient conditions for 12 hours, 18 hours or 24 hours. The spectra of the modified track-etched PET membranes are coded 24-APET, 18-APET, 12-APET and unmodified track-etched PET membrane CO-APET. The sample CO-APET also served as a control. The results of the reaction times studies are shown in Figure 4.3. The time of reaction was the variable parameter whilst the concentration of DETA was a fixed parameter at ambient conditions.

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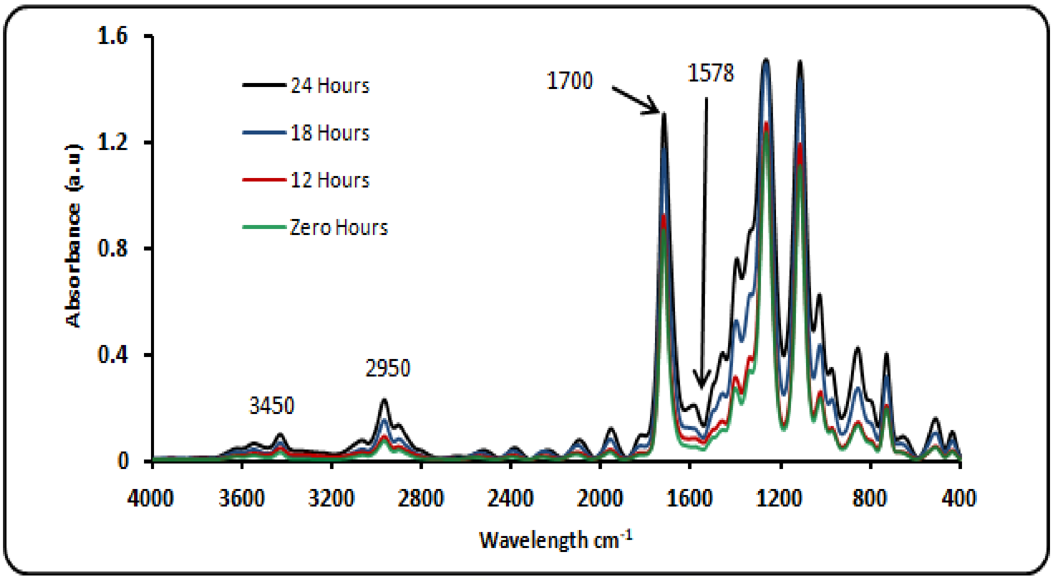

Figure 4.3: FTIR spectra of unmodified track-etched PET membrane (CO-APET) and modified track-etched PET membranes at 75% concentration of DETA and varied reaction times of 12 hours (12-APET), 18 hours (18-APET) and 24 hours (24-APET).

The FTIR results in Figure 4.3 show that there is a change in absorbance band between 1500 cm^{-1} and 1600 cm^{-1} mainly for C-N bond stretching of PET membrane that has been exposed to diethylenetriamine for 18 hours and 24 hours. The amide I bond absorbance peak occurs at 1648 cm^{-1} and amide II at 1578 cm^{-1} but when both exist in a molecule the most prominent one overshadows the less prominent one (Drobota *et al.*, 2013). In Figure 4.3, amide II is the most prominent one as observed from its absorbance peak which is appearing at 1578 cm^{-1}, thus overshadows that of amide I bond. Another notable change in absorbance peaks is between 3400 cm^{-1} and 3500 cm^{-1} contributed by the introduction of amine from DETA. The change in the absorbance peak at 3450 cm^{-1} arises from N-H bond stretching. The absorbance spectral peak increases in size and depth with an increase in reaction time from zero for the unmodified track-etched PET membrane coded CO-APET to PET membrane that was reacted with DETA for 24 hours (24-APET sample). There is an observed notable change in the absorbance peak at 2950 cm^{-1} which is attributed to the ethylene C-H bond stretching from the modifying agent, diethylenetriamine. Although there is a loss of glycol which has the ethylene moiety, the introduction of DETA brings in two

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ethylene moieties. The change in absorbance bands, 3400 to 3500 cm^{-1} of the introduced amine (N-H) is not very pronounced, which is consistent with observations made by Irena *et al*., (2009) where the change is attributed to the aliphatic amine in the range 3400 to 3500 cm^{-1}. The spectra of the PET membranes that were exposed for 24 hours to a diethylenetriamine solution clearly show the amide bonds' vibration band of 1500 to 1600 cm^{-1} is also reported by Drobota *et al*., (2013). The longer the solid/liquid interface reaction is left to occur the more prominent are the amide absorbance peaks. The results also show that the absorbance peaks (at 3450 cm^{-1} and 2950 cm^{-1}) of the track-etched PET spectra changes with the time of reaction. It can therefore be inferred that the longer the time of reaction between the surface of PET membrane and diethylenetriamine, the more significant the observed changes in absorbance peaks. The sample 24-APET, that was for 24 hours of reaction showed a noticeable change in absorbance peak intensity which is also indicative of the surface modification of the PET membrane.

The results in Figure 4.3 confirm the proposed changes as presented in Figure 4.2 which shows the proposed reaction mechanism. Figure 4.2 shows that an amide bond was introduced on the surface of the PET membrane through a scission of the ester bond in polyethene terephthalate and the formation of an amide (C-N) bond (Drobota *et al*., 2013). Therefore the results in Figure 4.3 agree with literature stating that the modification of the track-etched PET membrane surface with amines results in the formation of the amide bond and the introduction of amines on the surface (Fatiyants *et al*., 2013).

In this study, only the concentration of diethylenetriamine and the reaction time were changed to determine the optimal surface modification conditions for the track-etched PET membrane. In the reviewed literature, it was noted that treating the membrane at high temperatures degrades its tensile strength (Nissen *et al*., 2008).

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4.2.1.2 Concentration studies for the modification

The concentration of diethylenetriamine studies were conducted as described in Section 3.2.1 of Chapter 3. In brief, equal pieces of 2x2 cm track-etched polyethene terephthalate (PET) membranes were immersed in aqueous solution of 75%, 60% and 45% diethylenetriamine (DETA) concentrations. The reaction time was kept constant at 24 hours. The reaction was carried out at ambient conditions. The FTIR spectra of the modified track-etched PET membranes are coded 75A-PET, 60A-PET, 45A-PET and unmodified track-etched PET membrane CO-APET. The sample that was coded CO-APET served as a control. The results of the concentration of DETA studies are shown in Figure 4.4. The concentration of DETA was the variable parameter whilst time of reaction the was a fixed parameter at ambient conditions

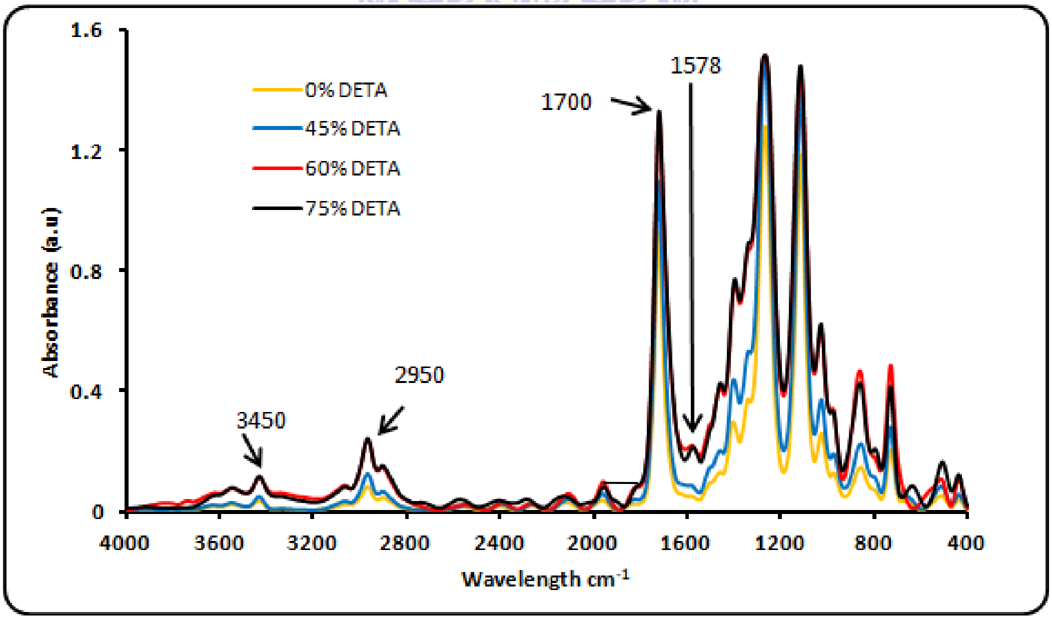

Figure 4.4: FTIR spectra of unmodified track-etched PET membrane (CO-APET) and modified track-etched PET membranes at 24 hours reaction time and variable concentration of DETA of 75% (75A-PET), 60% (60A-PET) and 45% (45A-PET).

The FTIR results arising from concentrations of DETA as a variable parameter in the aminolysis reaction are shown in Figure 4.4. The results in Figure 4.4 have similar trends as those observed from results of the reaction time studies, where reaction time was a variable parameter and concentration of DETA a fixed

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parameter as shown in Figure 4.3. The results in Figure 4.4 show that the absorbance peak centred at 2950 cm^{-1} broadens as the concentration of DETA was increased. The absorbance peak at 2950 cm^{-1} is attributed to C-H bond stretching from the ethylene moieties. The broadening of the absorbance peak is as a result of the surface of PET membrane having been modified with DETA which has two ethylene moieties in its molecular structure. Similar broadening of the absorbance peak centred at 3450 cm^{-1} is also observed. The partial broadening of the absorbance peak at 3450 cm^{-1} is attributed to N-H stretching. The N-H stretching vibrations are as a result of the amine moieties introduced on the surface from DETA. The absorbance band appearing in the region of 1500 to 1600 cm^{-1} is observed in the samples 75A-PET, 60A-PET and 45A-PET which were reacted with aqueous diethylenetriamine at concentrations of 75%, 60% and 45% respectively. Similar trends as observed in Section 4.2.1.1 regarding the time studies are also observed in Figure 4.4. The amide I band appears more pronounced in the spectral region of 1500 to 1600 cm^{-1}, when the track-etched PET membrane was reacted with 75% concentration of DETA. Similarly, in literature, it was reported that amide I and II bands were observed as a single absorbance peak instead of separate absorbance peaks for a modified track-etched PET membrane that was subjected to aminolysis using other amines such as ethylenediamine (Xue *et al.*, 2013). The aqueous solution of DETA with 75% v/v resulted in the appearance of amide I and II bands for stretching vibrations (N-C=O) overlapping each other between 1500 cm^{-1} and 1600 cm^{-1}. The presence of amide I and II bands on the FTIR spectra of the PET membrane subjected to DETA at different concentrations confirms that the surface of the track-etched PET membrane was modified in each case. The sample 75A-PET that had 75% concentration of DETA showed the greatest modification. Any higher concentration above 75% resulted in cracked and easily torn PET membranes that could not be properly characterised by Fourier transform infrared.

The next section presents results of the surface of track-etched PET membrane pieces as characterised by X-ray photoelectron spectroscopy following aminolysis reaction.

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4.2.2 X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) results complement those of the Fourier transform infrared (FTIR). The aim of characterising the modified and unmodified track-etched polyethene terephthalate membrane using XPS is to carry out elemental analysis of the track-etched PET membrane surfaces. XPS results presented in this section are only those of the unmodified track-etched polyethene terephthalate (PET) membrane and a diethylenetriamine-modified surface of PET membrane, which are coded CO-APET and 75A-PET respectively. The sample, 75A-PET was chosen among other samples, because it is the one that had the most clear FTIR results, whilst CO-APET is a control sample, the unmodified track-etched PET membrane. The procedure of carrying out aminolysis of the surface of PET membrane is described in Section 3.2. In brief sample 75A-PET was modified by immersing a 2x2 cm PET membrane in 75% diethylenetriamine aqueous solution for 24 hours. The samples coded 75A-PET and CO-APET were characterised as described in Section 3.5.2. The variable and fixed parameters of each sample are as described in Table 4.1 The elemental percentages on the surface of CO-APET and 75A-PET samples are shown in Table 4.2.

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Table 4.2: Elemental percentages from X-ray photoelectron spectroscopy for the surface of unmodified (CO-APET) and modified (75A-PET) track-etched PET membranes

PET Membrane	**Atomic percentages**		
	Carbon (C1s)	Oxygen (O1s)	Nitrogen (N1s)
C0-APET	72.59	27.41	0
75A-PET	72.54	22.50	4.96

The XPS results in Table 4.2 show that only elemental carbon (C1s) and oxygen (O1s) were present on the surface of unmodified track-etched PET membrane coded CO-APET, before exposing the membrane to diethylenetriamine (DETA)

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solution. The sample CO-APET had no nitrogen (N1s) atoms on the surface. The sample 75A-PET had a 4.96% nitrogen (N1s) atom content on the surface of amine-modified track-etched PET membrane. The sample 75A-PET shows the presence of nitrogen (N1s) from the diethylenetriamine that has replaced some oxygen that has been displaced via the aminolysis process, which involves ester bond scission and formation of an amide bond (Noel *et al*., 2011). The surface of amine-modified track-etched PET membrane has amine and amide moieties, whose nitrogen is prominently present as shown in Table 4.2. This shows that nitrogen containing moieties are present on the surface of track-etched PET membrane due to the aminolysis reaction. The results show the change in elemental percentages between the unmodified and modified samples.

The elemental compositions are also presented in the general survey graphs of the X-ray photoelectron spectroscopy taken for both track-etched PET membrane samples (CO-APET and 75A-PET). The general surveys are shown in Figure 4.5.

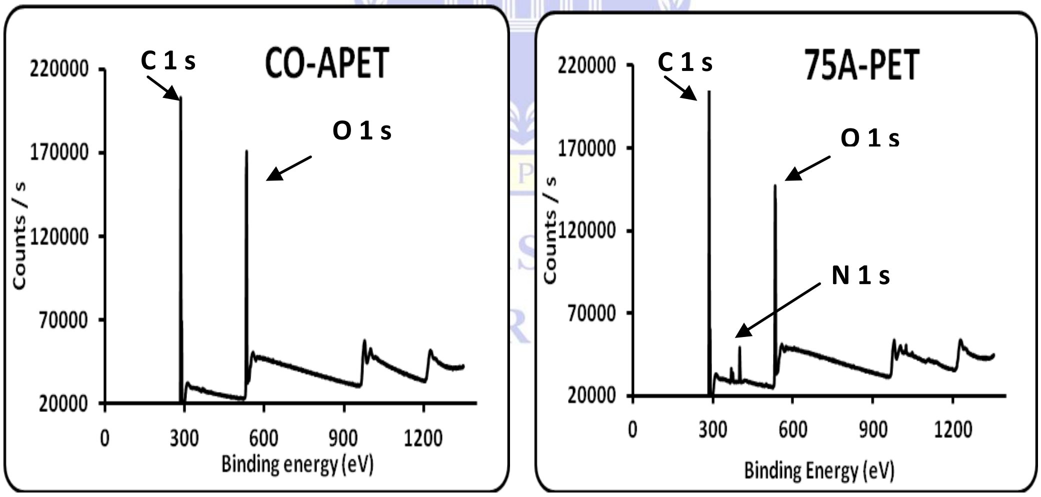

Figure 4.5: X-ray photoelectron spectroscopy general survey graphs of unmodified track-etched PET (CO-APET) and modified track-etched PET (75A-PET) showing elements within the detection limits

The general survey graphs in Figure 4.5 show elemental peaks making up the surface composition of PET before and after modification with diethylenetriamine. The XPS general surveys in Figure 4.5 show elements within the detection limits based on the chemical composition of the surface of the track-

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etched PET membrane. The general survey graphs of samples CO-APET and 75A-PET show that peaks of carbon (C1s), oxygen (O1s) and nitrogen (N1s) are in the binding energy regions of 285.21 eV, 532.63 eV and 399.61 eV respectively. The general survey graph for CO-APET has no nitrogen peak, while that of 75A-PET has the nitrogen peak. The general survey graph of 75A-PET shows that nitrogen is present on the surface of the modified track-etched PET membrane. The binding energies in Figure 4.5 agree with those reported in literature (Awasthi *et al.*, 2014; Xue *et al*, 2013).

The chemical states of nitrogen (N1s) and carbon (C1s) on the surface of amine-modified track-etched PET membranes are represented in Figure 4.6, The chemical state graph for nitrogen (N1s) is from the sample 75A-PET. The chemical state graph for carbon (C1s) presents results for both samples CO-APET and 75A-PET. The carbon (C1s) chemical state graph shows the chemical states of carbon when the PET membrane was not modified (sample CO-APET) and the changes that occured after modification of the track-etched PET membrane (sample 75A-PET).

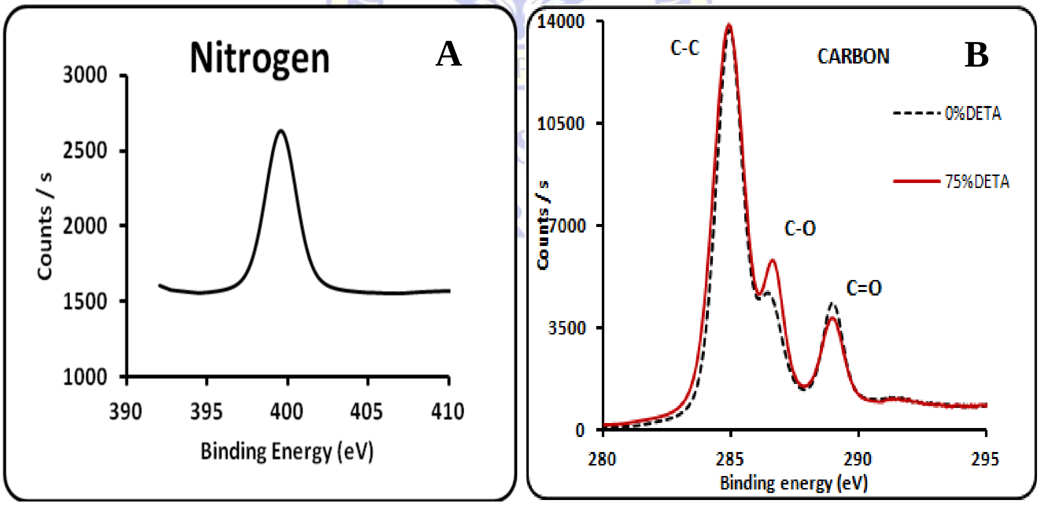

Figure 4.6: XPS spectra of N1s peaks of amine-modified track-etched PET (A) and C1s peaks for both unmodified (black) and amine-modified (red) PET membrane (B).

Further to the general survey, the magnified N1s shell scan in Figure 4.6A shows the chemical state of nitrogen on the surface of the modified track-etched PET

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membrane sample coded 75A-PET. The graph in Figure 4.6A shows that the spectra peak for N1s is at a binding energy of 399.61 (≈400) eV which is known to be for nitrogen in the chemical state of C-NH_2 (Makiabadi *et al.*, 2010). Furthermore, the C1s shell scan in Figure 4.6B shows the chemical states of carbon from samples CO-APET and 75A-PET. The C1s shell scan shows three symmetrical peaks with binding energies at 284.9, 286.6 and 288.9 eV for the chemical states of C-C, C-O and O-C=O respectively (Vesel *et al.*, 2008). These C1s spectra peaks are characteristic peaks observed for polyethene terephthalate polymers. The observed satellite peak π-π*, which is not so pronounced between 291 and 292 eV is characteristic of polyethene terephthalate polymer materials (Awasthi *et al.*, 2014: Basri *et al*., 2011). Figure 4.6B shows changes in the peak heights of C-C and O-C=O, which are as a result of the introduction of two ethylene (C-C) moieties from the diethylenetriamine, replacing one ethylene moiety in glycol and the formation of an amide bond (C-N) which replaces O-C=O with N-C=O.

The changes peak heights that occurred as a result of changes in chemical state of carbon are tabulated in Table 4.2.

Table 4.3: Changes in peak heights of carbon chemical states.

Chemical state of elements	Peak height (count/second)	
	CO-APET (PET)	75A-PET (Amine-PET)
C-C	13, 158	13, 362
C-O	3, 209	4, 226
O-C=O	3, 428	2, 888

The amide bond formation gives rise to a change in the chemical state of carbon in O-C=O as observed in the reduction of the O-C=O peak height from 3428 to 2888 counts per second. The conspicuous change in C-O peak height is not

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expected, the expected observation would be the reduction in height of the C-O spectrum peak due to loss of glycol during the aminolysis reaction. This could be contributed from atmospheric carbon existing in C-O chemical state during aminolysis reaction or storage.

4.3 Synthesis and immobilisation of silver nanoparticles on polyethene terephthalate membrane

The experimental results in this section and related subsections are for the synthesis and immobilisation of silver nanoparticles on the modified surface of the track-etched polyethene terephthalate (PET) membrane. The experimental procedure for the synthesis of silver nanoparticles is described in Section 3.2.2 of Chapter 3. The experimental procedures for immobilisation of silver nanoparticles on the modified surface of the polyethene terephthalate membrane is described in Section 3.3. The results and discussion of the synthesis of silver nanoparticles are presented in the following Section 4.3.1 and that of the immobilisation of silver nanoparticles on amine-modified track-etched PET membrane are presented in the Section 4.3.2 of this chapter. The fixed and variable parameters for the synthesis of silver nanoparticles and immobilisation of silver nanoparticles on the amine-modified track-etched PET membrane are outlined in Table 4.4 with their sample codes. All reactions were carried out at ambient conditions.

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Table 4.4: Sample codes for synthesis and immobilisation of colloidal silver nanoparticles on track-etched polyethene terephthalate membrane surface with fixed and variable parameters (time and temperature of reaction and volume of 1% trisodium citrate solution)

Sample code	**Fixed conditions**	**Variable conditions**
Synthesis of silver nanoparticles		
90C-Ag	Time 20 minutes; volume of 1% trisodium citrate 2 mL	Temperature 90 ^{o}C
75C-Ag	Time 20 minutes; volume of 1% trisodium citrate 2 mL	Temperature 75 ^{o}C
60C-Ag	Time 20 minutes; volume of 1% trisodium citrate 2 mL	Temperature 60 ^{o}C

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1-TriNa	Temperature 90 ^{o}C and time of reaction 20 minutes	Volume of 1% trisodium citrate 1 mL
2-TriNa	Temperature 90 ^{o}C and time of reaction 20 minutes	Volume of 1% trisodium citrate 2 mL
3-TriNa	Temperature 90 ^{o}C and time of reaction 20 minutes	Volume of 1% trisodium citrate 3 mL
30-AgNP	Temperature 90 ^{o}C; volume of 1% trisodium citrate 2mL	Time of reaction 30 minutes
20-AgNP	Temperature 90 ^{o}C; volume of 1% trisodium citrate 2mL	Time of reaction 20 minutes
10-AgNP	Temperature 90 ^{o}C; volume of 1% trisodium citrate 2mL	Time of reaction 10 minutes
Immobilisation of silver nanoparticles on PET membrane		
Co-AgPET	Control sample used as received	Control sample used as received
10-AgPET	Temperature 90 ^{o}C: volume of trisodium citrate 2 mL	Time of reaction 10 minutes
15-AgPET	Temperature 90 ^{o}C: volume of trisodium citrate 2 mL	Time of reaction 15 minutes
20-AgPET	Temperature 90 ^{o}C: volume of trisodium citrate 2 mL	Time of reaction 20 minutes
25-AgPET	Temperature 90 ^{o}C: volume of trisodium citrate 2 mL	Time of reaction 25 minutes
30-AgPET	Temperature 90 ^{o}C: volume of trisodium citrate 2 mL	Time of reaction 30 minutes

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4.3.1 Synthesis and characterisation of silver nanoparticles

The section presents the results of ultraviolet-visible spectroscopy (UV-Vis) of the colloidal silver nanoparticles. The results are of optimisation studies for the synthesis of colloidal silver nanoparticles. The optimisation studies are based on the following experimental parameters: temperature of reduction, reducing agent volume and time of reduction reaction. The reaction time studies have temperature of reaction and volume of trisodium citrate as a fixed parameters at ambient conditions and bearing sample codes 10-AgNP, 20-AgNP and 30-AgNP. The temperature of reaction studies have time of reaction and volume of trisodium citrate as fixed parameters bearing sample codes 90C-Ag, 75C-Ag and 60C-Ag. The volume of trisodium citrate as a variable parameter has temperature and time of reaction as fixed parameters and bear samples codes 1-TrNa, 2-TriNa and 3-TriNa.

In brief the synthesis of silver nanoparticles was carried out by adding varying volumes (1 mL, 2 mL and 3 mL) of 1% of trisodium citrate to the pre-heated 100 mL of 1 mM of silver nitrate solution for varying times (10 minutes, 20 minutes and 30 minutes) at varying temperatures (60 ^{o}C, 75 ^{o}C and 90 ^{o}C). As the temperature was varied other parameters such as volume of trisodium citrate and temperature were kept constant. The fixed and variable parameters of the experiments are as outlined in Table 4.4. All reactions were carried out at ambient conditions.

4.3.1.1 Ultraviolet-visible spectroscopy of silver nanoparticles

A widely used structural characterisation technique for silver nanoparticle is ultraviolet-visible (UV-Vis) spectroscopy technique. The silver nanoparticles, which have surface plasmon excitation, exhibit intense plasmonic peaks between the 380 nm and 450 nm absorption band of the ultraviolet-visible region. The subsections to follow present optimisation studies based on temperature, time of reaction and volume of 1% trisodium citrate as variable parameters. The experimental and sample codes are briefly described in Section 4.3.1. The next section presents results and discussion of the temperature of reaction studies.

4.3.1.1.1 Temperature studies for synthesis of silver nanoparticles

The temperature studies for the synthesis of silver nanoparticles were carried out as described in Section 3.2.2 of Chapter 3 and the sample codes are as presented in Table 4.4 in Section 4.3.1. The variable parameter was temperature of reaction at 90 ^{o}C, 75 ^{o}C or 60 ^{o}C. The fixed parameters were the volume of 1% trisodium citrate of 2 mL and time of reaction of 20 minutes. The results of temperature of reaction studies are shown in Figure 4.7.

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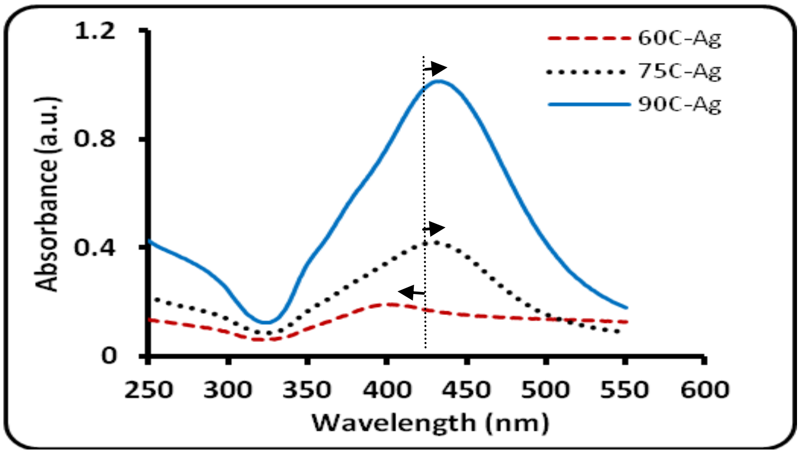

Figure 4.7: Ultraviolet-visible spectra of silver nanoparticles synthesised for 20 minutes using 2 mL of 1% trisodium citrate at varied temperatures of 90 ^{o}C (90C-Ag), 75 ^{o}C (75C-Ag) and 60 ^{o}C (60C-Ag)

The results presented in Figure 4.7 show changes in plasmonic peaks relative to the temperature at which the reaction was carried out. The sample 90C-Ag has a higher plasmonic peak compared to samples 75C-Ag and 60C-Ag. The peak height increased as the temperature was increased from 60 ^{o}C to 90 ^{o}C. The peaks showed a red shift (a wavelength shift towards longer wavelength) as the temperature was increased from 60 ^{o}C to 90 ^{o}C. The red shift in the peaks could be attributed to change in morphology of the silver nanoparticles such that as the temperature was increased, so did the size of nanoparticles. The trend of increasing peak height with an increase in temperature is in line with literature reviewed where it is known that temperature has an effect on the synthesis of silver nanoparticles (Khodashenas *et al*., 2015; Abour-el-Nour *et al.*, 2010). The peak heights show that there were a greater number of silver nanoparticles synthesised at a highest temperature than at lower temperatures. The results are speculated to show that silver ions are completely reduced to elemental silver that grows to form nanoparticles.

4.3.1.1.2 Effect of volume of trisodium citrate on synthesis of silver nanoparticles

The volume of trisodium citrate studies for the synthesis of silver nanoparticles were carried out as described in Section 3.2.2 of Chapter 3 and the sample codes

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are as presented in Table 4.4 in Section 4.3.1. The variable parameter was volume of 1% trisodium citrate at 1 mL, 2 mL or 3 mL. The fixed parameters were the temperature of reaction at 90 ^{o}C and time of reaction of 20 minutes. The results of volume of 1% trisodium citrate studies are shown in Figure 4.8.

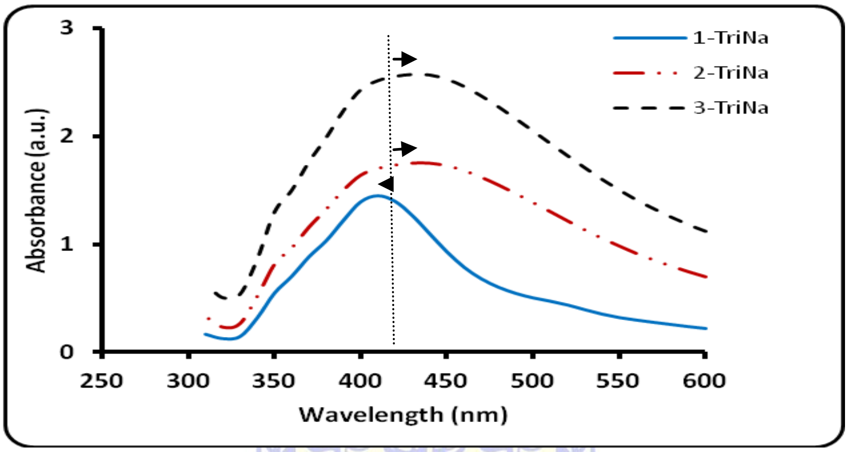

Figure 4.8: Ultraviolet-visible spectra of silver nanoparticles synthesised for 20 minutes at temperature of 90 ^{o}C at varied volumes of 1% trisodium citrate of 1 mL (1-TriNa), 2 mL (2-TriNa) and 3 mL (3-TriNa)

The results in Figure 4.8 show that the plasmonic peak height increased with an increase in the volume of 1% trisodium citrate that was added to silver nitrate solution. The results in Figure 4.8 also show that as the volume of 1% trisodium citrate added to silver nitrate solution at pre-heated 90 ^{o}C was increased there was a red shift, which is a wavelength shift towards longer wavelength. The red shift could be as a result of an increase in size of nanoparticles with an increase in volume of 1% trisodium citrate. It was also observed that the plasmonic peaks became broader in shape, which is characteristic of plasmonic peaks of silver nanoparticles synthesised by reduction silver nitrate by trisodium citrate (Qin *et al.*, 2010). The 1-TriNa plasmonic peak representing 1 mL of added 1% trisodium citrate was narrower compared to the 2 mL and 3 mL plasmonic peaks, which were similarly observed by Bastus *et al.*, (2014) and Qin *et al.*, (2010). This indicated that the lower the volume of 1% trisodium citrate added the narrower the peak and the smaller the nanoparticles. The addition of a high amount of 1% trisodium citrate resulted in rapid nucleation and growth of elemental silver to form nanoparticles larger in size, as reported by Taurozzi and Tarabara, (2007).

4.3.1.1.3 Time of reaction studies for synthesis of silver nanoparticles

The time studies for the synthesis of silver nanoparticles were carried out as described in Section 3.2.2 of Chapter 3 and the sample codes are as presented in Table 4.4 in Section 4.3.1. The variable parameter was time of reaction of 10 minutes, 20 minutes or 30 minutes. The fixed parameters were the volume of 1% trisodium citrate of 2 mL and temperature of reaction at 90 °C. The results of time of reaction studies are shown in Figure 4.7.

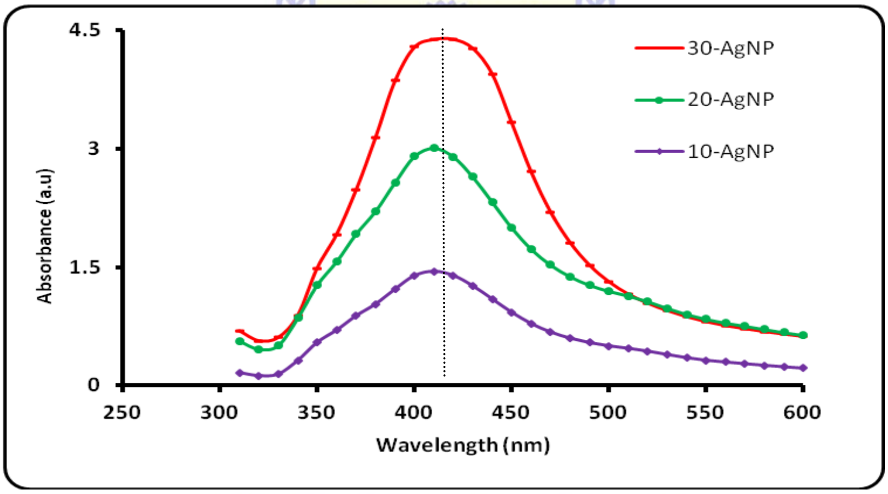

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Figure 4.9: Ultraviolet-visible spectra of silver nanoparticles synthesised at temperature of 90 °C and 2 mL volume of 1% trisodium citrate at varied times of 10 minutes (10-AgNP), 20 minutes (20-AgNP) and 30minutes (30-AgNP)

The results in Figure 4.9 show the increase in peak height as the time of reaction was increased from 10 minutes to 30 minutes. The results also show that plasmonic peak height had doubled after 20 minutes and tripled after 30 minutes.. The narrowing of the plasmonic peaks with an increase in the time of reduction could be attributed to the formation of silver nanoparticles within a narrow size range. The results in Figure 4.9 show slight shift in plasmonic peak, which can be attributed to the other parameters (temperature and volume of 1% trisodium

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citrate) having reached their optimum. The results show a trend that is in agreement with what has been reported in literature (Khan *et al*., 2013). The steps for synthesis of silver nanoparticles are inferred to involve the reduction of silver ions by 1% trisodium citrate to elemental silver, which then undergoes nucleation and growth to form silver nanoparticles (Kruszewski *et al.*, 2011). The ionic reaction mechanism of the reduction of the silver nitrate by citrate can be expressed as follows (Kruszewski *et al.*, 2011):

$$4Ag^{+} + C_6H_5O_7Na_3 + H_2O \longrightarrow 4\ Ag^{0} + C_6H_5O_7H_3 + 3\ Na^{3+} + H^{+} + O_2\uparrow$$

The nucleation stage of the synthesis is dependent on the time of reaction and the relative concentration of silver salt precursor as well as the reducing agent (Khan *et al.*, 2013). The best conditions for the synthesis of the silver nanoparticles were a temperature of 90 °C and 30 minutes of reduction reaction because at that temperature the plasmonic peak was of highest. These optimum conditions (90 °C, 30 minutes and 2 mL volume of 1% trisodium citrate) were used during the direct immobilisation of silver nanoparticles on the surface of amine-modified track-etched polyethene terephthalate membrane.

4.3.2 Transmission electron microscopy

The transmission electron microscopy (TEM) was used to characterise the colloidal silver nanoparticles to determined their morphology (shape and size). The TEM characterisation was carried out as described in Section 3.5.4 of Chapter 3. The sample that was characterised was 20-AgNP which was prepared as described in Section 3.2.2. The conditions under which silver nanoparticles coded 20-AgNP were synthesised are described in Table 4.4. The sample 20-AgNP was chosen because the silver nanoparticles were smaller than the reported average size of 58 nm (Taurrozzi and Tarabara (2007) and were more dispersed. The results of transmission electron microscopy for sample 20-AgNP are presented in Figure 4.10. Included in the results is the size distribution graph showing spread of the sizes of silver nanoparticles.

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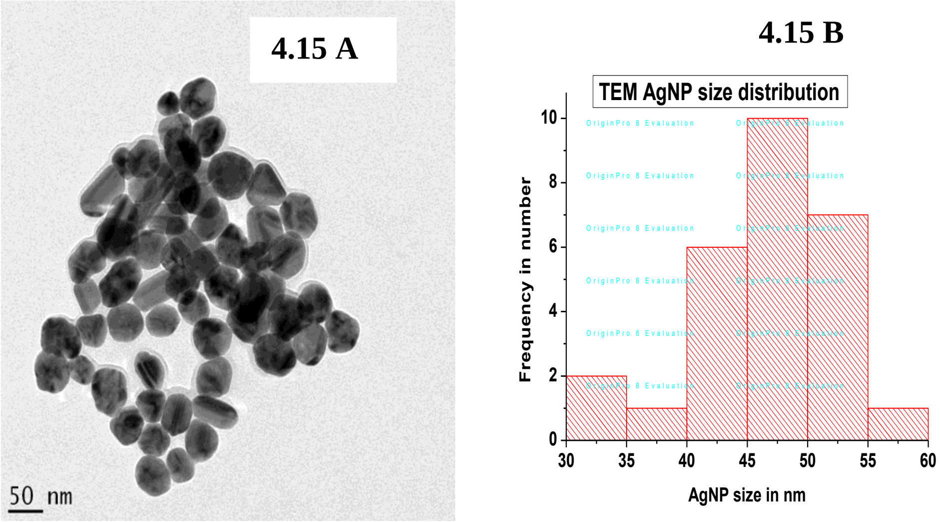

Figure 4.10: Transmission electron microscopy image showing colloidal silver nanoparticles synthesised for 20 minutes at 90 oC using 2 mL of 1% trisodium citrate (20-AgNP) and histogram showing the silver nanoparticle size distribution

The TEM image in Figure 4.10 A has an average silver nanoparticle size of 46.5 nm. The TEM images indicate that the majority of the silver nanoparticles are spherical in shape with a few rod-like and triangular nanoparticle The size distribution range of silver nanoparticles in Figure 4.10 B was from 30 to 60 nm. The results are in agreement with the results observed under UV-vis spectroscopy where polydispersed nanoparticles gave broad plasmonic peaks. The average size of colloidal silver nanoparticles of 46.5 nm is lower than reported by Taurozzi and Tarabara (2007) for SERS application, which size was averaged at 58 nm. The size range of colloidal nanoparticle results agree with the nanoparticle size immobilised on amine-modified track-etched PET membrane discussed in the next sections. This size is also in agreement with literature in cases where silver nanoparticles were synthesised via reduction of silver nitrate by trisodium citrate being polydispersed (Taurrozzi and Tarabara, 2007).

The next section presents results of the Zeta potential of the colloidal silver nanoparticles.

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4.3.3 Zeta potential of silver nanoparticles

The zeta potential of the silver nanoparticles that were synthesised was determined in order to determine how stable the colloidal silver nanoparticles were dependent on the duration of synthesis. The silver nanoparticles were synthesised as described in Section 3.2.2 and characterised as per Section 3.5.9 of Chapter 3. The results presented in this section are only for samples coded 10-AgNP, 20-AgNP and 30-AgNP, whose conditions of synthesis are described in Table 4.4 in Section 4.3. These samples were chosen because the silver nanoparticles were synthesised using optimum temperature and volume of 1% trisodium citrate. The time (10 minutes, 20 minutes, or 30 minutes) of synthesising silver nanoparticles was a variable parameter whilst the temperature (90 ^{o}C) and volume of 1% trisodium citrate (2 mL) that was added to pre-heated silver nitrate were fixed parameters.. The Zeta potential characterisation technique is described in Section 3.5.9 of Chapter 3. The results of the Zeta potential measurement are presented in Table 4.5.

Table 4.5: Zeta potential of the colloidal silver nanoparticles synthesised at 90 oC and with 2 mL volume of 1% trisodium citrate at 10 minutes (10-ANP), 20 minutes (20-AgNP) and 30 minutes (30-AgNP)

Silver Nanoparticle Sample	Zeta (ζ) Potential (mV)
10-AgNP	-23.7
20-AgNP	-24.8
30-AgNP	-25.4

The results in Table 4.5 show that the Zeta potential increased in the negative direction with an increase in time of synthesis. The potential values are changing from -23.7 mV for 10-AgNP, synthesised in 10 minutes to -25.4 for sample 30-AgNP that was synthesised for 30 minutes under same fixed conditions. Figure 4.11 shows the relationship between time of synthesis of silver nanoparticles and the zeta potential of the silver nanoparticles.

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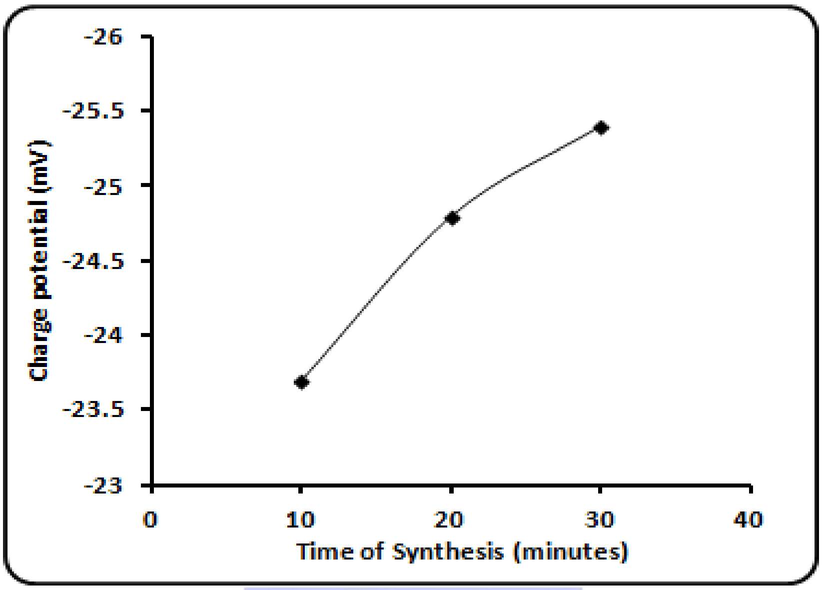

Figure 4.11: Graphical presentation showing the relationship between charge potential of silver nanoparticles and time of synthesis.

The trend in Figure 4.11 shows that the Zeta potential increased in the negative direction with an increase in the time of reaction. The increase in the negative direction could be attributed to build up of negative charge as the nanoparticles increase in size. The stability of colloidal silver nanoparticles is related to their zeta potential values in such a way that any potential value within the range of +20 to -20 mV is considered as an unstable region (Makabiadi *et al*, 2008). The nanoparticles in this region of -20 to +20 mV tend to cluster and agglomerate due to lack of strong repulsion forces between the nanoparticles' nuclei. The silver nanoparticles for all samples had their Zeta potential outside the region -20 to +20 mV, which show that they were stable.

The next section presents results of the characterisation of the unmodified track-etched PET membrane and silver-coated track-etched PET membrane.

4.3.4 Immobilisation of silver nanoparticles and characterisation of track-etched polyethene terephthalate membrane

The section and its subsequent subsections presents results and discussion of the immobilisation of silver nanoparticles on the modified surface of track-etched polyethene terephthalate (PET) membrane. The section covers results from the

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following characterisation techniques: scanning electron microscopy (SEM), ultraviolet-visible (UV-Vis) spectroscopy and X-ray photoelectron spectroscopy (XPS). The aim was to investigate silver nanoparticle immobilisation relative to the time of exposure of the amine-modified track-etched PET membrane during reduction of silver nitrate by trisodium citrate. The experimental procedures for immobilisation of silver nanoparticles on the modified surface of the track-etched PET membrane are described in Section 3.3.

Briefly the immobilisation of silver nanoparticles were achieved by immersing acid-activated 2x2 cm pieces of amine-modified track-etched PET membranes during reduction of silver nitrate by 2 mL of 1% trisodium citrate at 90 ^{o}C for varying times (10 minutes, 15 minutes, 20 minutes, 25 minutes and 30 minutes). The amine-modified track-etched PET membrane was first acid activated in 100 mL of 1 mM hydrochloric acid for 1 hour under agitation. The sample codes are presented in Table 4.4 together with variable and fixed parameters for each sample.

4.3.4.1 Ultraviolet-visible spectroscopy

The section presents ultraviolet-visible spectroscopy results and discussion of track-etched polyethene terephthalate (PET) membranes that have been coated with silver nanoparticles and the unmodified track-etched polyethene terephthalate (PET) membrane. The sample codes for the silver-coated track-etched PET membranes and unmodified track-etched PET membrane are described in Table 4.4 of Section 4.3.1. The experimental procedure for the immobilisation of silver nanoparticles on the surface of amine-modified track-etched PET membranes is described in Section 3.3. The characterisation technique is described in Section 3.5.3. The time (10 minutes, 15 minutes, 20 minutes, 25 minutes or 30 minutes) of immobilising silver nanoparticles was a variable parameter whilst the temperature (90 ^{o}C) and volume of 1% trisodium citrate (2 mL) were fixed parameters.

The results for sample codes 10-AgPET, 15AgPET, 20AgPET, 25AgPET and 30-AgPET are in Figure 4.12.

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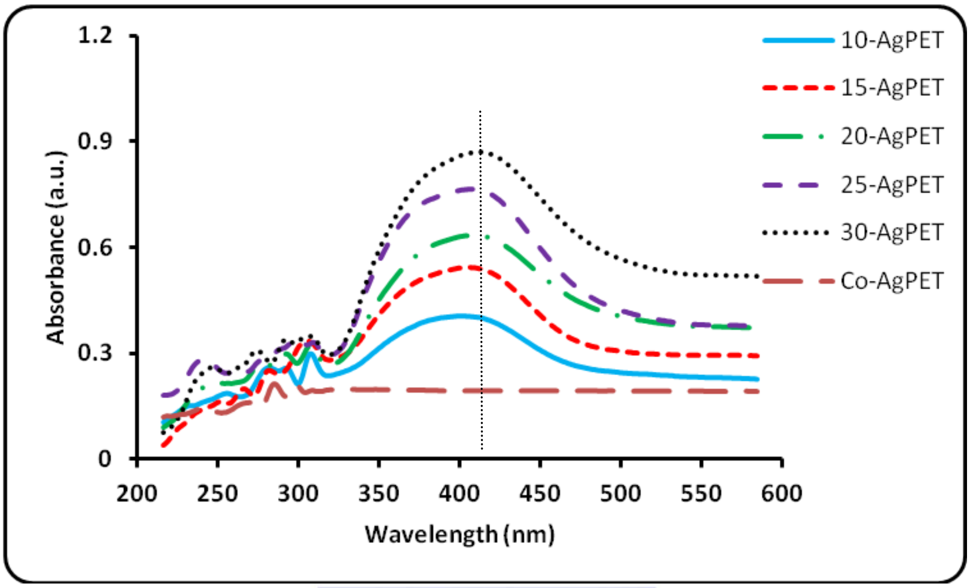

Figure 4.12: Ultraviolet-visible spectra of track-etched PET membranes coated at 90 ^{o}C and with 2 mL of 1% trisodium citrate for different immobilisation times of 10 minutes (10-AgPET), 15 minutes (15-AgPET), 20 minutes (20-AgPET), 25 minutes (25-AgPET), 30 minutes (30-AgPET) and 0 minutes (Co-AgPET).

The results in Figure 4.12 show an increase in the plasmonic peak height of silver-coated track-etched PET membranes. The sample 10-AgPET had the lowest peak and sample 30-AgPET had the highest peak, whilst the rest were in between. The plasmonic peak heights showed a trend that increased from the sample that was immersed for 10 minutes (10-AgPET) to that for 30 minutes. The sample Co-AgPET, a control sample showed no plasmonic peak due to lack of silver nanoparticles on the track-etched PET membrane surface. In agreement with results in Figure 4.12 is the correlation graph in Figure 4.13 showing the relationship between absorbance peak height and time of immobilising silver nanoparticles on the surface of amine-modified track-etched PET membrane.

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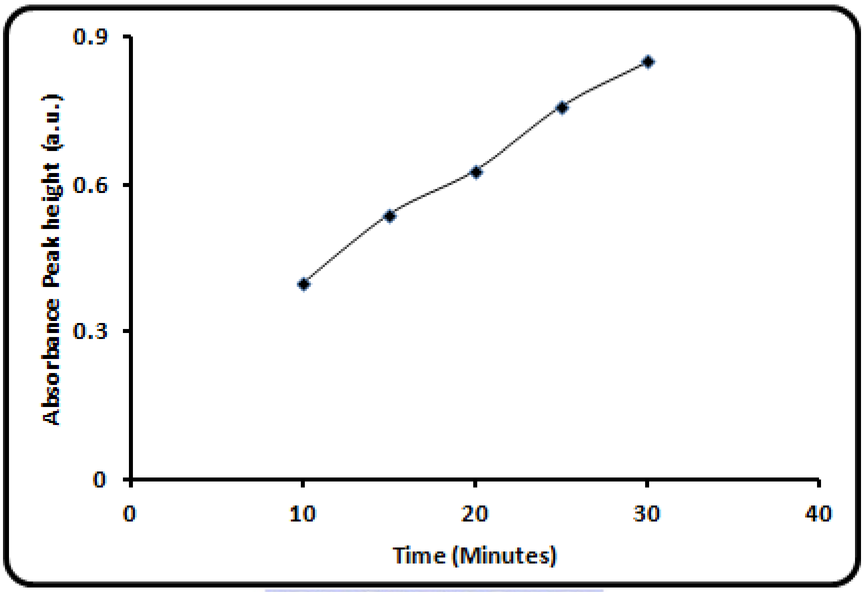

Figure 4.13: Graphical presentation showing correlation of absorbance peak height to time of silver nanoparticle immobilisation

The correlation in graph shown in Figure 4.13 shows that as time of immobilisation was increased from 10 to 30 minutes the absorbance peak height also increased from 0.40 to 0.85 arbitrary units. The plasmonic peak height trend showed that the amount of silver nanoparticles immobilised on the track-etched PET membrane surface was directly proportional to the time of immobilisation. The trend in peak height is in agreement with literature where it is stated that as time of synthesis of silver nanoparticles increases so does the amount of nanoparticles (Solov'ev *et al.*, 2007). The plasmonic peaks show a red shift as the immobilisation time was increased from 10 minutes to 30 minutes. The red shift, which is a change in the plasmonic peak position from short wavelength towards long wavelength meant that the size of silver nanoparticles changed with an increase in the time of immobilisation.

Further ultraviolet-visible spectroscopy was used to investigate different areas of the same membrane sample to ascertain the uniformity of the immobilised silver nanoparticles for randomly chosen samples 10-AgPET and 20-AgPET. The samples 10-AgPET and 20AgPET were prepared as described in Section 3.3. The fixed parameters were temperature and volume of 1% trisodium citrate, while time was the variable parameter. The characterisation was carried out as

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described in Section 3.5.3. The results presented in Figure 4.14 show the disparity in the amount of silver nanoparticles immobilised on amine-modified track-etched PET membrane for samples 10-AgPET and 20-AgPET.

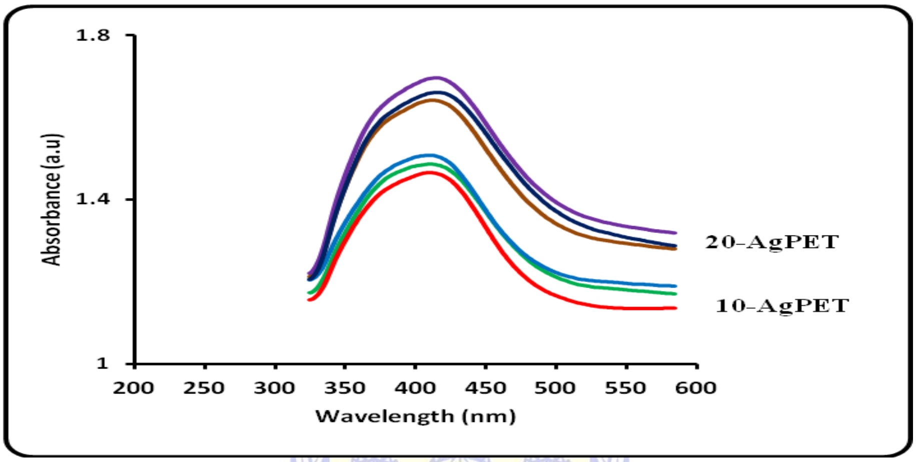

Figure 4.14: Ultraviolet-visible spectra of different areas on track-etched PET membranes coated at 90 ^{o}C and with 2 mL of 1% trisodium citrate for samples of 10-AgPET (10 minutes) and 20-AgPET (20 minutes)

The results in Figure 4.14 show different peak heights of the plasmonic peaks obtained from different areas on the surfaces for samples 20-AgPET and 10-AgPET. The different plasmonic peak heights obtained on the same sample but at different areas show that the silver nanoparticles were not uniformly immobilised on the surface of the amine-modified track-etched PET membranes. The non-uniform trend was not expected as it was presumed that the track-etched PET membrane surface would be uniformly modified chemically with diethylenetriamine. This could be attributed to some ester bonds of PET polymer not undergoing bond scission which led to no amide bond formation, which resulted in uneven immobilisation of silver nanoparticles on the amine-modified track-etched PET membranes.

The next section presents X-ray photoelectron spectroscopy results and discussion of samples 10-AgPET, 20-AgPET, 30-AgPET and Co-AgPET.

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4.3.4.2 X-ray photoelectron spectroscopy of silver-coated track-etched polyethene terephthalate membrane

The section presents results and discussion of X-ray photoelectron spectroscopy (XPS) for the silver-coated track-etched polyethene terephthalate (PET) membranes. The experimental procedure for preparation of the silver-coated track-etched PET membrane was described in Section 3.3 of Chapter 3. The time (10 minutes, 20 minutes, or 30 minutes) of immobilising silver nanoparticles was a variable parameter whilst the temperature (90 °C) and volume of 1% trisodium citrate (2 mL) were fixed parameters. The sample were characterised as described in Section 3.5.2. Table 4.6 shows the results of samples 10-AgPET, 20-AgPET and 30-AgPET.

Table 4.6: X-ray photoelectron spectroscopy results showing the percentage of silver relative to times of immobilisation on PET membrane surface at 10 minutes (10-AgPET), 20 minutes (20-AgPET), 30 minutes (30-AgPET).

Elements	**Silver-coated track-etched PET membranes / amount in percentage (%)**		
	10-AgPET	**20-AgPET**	**30-AgPET**
Carbon	70.65	69.70	67.8
Oxygen	21.77	21.96	22.15
Nitrogen	5.05	4.67	4.85
Silver	2.53	3.67	5.20

The XPS results in Table 4.6 show elemental percentages of carbon, oxygen, nitrogen and silver on the surface of silver-coated track-etched PET membranes at various times (10 minutes, 20 minutes and 30 minutes) of silver nanoparticles immobilisation. The results in Table 4.6 show that increasing the time of immobilisation of silver nanoparticles from 10 minutes to 30 minutes give rise to an increase in the percentage of silver on the PET surface from 2.53% to 5.20%.

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The trends in the results show that as the silver ions are reduced to elemental silver during reduction of silver nitrate by trisodium citrate, it caused an increase in the amount of silver immobilised on the surface of PET membrane over time. The trends shown in Table 4.6 are in agreement with results presented in Figure 4.12 which show an increase in plasmonic peak heights as the time is increased for the immobilisation of the silver nanoparticles on the surface of PET membrane. This conforms to observations made in literature, where it is stated that the elemental atoms in a sample with higher concentration results in higher number of photoelectrons released by that element compared to the element of lower atomic concentration (Basri *et al.*, 2011).

Furthermore, X-ray photoelectron spectroscopy results also show the state of existence of elemental silver on the surface of PET membrane. The elemental state of existence of silver is shown in Figure 4.15.

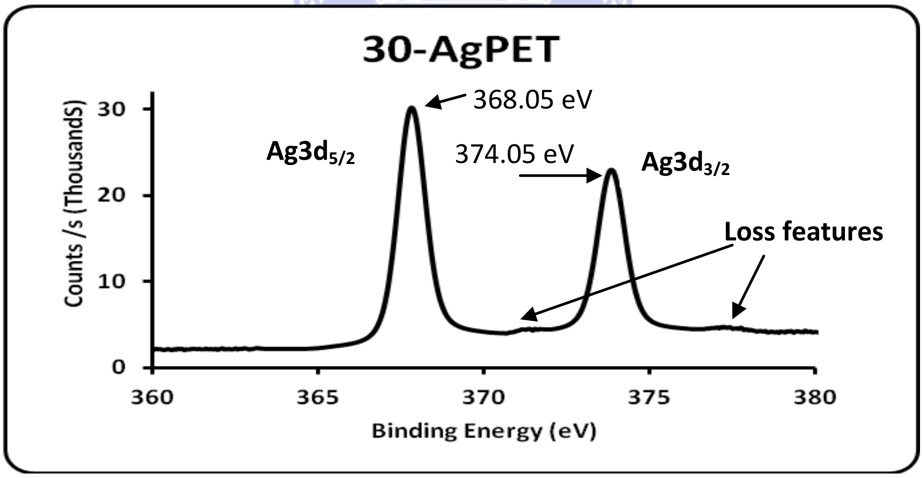

Figure 4.15: X-ray photoelectron spectroscpy scan showing binding energy spectra of silver in its elemental metal state of $Ag_3d_{5/2}$ and $Ag_3d_{3/2}$ and their relative binding energies (30-AgPET)

Figure 4.15 shows the peaks of silver ($Ag3d_{5/2}$ and $Ag3d_{3/2}$) which are asymmetrical and exhibit loss features towards the higher binding energy sides of the peaks. Elemental silver is shown to have a binding energy of 368.05 eV which shows that silver exists on the PET membrane surface in a metal state ($Ag3d_{5/2}$). The XPS results analysed also give information regarding the state in which silver ($Ag3d_{5/2}$ / eV) existed on the surface, either as a metal with a

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binding energy of 368.2 eV or as bromyrite (AgBr) with a binding energy of 267.5 eV (Basri *et al.*, 2011). The silver spectrum of the binding energy has loss features which only exist when silver is in a metal state. The results in Figure 4.15 confirmed the presence of silver as a metal nanoparticle on the surface of the amine-modified track-etched polyethene terephthalate (PET) membrane. This confirmation also complements results of ultraviolet-visible (UV-Vis) spectroscopy presented in Section 4.3.2.2.

The next section presents results and discussion of scanning electron microscopy characterisation of silver-coated track-etched polyethene terephthalate membrane.

4.3.4.3 Scanning electron microscopy

The section presents results and discussion of scanning electron microscopy (SEM) for the silver-coated track-etched polyethene terephthalate (PET) membrane. The experimental procedure for preparation of the silver-coated track-etched PET membrane is described in Section 3.3 of Chapter 3 and briefly stated in Section 4.3.2 of this chapter. The time (10 minutes, 15 minutes, 20 minutes, 25 minutes or 30 minutes) of immobilising silver nanoparticles was a variable parameter whilst the temperature (90 ^{o}C) and volume of 1% trisodium citrate (2 mL) were fixed parameters. The samples were characterised as described in Section 3.5.2. The experimental parameters are outlined in Table 4.4.

Figure 4.16 shows scanning electron micrograms of silver-coated track-etched polyethene terephthalate membranes coded 10-AgPET, 20-AgPET and 30-AgPET together with histograms showing size distribution of immobilised silver nanoparticles. Figures 4.16 A show the SEM microgram of the silver-coated track-etched PET membranes for sample 10-AgPET while 4.16 B and 4.16 C show those for samples 20-AgPET and 30-AgPET respectively.

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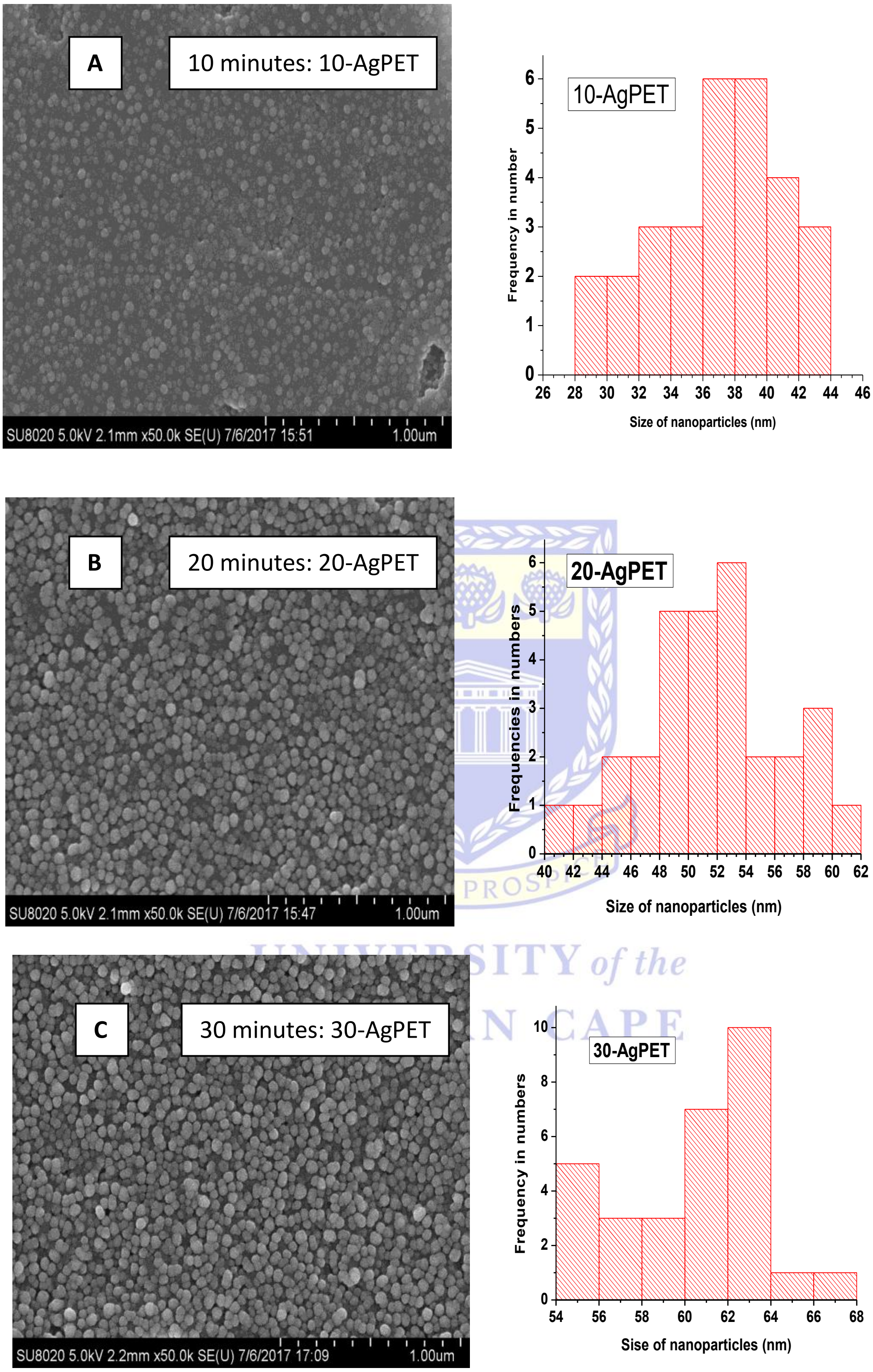

Figure 4.16: SEM images of silver-coated track-etched PET membrane prepared at 90 ^{o}C and with 2 mL of 1% trisodium citrate for samples of A - 10-AgPET (10 minutes), B - 20-AgPET (20 minutes) and C - 30-AgPET (30 minutes).

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The SEM microgram in 4.16A shows silver nanoparticles immobilised on track-etched PET membrane which are spherical in shape and the corresponding histogram shows a nanoparticle size range of 28 to 44 nm. The histogram for sample 10-AgPET is asymmetric, skewed to the right and has a high frequency of silver nanoparticle sizes between 36 and 40 nm. The average size of the silver nanoparticles was 37.5 nm for sample 10-AgPET which was immobilised for 10 minutes.

The SEM microgram in 4.16B shows silver nanoparticles immobilised on track-etched PET membrane which are spherical in shape and the corresponding histogram shows a nanoparticle size range of 40 to 62 nm. The histogram for sample 20-AgPET is symmetric and has a high frequency of silver nanoparticle sizes between 48 and 54 nm. The average size of silver nanoparticles was 51.4 nm for the 20 minutes of immobilisation (20-AgPET).

The SEM microgram in 4.16C shows silver nanoparticles immobilised on track-etched PET membrane which are spherical in shape and the corresponding histogram shows a nanoparticle size range of 54 to 68 nm. The histogram for sample 30-AgPET is asymmetric, partially skewed to the right and has a high frequency of silver nanoparticle sizes between 60 and 64 nm. The average size of the silver nanoparticles was 62 nm for sample 30-AgPET which was immobilised for 30 minutes.

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The results in Figure 4.16 show that the morphology of silver nanoparticles was mostly spherical in shape. The size of silver nanoparticles increased relative to the increase in the time of immobilisation of silver nanoparticles on the surface of track-etched PET membrane. The SEM results are in agreement with the ultraviolet-visible (UV-vis) spectroscopy results of the silver-coated membranes in Figure 4.12. The silver nanoparticle size was noted to increase with the time of immobilisation during reduction of silver nitrate by trisodium citrate. The SEM micrograms also show that silver nanoparticles on the track-etched PET membrane were not uniformly immobilised which complements ultraviolet-visible (UV-Vis) spectroscopy results presented in Section 4.3.2.1. The increase

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in size and variation in the shape of silver nanoparticles on the surface of the modified track-etched PET membrane concur with the broad plasmonic peaks and red shift of the plasmonic peaks in Figure 4.12, which was also reported by Reznikova *et al*., (2014). The SEM micrograms also show that silver nanoparticles on the PET membrane were not uniformly immobilised which complements UV-Vis spectroscopy at different points of the same sample. The histograms in Figure 4.16 show size distribution of the silver nanoparticles immobilised on the surface of amine-modified track-etched PET membrane. The results showing that as immobilisation time was increased, the nanoparticle sizes also were increased are in agreement with literature reviewed (Solove'v *et al.*, 2007).

4.4 Additional characterisation of the physical properties of track-etched polyethene terephthalate membrane and silver nanoparticles

Additional characterisation was done to investigate changes in the properties of the track-etched polyethene terephthalate (PET) membrane as a result of exposure to the wet chemistry reaction and high temperature. Therefore, thermogravimetric analysis and contact angle measurements were carried out. The thermogravimetric analysis technique was carried out to determine the thermal properties of the amine-modified track-etched PET membrane, silver-coated track-etched PET membrane and the unmodified track-etched PET membrane. The contact angle measurement was conducted to investigate wettability of the surface of the modified track-etched PET membrane in comparison with the unmodified membrane. The modification of the track-etched PET membrane would affect the filtration capabilities of the track-etched PET membrane if the surface became more hydrophobic.

4.4.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to determine and compare changes in the thermal profile of the polyethene terephthalate (PET) membrane samples. The analysis was used to quantify the weight loss relative to applied temperature

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gradient and quantify the silver nanoparticle loading. The comparison was amongst unmodified (CO-APET), amine-modified (75A-PET) and silver-coated amine PET membranes (30-AgPET), in order to monitor any thermal degradation as a result of the modification process. The samples 75A-PET and 30-AgPET were chosen because they were obtained under optimised conditions and CO-PET as a baseline sample. The TGA characterisation was carried out as described in Section 3.5.6 of Chapter 3. The samples that were characterised are 30-AgPET, 75A-PET and CO-APET which were prepared as described in Section 3.2. The conditions under which samples were prepared are described in Table 4.4. The results of the thermal profile of the samples 30-AgPET, 75A-PET and CO-APET are presented in Figure 4.17

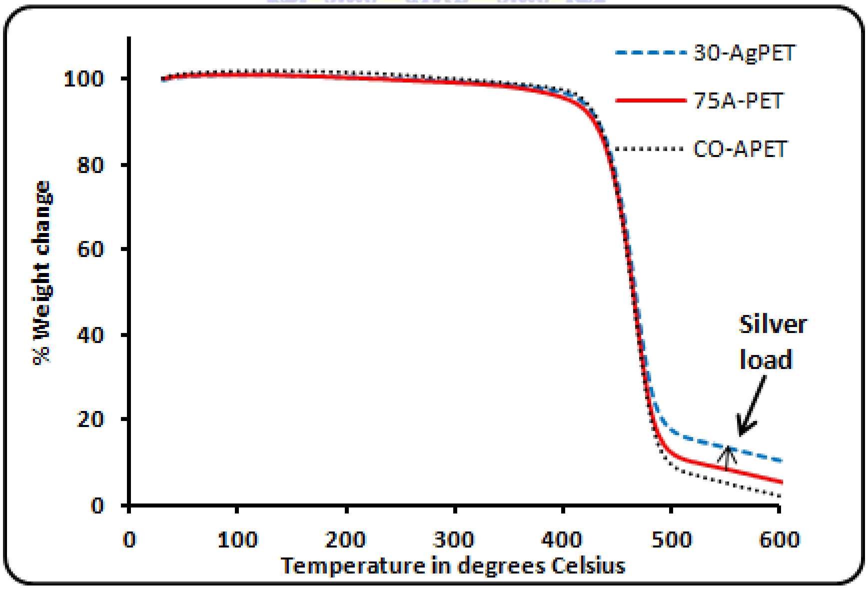

Figure 4.17: Thermogravimetric analysis graph showing the thermal profile of unmodified track-etched PET (CO-APET), amine-modified track-etched PET (75A-PET) and silver-coated track-etched PET (30-AgPET) membrane

The thermal profile in Figure 4.17 shows that all the membranes (30-AgPET, 75A-PET and CO-APET) are stable, without weight loss up to 300 ^{o}C where only a 2.5% weight loss is observed until reaching a temperature of 390 ^{o}C. After 390 ^{o}C the high percent weight loss was observed till reaching 490 ^{o}C. In between 390 ^{o}C and 490 ^{o}C range, the weight loss was 87.5% for unmodified track-etched PET and 83.5% for amine-modified track-etched PET, and 77.5% for silver-coated track-etched PET. The results indicate that after 490 °C, most of the polymer was lost and the remaining residue was mainly elemental carbon for samples CO-APET and 75A-PET and elemental silver and carbon for sample 30-AgPET which is silver-coated amine-modified track-etched PET membrane. The different profiles after 490 °C arose from different elemental compositions of residue which is made up of carbon and silver. At a temperature of 500 °C the silver-coated track-etched PET membrane sample coded 30-AgPET shows a 20% weight remaining, which is 10% more than CO-APET sample (unmodified track-etched PET membrane) and 6% than sample 75A-PET (amine-modified track-etched PET membrane). The difference in weight of 10% between 30-AgPET and CO-APET is due to elemental silver and additional carbon contributed by diethylenetriamine which was present as a residue after 490 °C. The 4% difference between sample 75A-PET and CO-APET would arise from carbon in diethylenetriamine that has been functionalised on the PET membrane surface. It can therefore be inferred that of 6% silver loading shows the amount of silver that was immobilised on the amine-modified track-etched membrane. This observation correlates with Figure 4.2, which shows a loss of ethylene glycol (two carbon atoms) that is replaced by four carbons from diethylenetriamine functionalised on the surface of PET.

The next section presents results of the contact angle measurements of the modified and unmodified surface of polyethene terephthalate membranes.

4.4.2 Contact angle measurements

The contact angle measurements were conducted in order to understand changes made to surface structures of the amine-modified and silver-coated track-etched polyethene terephthalate (PET) membrane. The measurements of contact angles were carried out using distilled water at ambient conditions as described in Section 3.5.8 of Chapter 3. The contact angle measurements were carried on samples CO-APET (unmodified track-etched PET membrane), 75A-PET (amine-modified track-etched PET membrane) and 30-AgPET (silver-coated track-

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etched PET membrane). The results of contact angle measurements are presented in Table 4.7.

Table 4.7: Contact angles measurements of CO-PET, 75A-PET and 30-AgPET samples.

PET membranes	Average Contact angle (degrees)
CO-APET	88.5
75A-PET	46.4
30-AgPET	53.7

The results in Table 4.7 show a decrease in average contact angle following modification of the PET membrane by diethylenetriamine (DETA). The average contact angle decreased from 88.5^o for sample CO-APET which is unmodified track-etched PET membrane to 46.4^o for amine-modified track-etched PET membrane (sample 75A-PET). The introduction of amines on the surface improved the wettability of the sample 75A-PET, the amine-modified track-etched PET membrane surface. The membrane surface became more hydrophilic as the track-etched PET membrane was modified with diethylenetriamine which bears ionisable groups, the amines (NH_2). The amines were introduced onto the surface of track-etched PET membrane as shown in reaction mechanism Figure 4.2. The observation agrees with the literature that ionisable functional groups on the surface of membranes improve hydrogen bonding between water molecules and ionisable moieties on the surface of the membrane (Goddard *et al*., 2007). The contact angle increased upon immobilising silver nanoparticles on the surface due to loss of ionisable moieties (nitrogen) which has been partly hindered by the silver nanoparticles.

The next section presents the summary of the chapter.

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4.5 Summary of chapter

The achievements described in this chapter are the successful chemical modification of the track-etched polyethene terephthalate (PET) membrane via a wet chemistry method involving a solid/liquid interface reaction, resulting in the immobilisation of silver nanoparticles on the track-etched PET membrane surface. This type of track-etched PET membrane surface modification using diethylenetriamine and then immobilisation of silver nanoparticles on the surface has not been reported in literature. The results have shown that the ester bond scission and formation of amide bond occurred at the solid/liquid interface of diethylenetriamine solution and surface of the track-etched PET membrane. Wet chemistry modification of the track-etched PET surface was confirmed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR). The immobilisation of silver nanoparticles on the surface of the track-etched PET membrane during reduction of silver nitrate by trisodium citrate was confirmed by scanning electron microscopy (SEM), ultraviolet-visible (UV-vis) spectroscopy and XPS. Transmission electron microscopy (TEM) was used to confirm the shape and size of colloidal silver nanoparticles while SEM was used to show shape of silver nanoparticles that were immobilised on track-etched PET membrane surface. The chapter linked results of different characterisation techniques in ascertaining modification of the surface of track-etched PET membrane, finding the optimum conditions for synthesis of silver nanoparticles then reports immobilisation of silver nanoparticles. The initial characterisation of the modified track-etched PET membrane caused more challenges as the FTIR results gave very little observable changes in the absorbance spectra. The presence of silver was therefore determined with XPS showing the amount in percentage of elemental silver immobilised on the surface. Further size distribution and concentration of silver nanoparticles on the amine-modified track-etched PET surface was confirmed by SEM and UV-vis spectroscopy respectively. ImageJ software was used to calculate the size of nanoparticles immobilised on the surface of amine-modified track-etched PET membrane from the SEM and TEM monograms.

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The use of the surface-enhanced Raman spectroscopy (SERS) for the detection of acetaminophen using the silver-coated track-etched polyethene terephthalate membrane is presented in the next chapter. The next chapter also discusses the characterisation of silver-coated track-etched PET membranes using Raman spectroscopy in order to determine the silver-coated track-etched PET membrane sample which would serve the purpose as a platform for SERS application.

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CHAPTER FIVE

Applications

5 Introduction

This chapter presents results and discussion of the detection of acetaminophen on a modified surface of track-etched polyethene terephthalate (PET) membrane that was fabricated as outlined in chapter three. The chapter also lays out the results and the applicability of surface-enhanced Raman spectroscopy using silver-coated surface of track-etched PET membranes (10-AgPET, 20-AgPET and 30-AgPET samples) for detection of acetaminophen,. The sample codes 10-AgPET, 20-AgPET and 30-AgPET are as defined in Table 3.3 and their fixed and variable experimental parameters are given in Table 4.4. The focus is on whether the silver-coated track-etched PET membranes would be able to enhance a weak Raman signal resulting from Raman scattering by acetaminophen molecules on the surface as reviewed in Section 2.5 of Chapter 2. The samples 10-AgPET, 20AgPET and 30-AgPET were prepared as described in Section 3.3 of Chapter 3. The samples were characterised by Raman spectroscopy as described in Section 3.5.7 of Chapter 3. A discussion of the challenges encountered to detect acetaminophen on the surface of both unmodified track-etched PET (Co-AgPET) and silver-coated track-etched PET membrane (10-AgPET, 20-AgPET and 30-AgPET samples) using the Raman spectrometer is also presented in the chapter.

The moieties of acetaminophen have specific vibration modes that produce a Raman spectrum specific to acetaminophen (Kauffman *et al.*, 2008). The chemical structure of acetaminophen is shown in Figure 5.1.

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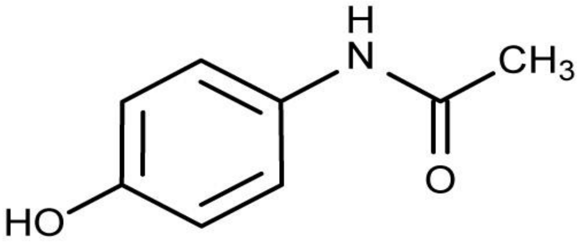

Figure 5.1: Chemical structure of acetaminophen

Acetaminophen has functional groups that have peaks in its Raman spectrum, which are also common to other chemicals. The functional groups are phenyl, amide, carbonyl and hydroxyl. Although acetaminophen has similar peaks to common functional groups, its overall Raman spectrum is specific to acetaminophen only, making the Raman spectrum, a fingerprint signature. The typical acetaminophen peaks identified in its spectrum are outlined in Table 5.1 (Kauffman *et al.*, 2008).

Table 5.1: Peaks in Raman spectrum of acetaminophen.

Proposed bond	**Spectral peak cm^{-1}**
C-O	854, 861, 1170
C-N	1245, 1281, 1328
C=C	1557, 1565, 1576
C=C	1608, 1615, 1623
C=O	1646, 1650

The peaks of the Raman spectrum in Table 5.1 were used to ascertain the presence of acetaminophen on the prepared surfaces of unmodified track-etched PET membrane (CO-AgPET), silver-coated track-etched PET membrane (30-AgPET) and a control surface made of silver nanoparticles sputtered on a glass support (Quartz).

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5.1 Preparation for Surface-enhanced Raman Spectroscopy platform

The platform for the performance of surface-enhanced Raman spectroscopy (SERS) for detection of acetaminophen was fabricated as described in Section 3.3 of Chapter 3. The characterisation of the silver-coated surface is discussed in Section 4.3.2 of Chapter 4 of the thesis. The silver nanoparticles were coated on the surface of modified track-etched polyethene terephthalate (PET) membranes as surface-enhanced Raman spectroscopy active materials to intensify the weak Raman scattering signal with an aim of detecting acetaminophen molecules on the surface. The immobilisation of silver nanoparticles was done at different times in order to find the best conditions that would suppress the polyethene terephthalate Raman signal. The conditions and sample codes are as presented in Table 3.4. Figure 5.2 shows the Raman spectra of the silver-coated track-etched PET membranes (10-AgPET, 20-AgPET, 30-AgPET) and the unmodified track-etched PET membrane (Co-AgPET) as a baseline (control sample).

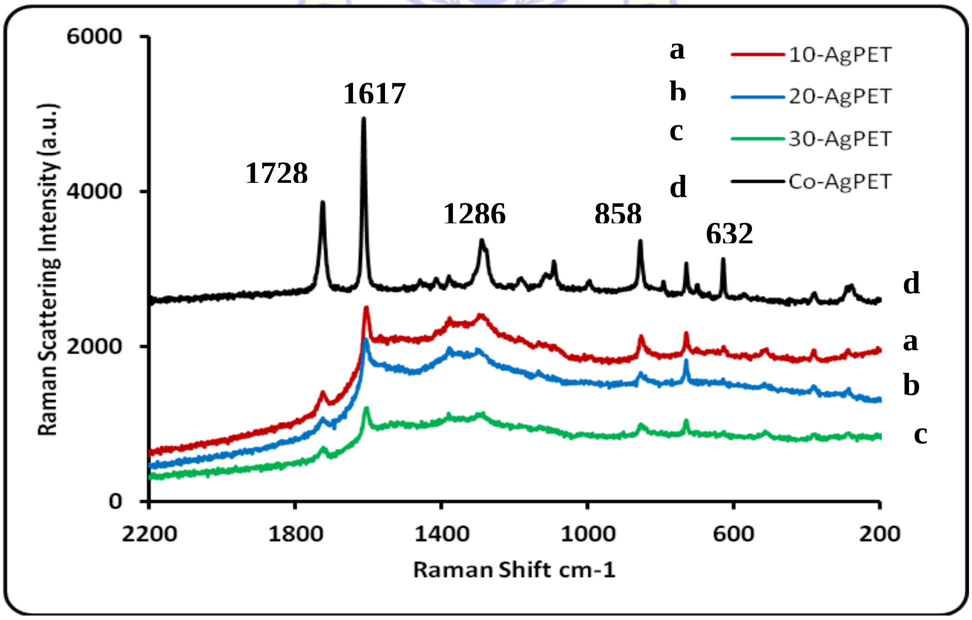

Figure 5.2: Raman spectra of silver-coated track-etched PET membranes at reaction times (a) 10 minutes (10-AgPET), (b) 20 minutes (20-AgPET), (c) 30 minutes (30-AgPET) prepared at 90 ^{o}C using 2 mL of 1% trisodium citrate and unmodifed PET membrane (d) control (CO-AgPET).

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The results for Raman spectra in Figure 5.2 show that as the time of silver nanoparticle immobilisation increased, the intensity of the peaks relating to the PET membrane were reduced with the lowest signal at 30 minutes as shown by the spectrum of 30-AgPET in Figure 5.2. The Raman spectra of silver-coated track-etched PET membranes (10-AgPET, 20-AgPET, 30-AgPET) show suppressed peaks relating to the polyethene terephthalate membrane and these peaks were not as prominent as for the unmodified track-etched PET membrane (Co-AgPET). The Raman spectra peaks of silver-coated track-etched PET membranes show that as the silver nanoparticle immobilisation time was increased from 10 minutes to 30 minutes, the PET peaks' intensities were suppressed. The reduction in the PET peaks' intensities follows the trend of size of silver nanoparticles immobilised on the surface of amine-modified track-etched PET membranes as discussed in Section 4.3.2.3. The trend observed in Section 4.3.2.3 showed that as the time of reduction reaction increased, so did the size of silver nanoparticles immobilised on the surface of PET. The silver-coated track-etched PET membrane coded 30-AgPET was therefore chosen as the most suitable platform for detection of acetaminophen using surface-enhanced Raman spectroscopy. The Raman spectrum of sample 30-AgPET was chosen as baseline because this sample of silver-coated track-etched PET membrane showed the minimum peak intensities of the PET membrane itself. The cut-off point of immobilising silver nanoparticles on modified track-etched PET membrane was set at 30 minutes because the size of silver nanoparticles of sample 30-AgPET, as observed in Section 4.3.2.3, fell within the average range of 58 nm as stated by Taurozzi and Tarabara, 2007.

5.2 Detection of acetaminophen using fabricated silver-coated track-etched polyethene terephthalate membrane.

Similar to Fourier transform infrared spectrum, a Raman spectrum comprises wavelength distribution of peaks equivalent in character to molecular vibrations specific to the analyte being characterised (Ferraro *et al.*, 2003). Surface-enhanced Raman spectroscopy (SERS) as an advanced Raman spectroscopy

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technique was used to detect acetaminophen using silver nanoparticles as SERS active materials to enhance the Raman signal.

The detection of the molecules of acetaminophen on the silver-coated track-etched polyethene terephthalate membrane was carried out at ambient conditions as described in Chapter 3 under the Raman spectroscopy Section 3.5.7. A solution of 20 µL of 1.51 mg/L aqueous acetaminophen was dropped and dried on the surfaces of the selected samples. The Raman spectra of acetaminophen detected on the surface of silver-coated track-etched polyethene terephthalate (PET) membrane (30-AgPET), unmodified track-etched PET (Co-AgPET) and Quartz, a silver-coated glass surface (non-porous) as described in Section 3.1 are shown in Figure 5.3.

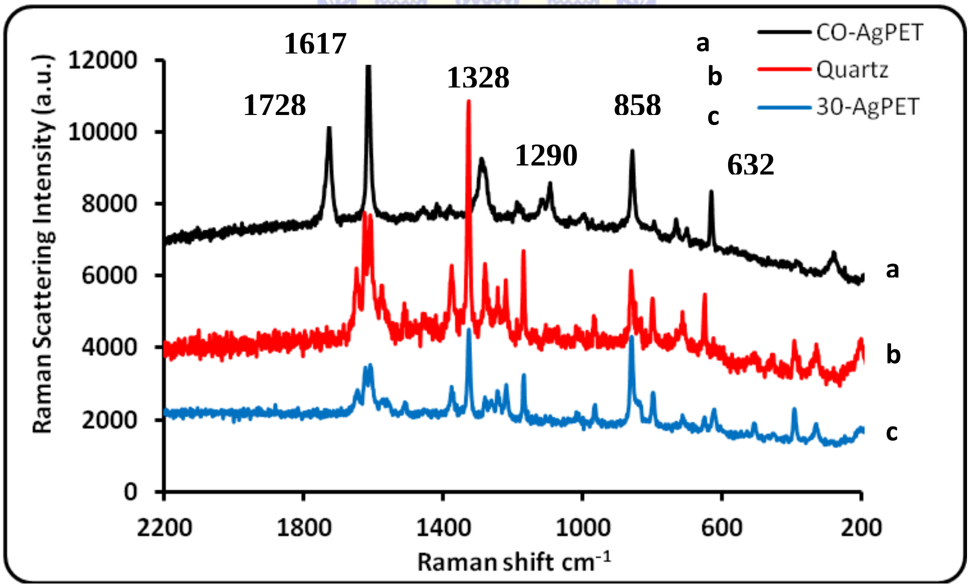

Figure 5.3: Raman spectra of 1.51 mg/L of acetaminnophen on the surface of (a) Co-AgPET (unmodified track-etched PET) membrane (b) Quartz (Non-porous) and (c) 30-AgPET (silver-coated track-etched PET membrane).

Figure 5.3 shows that the peak intensities are higher for the sample coded Quartz (a non-porous silver-coated glass) than that of 30-AgPET, the track-etched silver-coated track-etched PET membrane. In the case of the control sample, Co-AgPET, which is unmodified track-etched PET membrane, no characteristic peaks of acetaminophen could be observed among the overall prominent peaks of polyethene terephthalate membrane. This could be attributed to lack of SERS signals on the surface of sample Co-AgPET membrane to enhance the Raman signal of acetaminophen. Therefore it is inferred that the lack of silver nanoparticles is the main cause of the lack of acetaminophen peaks for the sample Co-AgPET. When comparing the Raman signal intensity of acetaminophen on sample Quartz (a non-porous SERS surface) against 30-AgPET (a track-etched silver-coated track-etched PET membrane), most of the acetaminophen vibrational bands on 30-AgPET are rather weak. The limited SERS intensity and the low spectral intensities could be due to the loss of some molecules of acetaminophen that may leach through the pores.

5.3 Concentration studies for detection of acetaminophen

Concentration studies were carried out using a silver-coated track-etched polyethene terephthalate (PET) membrane sample 30-AgPET for detection of acetaminophen in different concentrations as described in Section 3.4. Acetaminophen solution was prepared using distilled water. The following concentrations were prepared 15.10 mg/L, 1.51 mg/L and 0.151 mg/L which were coded Acet-100, Acet-010 and Acet-001 respectively. Acetaminophen solution of volume 20 μL for each concentration was dropped and dried on the surface of 30-AgPET. Figure 5.4 shows the Raman spectra for the concentrations of the acetaminophen at 15.1 mg/L, 1.51 mg/L and 0.151 mg/L detected from the surface of 30-AgPET membrane.

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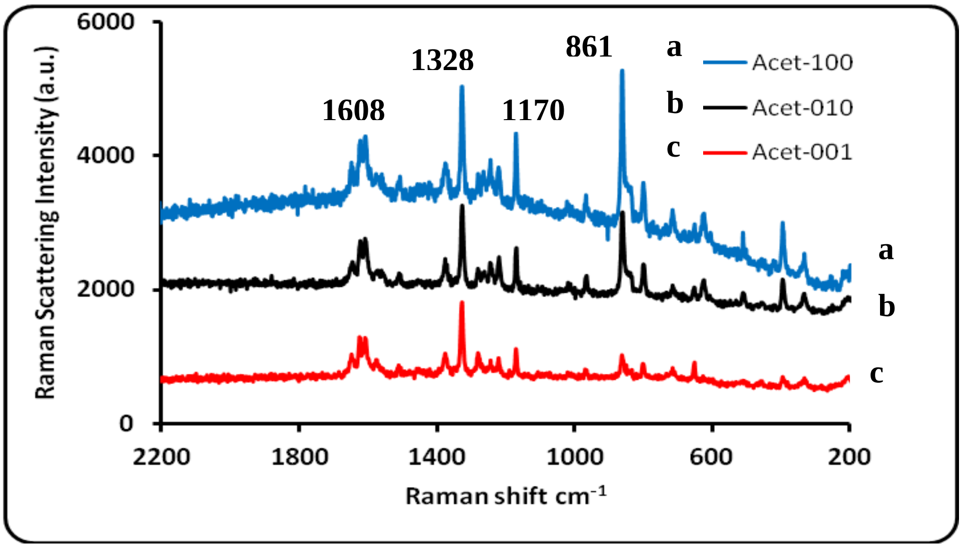

Figure 5.4: Raman spectra showing variations in intensity of different concentrations of acetaminophen in aqueous media (a) 15.1 mg/L, (b) 1.51 mg/L and (c) 0.151 mg/L.

Figure 5.4 shows that the intensity of the Raman peaks increased with an increase in acetaminophen concentration. The trend agrees with what was reviewed in the literature that Raman peak intensity is a function of the concentration of analyte (Taurozzi and Tarabara, 2007). Sample Aceta-100 which is 15.1 mg/L has its acetaminophen peak intensity greater than those of lower concentration (Aceta-010 and Aceta-001) which were 10 and 100 times more dilute, respectively. The changes in the intensity of the peaks of the acetaminophen spectrum are consistently changing with change in concentration. This finding of detecting acetaminophen upon the surface of silver-coated track-etched PET membrane using surface-enhanced Raman spectroscopy has not been reported in literature.

Theoretically, when there is a higher number of molecules on the surface-enhanced Raman spectroscopy surface hot sites, there is a greater chance of observing medium to strong Raman signals (Strachan *et al*., 2007). This is also shown in peaks of the spectra in Figure 5.4. When more acetaminophen molecules covered the surface of silver-coated track-etched PET membrane, the possibility of observing a strong to medium Raman signal was greater. The SERS effect is provided by the localised surface plasmon of silver nanoparticles. The higher Raman scattering intensity could be as a result of SERS contributions

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from both electromagnetic effects and chemical effects (charge transfer) arising from adsorption of acetaminophen molecules on the silver nanoparticles. There is a greater probability for the acetaminophen to be adsorbed on the surface if it exists in high concentration on the surface.

5.4 Application of spectral peaks for quantification

Theoretically, quantification of an analyte in a sample is possible with Raman spectroscopy since the Raman scattering is proportional to the concentration of the analyte. The intensity of Raman scattering of a particular vibration mode is directly proportional to vibrating moieties' concentration (Strachan *et al*., 2007). Raman spectra analysis could be used to extract information from the peak height or area, and/or use the ratio of peak height or area to quantify the analyte. This could be possible only if spectral peaks do not overlap, and all analyte samples are exposed to the same conditions so as to be affected equally by undetected interferents. In reference to Figure 5.4 showing Raman spectra of concentrations 15.10 mg/L, 1.51 mg/L and 0.151 mg/L represented as Acet-100, Acet-010 and Acet-001 respectively, Figure 5.5 shows the trend in specific Raman intensity peak height relative to concentration of acetaminophen.

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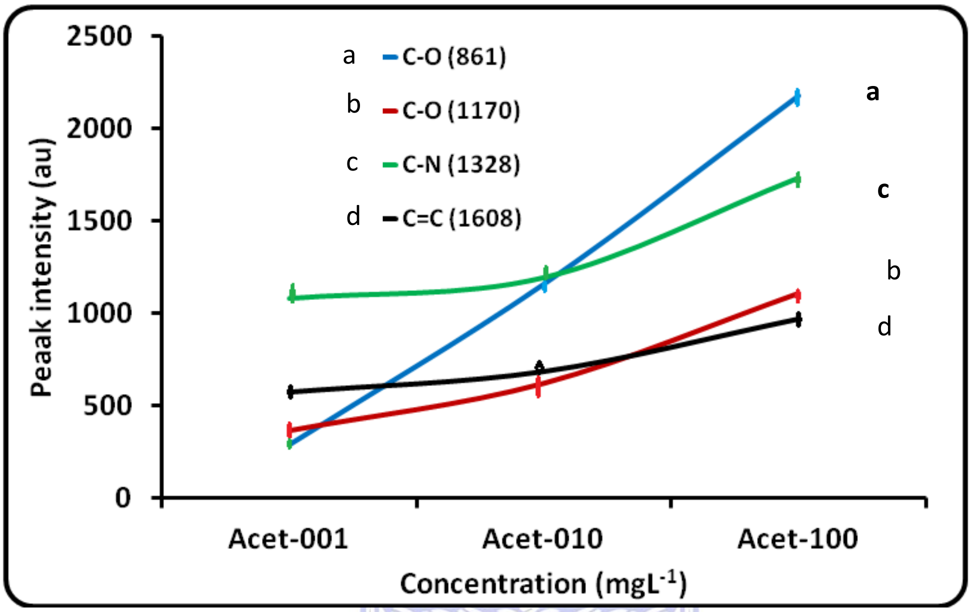

Figure 5.5: Graphical presentation of relationship between concentration of acetaminophen and trends in Raman intensity peak height at specific bond vibrations (a) C-O (861), (b) C-O (1170), (c) C-N (1328) and C=C (1608)

The general trend in Figure 5.5 shows that as the concentration increased so did the peak intensity height. The difference in the trends is observed when comparing the rate of change amongst the specific bonds. For instance the rate of change of C=C (1608) and C-0 (1170) are not correlated, but rates of change for C-O (1170) and C-N (1328) have a similar trend. The peak intensity trend for the C-O (861) vibration shows a linear response. The linearity of peak intensity of the C-O bond versus the concentration has the best correlation of the two factors. The other bond vibrations C-O (1170), C-N (1328) and C=C (1608) show no linearity and if extrapolated towards zero concentration they cross the peak intensity axis instead of the concentration axis. The linear correlation line of C-O (861) when extrapolated would give a limit of detection of approximately 0.0755 mg/L. The challenge with the peak intensity heights is that the proportionality does not seem to be the same for all peak intensity heights, that is the peak intensity increases were not the same for all spectrum peaks. The finding has not been reported anywhere else in literature and therefore this is the first observation to have been made by this study.

The detection of acetaminophen on the surface of silver-coated track-etched polyethene terephthalate (PET) or unmodified track-etched PET was faced with some challenges. The Raman spectrometer used for detection had limited options, for instance it was limited to one laser option of excitation wavelength of 532 nm, and lacked software to calculate peak heights and areas.

5.5 Summary of the chapter

The chapter has covered in detail the results and characterisation of using the silver-coated track-etched polyethene terephthalate (PET) membrane as a platform for the detection of acetaminophen by surface-enhanced Raman spectroscopy (SERS). The quartz platform was used as control to compare the detection using the surface-enhancement of silver nanoparticles of the silver-coated track-etched PET membrane against unmodified track-etched PET membrane. Silver nanoparticles were found to have enhanced the Raman signal of acetaminophen. Further Raman characterisation of the PET membranes that were immobilised with silver nanoparticles at different times showed how effective the amount of silver nanoparticles and their size suppressed the polyethene terephthalate signal. The chapter also made comparison of concentrations of acetaminophen which showed increase in peak height of spectra with an increase in concentration.

The next chapter presents the conclusions and recommendations of the research aims and objectives, findings and achievements in the thesis.

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CHAPTER SIX

Conclusion and Recommendations

6 Introduction

The chapter presents an overall conclusion of key findings and achievements of this study. This chapter also presents suggestions in the form of recommendations for further research as a result of the key findings accrued in this study.

6.1 Conclusion

The study outcomes have shown that the surface of a track-etched polyethene terephthalate (PET) membrane can be modified with diethylenetriamine (DETA) via aminolysis, a wet chemistry technique. The modified track-etched PET membrane surface was characterised by the ester bond scission and formation of an amide bond (C-N). This was confirmed by Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) spectra. The surface of track-etched PET membrane was successfully modified with DETA. The surface modification brought about changes in terms of wettability of the surface as evidenced by the contact angle measurements outcome. The chemistry of the surface was also changed by the introduction of amide bond and changes in chemical states of carbon (C1s) following ester bond scission and formation of amide bonds which resulted in a percentage increase of C1s in C-C chemical state and a decrease in the percentage in O-C=O chemical state as shown in XPS data. The observance of an amide II absorbance in FTIR spectrum of amine-modified track-etched PET membrane at 1578 cm^{-1} was complementary to XPS data.

The silver nanoparticles were successfully synthesised by reducing silver nitrate with trisodium citrate that served as a reducing and stabilising agent. The colloidal silver

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nanoparticles were found to be stable following their zeta (ζ) potential values of more than minus 20 mV. The transmission electron microscopy images of colloidal silver nanoparticles showed that they were of spherical shape with an average size of 46 nm for sample 20-AgNP. The plasmonic peaks of silver solution and silver-coated track-etched PET membranes were observed between 400 and 420 nm which is typical of silver nanoparticles synthesised via reduction by trisodium citrate. The scanning electron microscopy (SEM) images of the silver-coated track-etched PET membranes showed successful immobilisation of silver nanoparticles on the surface. The SEM images showed silver nanoparticles sizes ranging between 28 nm and 68 nm for silver nanoparticles immobilised between 10 minutes and 30 minutes. The SEM results were also in agreement with transmission electron microscopy (TEM) results regarding the spread in size of the silver nanoparticles as measured by ImageJ software. The SEM results also showed a trend in the increase of silver nanoparticles size with an increase in the time of immobilisation. Furthermore, the XPS results complemented the SEM results and UV-Vis results regarding the number of silver nanoparticles immobilised on the surface where XPS data showed an increase in the percentage from 2.53 to 5.20% of silver ($Ag_3d_{5/2}$) relative to the increase in time of immobilisation from 10 minutes to 30 minutes. The thermal properties of the track-etched PET membrane was found not to have been affected by aminolysis of the surface and immobilisation of silver nanoparticles at 90 ^{o}C. The thermogravimetric analysis (TGA) showed that at a temperature of 550 ^{o}C, the silver-coated track-etched PET membrane still had 20% of its original weight, which was calculated to be 6% more than the amine-modified track-etched PET membrane. and 10% than unmodified track-etched PET membrane. The 6% weight of silver-coated track-etched PET membrane which was over and above amine-modified track-etched PET membrane weight was due to residual silver nanoparticles that were immobilised on the surface. The Raman spectra of the silver-coated track-etched PET membrane confirmed immobilisation of a layer of silver nanoparticles that suppressed the Raman signal of polyethene terephthalate. The more silver nanoparticles that were

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immobilised on the surface of PET membrane, the more the reduction of interference was observed by suppression of the PET scattering signal. This was found to be of importance as any analyte on the surface could be detected without interference from PET membrane spectrum.

The silver-coated track-etched PET membrane was successfully used to detect acetaminophen as low as 0.151 mg/L (parts per million). In comparison to a quartz platform which was non-porous, it was observed that the spectra of acetaminophen detected from the surface of silver-coated track-etched PET membrane were of lower intensity. This was attributed to the loss of some of the acetaminophen molecules that leached through the pores of the track-etched PET membrane. The unmodified track-etched PET membrane did not show any peaks of acetaminophen in the Raman spectrum obtained. The Raman spectrum obtained was mainly of polyethene terephthalate monomer of the track-etched PET membrane itself. In the concentration studies of detecting acetaminophen, the Raman peak intensities of acetaminophen decreased with a decrease in concentration of acetaminophen. The correlation o f the Raman peak intensity heights and concentration of acetaminophen for C-O bond vibrations at Raman shift of 861 cm-1 had a linearity response. The other bond vibrations C-N at 1328 cm-1, C=C at 1608 cm-1 and C-O at 1170 cm-1 showed no linearity response. The best correlation from the peak when extrapolated gave 0.0755 mg/L as limit of detection for acetaminophen using a track-etched PET membrane that was amine modified with 75% DETA for 24 hours and immobilised with silver nanoparticles for a duration of 30 minutes.

The fabricated silver-coated track-etched PET membrane was successfully used as a platform to detect acetaminophen.

6.2 Recommendations

The results obtained in this study inspire further research in order to ascertain some parameters that led to the above conclusions in section 6.1. The observed reduced Raman spectra of track-etched PET membrane could further be studied by using PET

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membranes of different pore densities and pore sizes, mainly targeting smaller pore sizes and lower pore densities for improved pre-concentration. This is to observe if there could be an improved Raman scattering intensity, on the fact that less analyte would leach through the PET membrane. The silver nanoparticles were found not to be uniformly immobilised in a monolayer arrangement and this could either have created SERS hot spots or reduced the number of hot spots on the surface. Therefore, there is need to explore this further. The other area of interest generated from the findings of this study is the size of nanoparticles that would enhance the Raman signal. It would be of greater scientific importance to find out how the sizes of silver nanoparticles affect the enhancement of Raman signal when immobilised on the surface of PET membrane. Therefore further research could be explored with much smaller nanoparticles. As regards quantification of analyte from the Raman spectra intensity, further investigations could be explored to focus on the relationship between concentration and Raman intensity of prominent peaks in the spectra for different compounds. This could lead to a calibration curve of Raman scattering intensity versus concentration of an analyte as is done in chromatography studies.

The surface-enhanced Raman spectroscopy technique could be modified and combined with another quantitative analytical technique. This could also be explored in the future research. The SERS technique should be part o f the hyphenated technique where compounds are isolated by before analysis as is done in gas chromatography and high performance liquid chromatography.

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