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Synthesis and Performance Evaluation of Iron Nanoparticles / Polyethersulphone (Fe-NPs/PES) Membrane for BTEX Removal from Wastewater

Chinwe. F. Unuigbe

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Supervisor: Prof. M.O. Daramola

February, 2019

DECLARATION

I, Chinwe Unuigbe, solemnly declare that this dissertation is my unaided work. It is being submitted for the degree of Master of Science in Engineering at the University of the Witwatersrand Johannesburg, South Africa. It has not been submitted before for any other degree or examination at any other university.

_____ 11th Day of February, 2019

Chinwe Fidelia Unuigbe Date

ABSTRACT

Global concern has increased in recent years regarding the potential negative effects of produced water discharged to the marine and estuarine environment. Water is an integral part of life and health which is generally used in every home and industries. Having clean water solves many problems associated with diseases but obtaining it can be difficult. The inadequate measures of handling industrial wastewater are becoming a problem and more difficult to manage than sewage. One of the most serious environmental pollutants in groundwater are organic compounds. These compounds are in abundance in crude oil petroleum products and coal tar. They are volatile in nature and highly soluble in water. These compounds are monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene, and are commonly known as BTEX compounds. BTEX compounds are sometimes neglected, unattended and untreated by the municipal water treatment system notwithstanding their negative effects on our health relating to ingestion.

Nanotechnology has the potential to significantly impact positively on the environmental protection through development of green technologies that minimize the production of undesirable by-products, and remediation of existing sites and polluted water sources. This study focuses on synthesizing iron nanoparticles (Fe-NPs) using plant extract (pomegranate leaves) and embedding the nanoparticles in a Polyether sulphone polymer to obtain mixed matrix membranes (MMMs) for removing BTEX compounds from wastewater. Polyethersulphone (PES) membranes are known for their cost-effective, good mechanical, thermal and chemical stability. However, the inherent hydrophobicity of PES has limited its application in water and wastewater treatment. This inherent nature of hydrophobicity of PES has resulted in research on how to make PES membranes more hydrophilic. Iron nanoparticle infused membrane has^^ promising advantages over the PES membrane, whereby it improves the properties of polymeric membrane such as antifouling, permeation and mechanical properties. Polymer membranes are commonly used in the preparation of microfiltration and ultrafiltration membrane especially, ultrafiltration membrane. In

this study, Fe-NPs and PES composite membranes were fabricated by phase inversion method and evaluated at different percentage loading of iron nanoparticles namely 0 wt.%, 5 wt.%, 10 wt.%, 15 wt.% and 20 wt. %. The physiochemical properties of the composite membrane was investigated using scanning electron microscopy (SEM) for morphology, Fourier transform infrared spectroscopy (FTIR) for surface chemistry, Thermogravimetric analysis (TGA) for thermal stability, water contact angle determination for wettability, and Atomic force microscopy (AFM) for the roughness. The performance of the composite membrane in terms of water flux and BTEX removal efficiency during wastewater treatment was investigated.

The results show that the composite membranes with Fe-NPs were improved significantly and has the potential for removal of BTEX compounds in wastewater. Contact angle measurement indicates enhanced hydrophilicity by incorporating Fe-NPs in the polymer matrix. At 10 wt. % Fe-NPs, the membrane-displayed BTEX rejection of 63.8 %, 56.86 %, 53.42 % and 84.12 %, respectively. The membrane mechanical strength at 20 wt. % Fe-NPs loaded displayed the highest tensile strength of 8.94 MPa compared to 0 wt. % Fe-NPs loaded which gave 1.2 MPa. This indicates that mechanical properties were enhanced at increasing Fe-NPs loading. When the Fe-NPs loading was 10 wt. %, the water flux reached the maximum at 80.50 L m^{-2} h^{-1}, about 62 % higher than the pure PES membrane. It is an indication of enhanced membrane properties as nanoparticles loading are increased.

DEDICATION

This work is dedicated to God Almighty in whom I live, move and have my being.

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NOMENCLATURE

A	Area
AFM	Atomic force microscope
AMD	Acid mine drainage
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CWA	Clean Water Act
DMAC	Dimethylacetamide
EPA	Environmental Protection Agency
EDC	Endocrine disruptive chemicals
EDS	Energy dispersive spectroscopy
Fe	Iron
F	Flux
FAO	Food and Agriculture Organization of the United Nation
FTIR	Fourier Transform infrared spectrometer
GAC	Granular activated carbon
TGA	Thermogravimetric analysis
TMP	Trans-membrane pressure
THMs	Trihalomethanes
TFCM	Thin film composite membrane

MTBE	Methyl tertiary-butyl ether
MMM	Mixed Matrix Membrane
MF	Microfiltration
MWCO	Molecular Weight Cut-off
NPs	Nanoparticles
NF	Nanofiltration
PES	Polyethersulphone
P	Pressure
PWF	Pure water flux
PWP	Pure water permeate
PAC	Powdered activated carbon
SEM	Scanning electron Microscopy
SDWF	Safe Drinking Water Foundation
UV	Ultraviolet
UF	Ultrafiltration
UN	United Nation
WHO	World Health Organization
W	Weight
Wt. %	Weight percentage
XRD	X-ray diffraction

PUBLICATIONS FROM THIS STUDY

(i) Unuigbe, C.F., Fayemiwo, O.M., Daramola, M.O. (2018) Performance evaluation of iron nanoparticles infused polyethersulphone (Fe-NPs/PES) membrane during treatment of BTEX-contaminated wastewater, Water and Environment Journal (under review)

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CHAPTER 1

INTRODUCTION

This chapter presents motivation, research objectives and justification.

1.1 Motivation

Global concern over the impact of wastewater on environment has generated increasingly urgent attention for research and development in water resource management. Water is a crucial mineral resource essential to life, used in every home and industry at various desirable times. To ensure availability of potable water, wastewater treatment processes had been applied for over centuries in industries and homes. Increase in industries joined with population growth have driven intense demand for global portable water resulting in more challenges in handling wastewater.

Water treatment originally focused on improving the quality of drinking water. Methods to improve the taste and odour of drinking water were reported as early as 400 BC (US EPA, 2000). The recommendation of wastewater treatment methods by the Ancient Sanskrit and Greek writings were straining, exposing to sunlight and filtration through charcoal. Egyptians, as early as 1500 BC used the chemical, alum to treat water (US EPA, 2000; Baker, 1981). During the 1700s, the filtration method was established as an effective means of removing solid particles from water. Water resources are vulnerable to pollution and recent studies have documented various pollutants such as trihalomethane (THMs), acid mine drainage (AMD), endocrine disruptive chemicals (EDC), heavy metals and hydrocarbons (Westerhoff et al., 2005; Zhang, 2003). The activities produced by human that use water mostly generate a lot of wastewater. Increase in demand for water is proportional to the quantity of

wastewater produced, thereby resulting in high water pollution load worldwide (UNESCO, 2017). The AQUASTAT database of Food and Agriculture Organization (FAO) of the United Nation (UN) estimates global freshwater withdrawals at 3,928 km^3 per year. An estimated 44 % of this water is consumed, mainly by agriculture. The remaining 56 % (2,212 km^3 per year) is released into the environment as wastewater in the form of municipal and industrial effluent and agricultural drainage water (UN- water,2017) as seen in Figure 1.1.

A country's level of industrial and municipal wastewater treatment is generally a reflection of its income level. On average, high-income countries treat 70 % of the wastewater they generate. The upper-middle-income countries treat 38 % while lower-middle-income countries treat 28 % and finally, in low-income countries, they only treat 8 % of the industrial and municipal wastewater they generate (Sato et al., 2013) These estimates support the often-cited approximation that, globally, over 80 % of all wastewater is discharged without treatment (UNESCO, 2017; UN-Water, 2015). However, the discharge of untreated wastewater remains common practices especially in developing countries, due to lack of technical and institutional capacity, infrastructure, and financing.

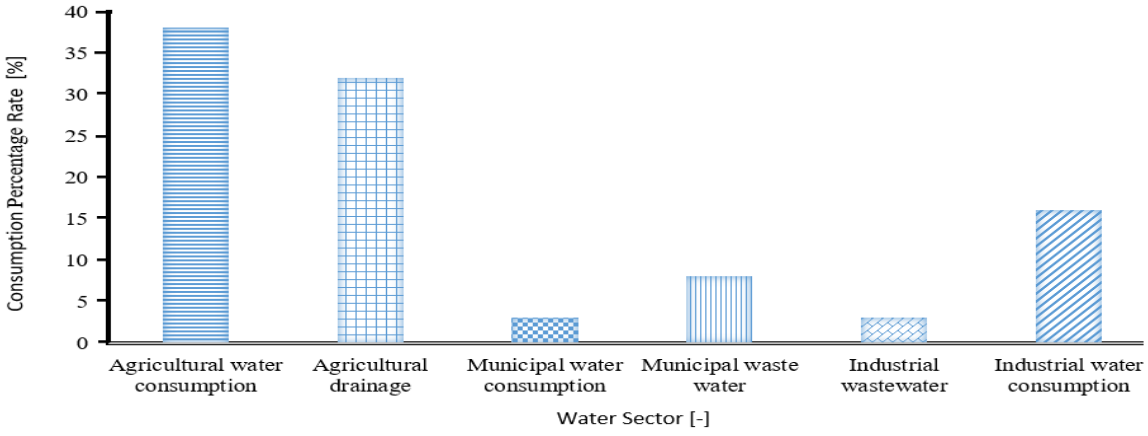


Figure 1.1: The fate of freshwater withdrawals: Global consumption and wastewater production by major water use sector.

The discharge of untreated wastewater has potentially more significant negative impacts on human health, environment and water resources. These effects include loss of biological diversity and ecosystem, water and vector-borne diseases. The world Health Organization (WHO), globally estimated over three million water-related deaths annually because of the prolonged existence of biological pathogens and chemical pollutants such as hydrocarbons (monoaromatic and polyaromatic) and heavy metals. According to WHO, about seven hundred and eight million people have not got access to a safe drinking water system (WHO, 2008; Muhammad et al., 2011). It has also been estimated that in the year 2020 about 76 million people will die from water-related illnesses (Galiani et al., 2005; Gleick, 2002). In order to avoid detrimental effect of wastewater on ecosystem, every wastewater generated should be treated.

Benzene, toluene, ethylbenzene, and xylene, which are commonly known as BTEX belong to monoaromatic ring compounds with a six-carbon benzene ring as their main structure (Fayemiwo et al., 2017). They are volatile organic compounds that are commonly used as a solvent in many industries and also in many household products such as plastics, paint, and insecticide in spite of their life-threatening effects on human health and environment (Singh et al., 2011). BTEX compounds can be released into the air and water which usually evaporate quickly into the air and can also dissolve in water (Mitra and Roy 2011). It may be found in surface water and groundwater contaminated sites or in close proximity to natural oil, coal, and gas deposits (Fayemiwo et al., 2017; Leusch and Bartkow 2010)..

The spillages of petroleum products and hydrocarbon leakage from underground storage tank over the years have become a major environmental concern (Qin et al., 2008). During drilling and refining operations in crude oil, a large volume of oilfield-produced water is accumulated and for most offshore, this produced water has the greatest volume of effluent. The percentage volume of waste produced may amount to 80 % of the wastewater in the production process (Krause 1995; Stephenson 1991). Oilfield produced water comprises of organic and inorganic compounds with a

variable amount of metals, salts, oil; radionuclide and treatment chemicals with high salinity (Fakhru'l-Razi et al., 2009). Among the organic compounds, one specific group that poses a serious threat to our health is BTEX. These compounds are collectively known as BTEX compounds (EUGRIS, 2007). BTEX compounds are monoaromatic compounds that are volatile and highly soluble in water, which substantially affects the health of water bodies (Reddy et al., 2012).

BTEX compounds are present at high concentration in untreated produced water as from 600 mg/l depending on the source (Qin et al., 2008). These compounds are classified as harmful and potentially carcinogenic under the Safe Drinking Water Act and Clean Air Act (US EPA, 2011). The persistence of BTEX in groundwater is of a great concern due to its negative impact on human health and resultant environmental degradation. Benzene-induced toxicity is related to blood disorders, including bone marrow depression and some types of cancer (Wan and Winn 2004; Wetmore et al., 2008). The toxicity of the organic compounds has proven harmful to human and wildlife (Sirotkin and Harrath, 2017) as shown in Table 1.1

Table 1.1: Effect of BTEX Compounds on human health (Andersen et al., 2013)

Chemical	**Carcinogen**	**Effects Liver**	**Affects Kidneys**	**Affects Nervous System**
Benzene	YES	NO	NO	NO
Toluene	NO	YES	YES	YES
Ethylbenzene	NO	YES	YES	NO
Xylene	YES	NO	NO	YES

Oilfield produced-water (OPW) when disposed into the ocean directly becomes unsafe and unhealthy to human and other aquatic bodies due to the presence of BTEX compounds. This method of direct discharging of OPW has been the disposal method over the years before the intervention of United States Environmental Protection

Agency (EPA) to preserve water bodies from degradation (Fakhru'l-Razi et al., 2009; US EPA, 2000). According to the US EPA, about 35 % of diesel fuel and gasoline underground storage tanks (USTs) are leaking and about 40 % of these leaking storage tanks might propagate groundwater and soil pollution (Pawlowski, 1998).

There are so many ways by which disposal and management of wastewater affect drinking water such as inadequate treatment of wastewater prior to discharge; accidental releases during transport or leakage from wastewater storage pits; unpermitted discharges; migration of constituents in wastewaters following land application; inappropriate management of residual materials from treatment (Caitlin et al., 2014). It is of great value to health for everyone to obtain safe drinking water, a basic human right and a factor of an effective procedure for health preservation. Attention should be given to the chemical substances that pose a serious threat to health in order to limit their concentration in water (WHO, 2017).

1. 2 Problem Statement

The WHO estimated that over three million people die from water-related diseases annually and about seven hundred and eight million people have not got access to a safe drinking water system (WHO, 2008). Global water quality is increasingly diminishing due to industrialization, population growth, climate change and economic inflation in developing countries. It is of utmost importance for every human being to have access to safe drinking water (Friedrich, 2015).

South Africa is a water scarce nation with erratic variable rainfall and water run-off (Ringwood, 2017). Currently, the quality of the scarce fresh water is decreasing due to an increase in pollution related to river catchment (Cole, 2017). The average annual rainfall in South Africa is about 450 mm, which is below the world average of about 860 mm (DWAF, 2008). It has been evaluated that rainfall could decrease as much as 10 % by the year 2050 and Consulting Engineers of South Africa (CESA) predicted that the demand for water in 2025 will surpass its supply (Misra, 2014; Roberts, 2010). So, it is of utmost importance to recycle wastewater from industries

and preserve them. Currently, the quality of South African borehole water is deteriorating; unable to meet with the standard water supply. In addition, the method of water treatment used in the municipal water allows pollutants to enter the water for the end users, making it unsafe and unhealthy for people (Le-Minh et al., 2010).

Drinking contaminated water causes diseases which are a burden on human health with even the treatment cost is burdensome for families. Intervention to revamp the standard of drinking water provides significant well-being to health (WHO, 2008; WHO, 2017). The conventional method of water treatment is no more effective and challenging as they are becoming more saline and eutrophic (Cole, 2017). There is a need to develop a treatment technique that will effectively remove BTEX compounds from BTEX contaminated water. Several methods have been proposed to do this, but the application of nanotechnology and membrane technology has been demonstrated to be effective in removing BTEX compounds from contaminated water. The use of nanoparticles in water treatment has been reported for their ability to remove some water pollutants like trichloroethylene and methyl-t-butyl ether (Karn et al., 2003). Recently, attention has been given to the use of nanomaterials incorporated in a membrane for water treatment.

In this work, iron nanoparticles were synthesized and incorporated within the polymer matrix (Fe-NPs/PES) via phase inversion method. The fabricated membrane was characterized and evaluated for BTEX water treatment. However, BTEX water treatment using a mixed matrix method is still limited in the literature.

1.3 Research questions

Specific questions posed in this study included:

- What will be the removal performance of pure Polyethersulphone (PES) membrane (0 wt. % Fe-NPs loading) during the treatment of BTEX contaminated water?

- Can BTEX removal efficiency of PES membrane be enhanced with subsequent loading of Fe-NPs during the treatment of BTEX – contaminated water when embedded with Fe-NPS?
- What will be the effect of operating conditions on the removal efficiency of Fe-NPs/PES membrane?

1.4 Research aim and objectives

The aim of this research was to fabricate and characterize the nanocomposite membrane (Fe-NPs/PES) and evaluate its performance for BTEX removal.

The specific objectives of the study were as follows:

i. To synthesis iron nanoparticles (Fe-NPs) from pomegranate leaves and characterize them.
ii. To fabricate PES membrane and Fe-NPs/PES composite membrane and characterize them.
iii. To evaluate the removal efficiency of PES membrane and Fe-NPs/PES membrane during the treatment of BTEX- contaminated water.
iv. To investigate the effect of operating variables such as operating pressure, concentration of BTEX content and pH on the performance of Fe-NPS/PES membrane during the treatment of BTEX contaminated water.

1.5 Dissertation layout

The structure of the remaining sections of the dissertation is presented as follows:

Chapter 2 discusses the detailed literature review of previous works done on wastewater treatment using membrane and other conventional methods with a focus on synthesis and incorporation of iron nanoparticles on the membrane.

Chapter 3 dwells on experimental methods reviewed in Chapter 2 employed for the synthesis and characterization techniques of iron nanoparticles from pomegranate leave, the fabrication of nanocomposite membrane (Fe-NPS/ PES) membrane. Also, a detailed description of the method used in the performance evaluation of the membrane is presented as well.

Chapter 4 is a presentation of results from the methodologies with a focus on the evaluation of removal efficiency of nanocomposite membrane when treated with BTEX contaminated water. (1) Synthesis of the nanoparticles and membrane; (2) Characterization of the nanoparticles and membranes; (3) Evaluation of the membrane during BTEX contaminated water.

Chapter 5 outlines the results of the effects of the operating variables such as pressure, concentration of BTEX, and pH investigated in this study on the performance of the nanocomposite membrane during the treatment of BTEX contaminated water. The results were compared to the literature.

Chapter 6 summarizes the findings of the study with general conclusion and recommendation of the research work.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Environmental protection is requiring more awareness every year because of the pervasive impingement of wastewater on environment. Industrial wastewater presents a complex and challenging problem to human beings and their environment (Austin, 1984). In recent years, research into the characteristics of wastewater has become more substantial and more comprehensive. The body of scientific knowledge has significantly expanded. Recent research in wastewater treatment has been developed and designed to deal with health and environmental concerns. However, the effectiveness in advanced treatment technology has not kept pace with improved detection capability of the constituents in wastewater. The impact of climate change on the quality and quantity of groundwater resources is of global importance. It has been reported that about 1.5-3 billion people rely on groundwater as a drinking water source (WHO, 2008; Kundzewicz and Döll 2009).

In the process to remediate wastewater, the US Federal government came up with strict laws. These laws are enforced by the United States Environmental Protection Agency (U.S.EPA). Federal water pollution laws were approved in 1984,1956, 1961, 1965, 1966, 1970. In 1972, the nation's initial program covering all navigable waterways was passed and it is known as the water Pollution Control Act of 1972 (Austin, 1984). Implementation in the United States of the Federal Water Pollution Control Act Amendments of 1972 also known as the Clean Water Act (CWA) arouses great interest with changes in wastewater treatment to achieve objectives such as: issuing wastewater standard for the industries, development of national water quality criteria recommendation for pollutants in surface waters and to ensure safe drinking water to protect human health and aquatic organisms. Many Countries both

developing and underdeveloped countries also established their own laws (US EPA, 2011).

2.1 Critical challenges

Preservation of water is one of the oldest actions taken by the ancient civilization in order to fulfil the required demand for water for domestic and agricultural purposes (US EPA, 2000). The conservation of water resources costs far less. It is more sustainable than treating non-portable and wastewater and supplying it for the required needs. The problem of adequately handling industrial wastewater is more complex and much more difficult since many organic compounds are toxic, resistant to natural degradation, and require special handling before they can be safely discharged (IEPA, 2011).

The goal of water treatment is to remove organic, inorganic and microbial contaminants as well as other unhealthy properties such as colour, odour and taste to obtain clean, safe and potable water. Wastewater is characterized in terms of its physical, chemical and biological constituents. The physical characteristics include colour, odor, solids and temperature; chemical characteristics include the amount or concentration of carbohydrate, fats oils and grease, pesticides, phenols, proteins, volatile organic compounds and surfactants, nitrogen, oxygen, heavy metals, sulphur, methane, alkalinity, chloride and sulphide; and biological characteristics include viruses, bacteria, and plants and animals (Saravanamuthu, 2009). Many of these parameters are interrelated. Tchobanoglous et al., (2003) outlined the sources of these various characteristics. Lots of studies focused on the remediation of wastewater has been proposed, ranging from physical, chemical and biological treatments. During the water treatment processes, the treatment method adopted depends on the water sources and its application. In other words, surface water which is near human activities tends to be more vulnerable and highly susceptible to contamination than groundwater. The treatment method of groundwater will be different from that of surface water due to their individual constituents and this is applicable for all water source (Mitra and Roy, 2011).

For the past decade, conventional water treatment technology has been used for primary and secondary water treatment. This conventional water treatment technology is no more effective and also more challenging as waters are becoming more saline and eutrophic as a result of industrialization. This treatment method includes disinfection and sand filtration, flocculation/sedimentation and coagulation (Cole, 2017).

2.2 Conventional water treatment technologies

Conventional water treatment method has been there over the years about the 20th century. In this method, polluted water was allowed to stand in a vessel for a period of time and a clear liquid could be observed on top while particles settle at the bottom of the vessel (Hazen, 1909; US EPA, 2000). This conventional wastewater treatment cannot remove all contaminants, as has been indicated by recent studies (Snyder et al., 2004; Parrott and Blunt 2005). Many of the conventional water treatment technologies are currently being used for primary and secondary water treatment. However, the shortcomings attached to them hinder their effectiveness and efficiency. In the subsequent sections, the merit and demerit of the conventional treatment methods will be treated in detail. After which, comes the emerging membrane technology for water treatment which is the focus of this study.

2.2.1 Filtration

Conventional filtration was established during the 1700s as an effective means of removing particles from water (Metcalf and Eddy, 2003). It is a treatment process of separating undissolved solids from a liquid by means of a filter containing filter media such as porous substances, membrane or permeable fabric. The filter media used can either be a granular filter (charcoal, gravel or sand etc.) or a membrane filter (Crittenden et al., 2005). It provides effective treatment for about any range of raw-water turbidity. Its success is due partially to the clarification that precedes filtration and follows coagulation and flocculation as seen in Figure 2.1

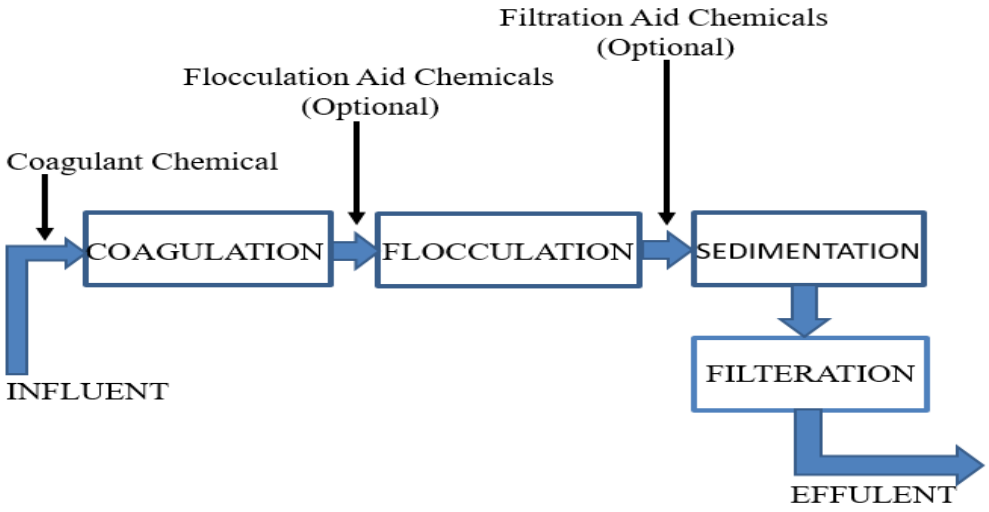


Figure 2.1: Schematic of conventional water treatment process (Hancoc, 2017)

There are two major filtration processes, namely: slow sand filtration and rapid sand filtration (Hancoc, 2017). Each filtration process depends upon the size of the filter. Slow sand filtration removes bacteria, protozoa, and viruses, and produces essentially clean water, though it is advisable to use disinfectant and the diameter of the pores is between 0.3-0.45 µm. Rapid sand filtration removes suspended particles, which have bacteria attached but does not remove bacteria, protozoa or viruses. In both cases, water is forced through the medium by gravity (SDWF, 2007). In slow sand filtration, the microorganisms spread into colonies and form a layer on top of the sand and this layer of microbes is called biofilm and it requires cleaning every couple of months (US EPA, 2000; SDWF, 2007). This biofilm layer later degrades suspended particles in water and dissolved organic solvents (Caitlin et al., 2014). Direct filtration plants have a lower capital cost. However, the process cannot handle large variation in raw turbidity.

2.2.2 Coagulation

The coagulation process involves adding positively charged chemical coagulants such as aluminium sulphate, ferric chloride, ferric sulphate or polymer to water in order to

bind the suspended particles, colloids and dissolved matter into heavier particles that can settle out of solution (Aboussabiq et al., 2014). The positively charged coagulants neutralize the negative charge of dissolved and suspended particles in the water. When this reaction occurs, the particles bind or coagulate; this process is also known as flocculation (Hancoc, 2017). The large particles or agglomeration of particles are often referred to as "flocs" and these flocs are settled at the bottom of the water supply known as sedimentation. Figure 2.2 illustrates the coagulation process and its basic reaction. The coagulation process is effective in removing suspended solute and dissolved organic particles but the process does not remove pathogens present in the water (SDWF, 2009). Addition of more chemicals may a pose threat to the environment. Aguiar et al. (1996) investigated the relationship between the optimum coagulant (ferric chloride) dosage and the organics in the water studied at optimum coagulation pH. The raw water studied have high concentration of iron and weak mineralization in common. The authors then concluded that the optimum pH for coagulation with ferric chloride is 4-5 when considered in relation to the removal of organics; and 5-6 in terms of residual iron occurrence. Secondly, the occurrence of residual iron after coagulation, clarification, and filtration increases when the dose of the coagulant is below the optimum. As coagulation does not remove all the viruses and bacteria in the water, it cannot produce safe drinking water.

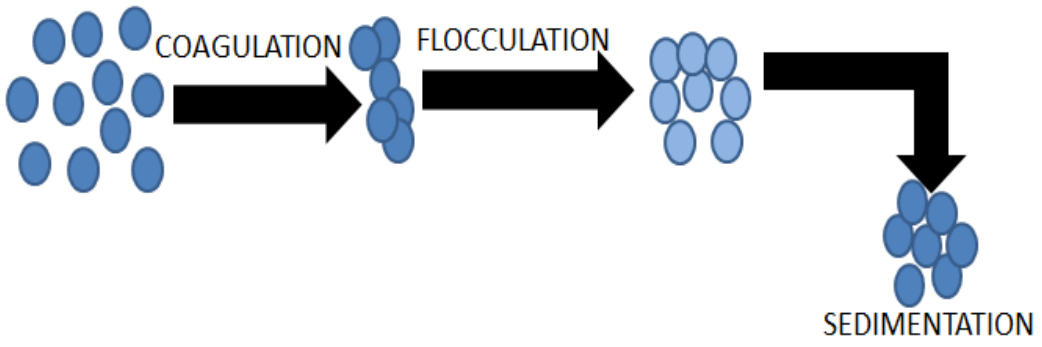


Figure 2. 2: Process of coagulation, flocculation and sedimentation (SDWF, 2009)

2.3 Adsorption

Adsorption is the process of accumulating substances that are in solution on a suitable interface for separation (Metcalf and Eddy, 2003). The substance that is being removed from the liquid phase of the interface is called the adsorbate. The principle of adsorption process in water treatment involves physical and surface separation in which organic organisms, as well as inorganic ions, can be removed from the aqueous phase (Worch 2012). The popular adsorbent materials applied in water treatment for wastewater, drinking water and groundwater landfill is activated carbon, zeolites and polymeric adsorbents as seen in Figure 2.3 (Worch 2012; Ali and Gupta 2006).

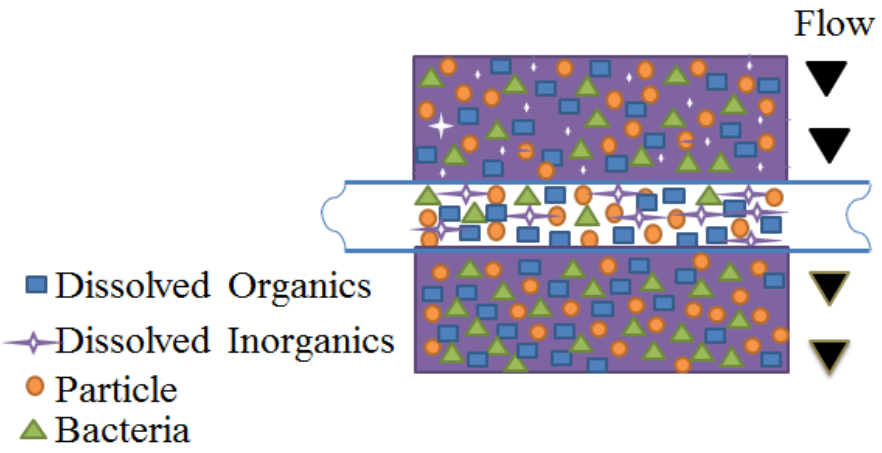


Figure 2. 3: Adsorption process (Worch, 2012)

Over a decade, activated carbon has been in use for water treatment as an adsorbent. It was mainly used to remove taste and odorous compounds that are often found in surface water supplies. Activated carbon is a member of carbonaceous substances characterized primarily by their surface area, pore size distribution and sportive catalytic properties (Mopoung et al., 2015). Furthermore, Crittenden et al. (2005) described adsorption as a process that occurs in the form of physical attachment driven by Van der Walls forces and electrostatic forces between adsorbate and adsorbent molecules. Activated carbon is being applied in two different forms such as

powdered activated carbon (PAC) which is applied in slurry reactors and as granular activated carbon (GAC) which is applied in fixed-bed adsorbers (Worch, 2012). These particles are ranges from medium micrometre for PAC (PAC<2000 µm) and lower millimetre for GAC (GAC >0. Activated carbon is locally prepared from a wide range of products such as coal, wood 1 mm) (Worch, 2012; Manahan, 1999). Both possess similar adsorption characteristics., clay, petroleum coke etc. (Gumbi, 2015). The adsorption method currently in use for water treatment is effective, there is however, one major drawback relating to capacity to address the issue of toxic or micro-pollutants. In dealing with toxic compounds, the results achieved is actually accumulating and transferring the pollution load from aqueous to the adsorbent phase, high cost (expensive distillation), poor capacity, in addition, PAC may also provide sludge ballasting (Shon et al., 2005; Jones and Tompeck 2006; Vigneswaran 2009).

2.4. Disinfection

Water disinfection is the removal, deactivation or killing of pathogenic organisms that can cause diseases to human (IEPA, 2011). To have an effective disinfection of water during water treatment, there are factors to be considered. These include maintaining adisinfectant residual level through the distribution system devoid of emergence of any significant problems from the use of disinfectant (Crittenden, 2005), and secondly, ensures the inactivation of traditional and emerging microorganisms in water. Commonly used disinfectants include:

- Chemical agent disinfectants such as chlorine, hypochlorite, chlorine dioxide (twin oxide) and chloramines; ozone; peroxide.
- Irradiation (UV radiation) and heating (boiling)
- Sonification, electrocution.

2.4.1 Ozone

Ozone (O_3) is an oxidizing agent that is used in water treatment. It is the chemical that can provide effective inactivation of bacteria such as Giardia or Cryptosporidium and reduce heavy metals into insoluble metal oxide at a lower dosage level not much

greater than those used in routine water treatment (Wang et al., 2014; US EPA, 2011) It is an expensive disinfection technology in terms of capital and operating cost.

2.4.2 Chlorine disinfection

Chlorine is a most widely used disinfectant for the inactivation of waterborne pathogens due to its capacity to maintain a measurable residual disinfectant level for continuous treatment (I EPA, 2011). It has a low operational cost as well as very easy to handle (Jones and Tompeck, 2006). Chlorine is routine chemical disinfectant used for water treatment and it has made greatest contribution to the prevention of waterborne diseases worldwide (US EPA, 2011; Jones and Tompeck, 2006). Treatment technology using chlorine reduces the finished water concentration of the disinfection when used as disinfection by-product by lowering their total organic carbon concentration before the point of chlorination. In bromine water, application of chlorine does not guarantee risk of impurity (Black et al., 2013).

2.4.3 Ultraviolet (UV)

Many municipal wastewater treatment plants have adopted the UV disinfection treatment over chemical chlorine disinfection as UV is safe, environmentally friendly and cost-effective (US EPA 1999). A UV disinfection system transfers electromagnetic energy from a mercury arc lamp to the organism (WHO 1996). The effectiveness of UV radiation system depends on the characteristics of the wastewater, the intensity of UV radiation, the amount; the amount of time the microorganisms are exposed to the radiation and the reactor configuration (Bolton and Cotton, 2008). UV light is very effective against protozoan pathogens with additional effectiveness against bacterial and, to some lesser extents, viruses in water (EPA, 2011). It has no effect on taste or odour issues should they arise in the water treatment.

The advantages and limitations of some disinfection methods are described in Table 2.1. They are separated into the use of system for primary disinfection and their use in the maintenance of a residual disinfectant in distribution system.

Table 2. 1: Advantages/ limitations of primary disinfection treatment (EPA, 2011)

Method	**Advantages**	**Limitations**
Chlorination	Well understood disinfection capability. Has dosing technology	Chlorination by-product and taste and odour problems can affect consumption. Ineffective against Cryptosporidium
Ozone	Strong oxidant and highly ineffective disinfectant compared to chlorine. Has the ability to destroy organic micropollutant such as pesticide, taste and odour.	Bromate by-product and increased absorbed organic carbon can impact on re-growth in distribution. Complex, energy-intensive equipment compared with chlorination. Residual insufficiently long lasting for distribution.
UV	Generally, highly effective for protozoa, bacteria and most viruses and particularly for Cryptosporidium. No by-product implication.	Less effective for viruses than chlorine. No residual for distribution

Generally, chemical disinfection methods are more effective against bacteria and viruses, with little or no effect in the case of chlorination (IEPA 2011)

2.5. Advanced technology for water treatment

2.5.1. Membrane technology

Membrane technology is a novel concept that has been applied in all water and wastewater treatment as well as in the broad range of applications such as medical, pharmaceutical industries and other production industries (Fenu et al., 2010; Van and Zydney 2007; Li and Chu, 2003). In chemical technology, membrane has acquired an important place (Baker 2004). The importance of membrane technology for wastewater treatment cannot be overemphasized. In the early 1960s, Loeb and Sourirajan (1963) developed industrial scale membrane processes for making defect-free, high-flux and anisotropic reverse osmosis membranes. A membrane is a selective barrier that separates mixtures and restricts transport of various chemical species (Daramola et al., 2012). The membrane acts as a semi-permeable layer between two-phases and it regulates the transportation between those two phases (Baker, 2004). In water treatment, membranes allow water to flow through while the suspended solid remains on the membrane surface (Padaki et al., 2015). Thin layer is a type of asymmetric membrane that is responsible for the separation and permeability of chemical species. The thin layer was developed on a thick substance that provides mechanical strength to the selective layer (Baker, 2004; Padaki et al., 2015; Loeb and Sourirajan, 1963). The contribution of Loeb and Sourirajan (1963) was significant in membranes for water treatment. Membrane flux is volume of permeate per unit area per unit time. The membrane flux produced by the members was 10 times higher than that of the membrane available then and made reverse osmosis membrane a practical application in water desalination. The discovery provided the fundamental basis through which other membrane designs were built (Baker, 2004).

The application of membrane technology has become a significant separation method over the years, which was proven to be very efficient, cost-effective, fast and practically applicable (Idris et al., 2012). Membrane technology is an important technique that implements process intensification and energy efficiency (Olajire, 2011). Conventional water treatment systems consume a huge amount of energy that can affect industrial operational cost, see Figure 2.4.

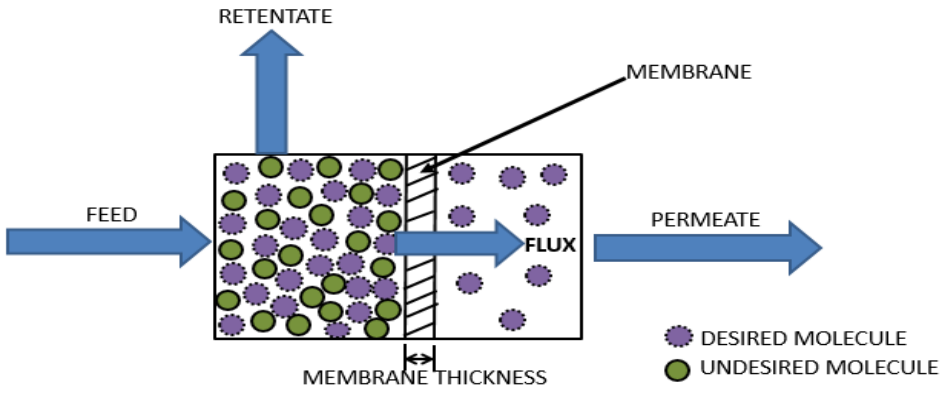


Figure 2. 4: A Schematic of a membrane unit separation (Daramola et al., 2012)

Membrane technology has been there over the years about 150 years ago. The first notable application of membranes was seen in the testing of drinking water at the end of second World War but in 1960, modern membrane science was developed (Baker 2004). Membrane filtration has been proven effective in treating oily water (Fakhru'l-Razi et al., 2009), municipal wastewater (Nicolaisen 2003; Channabasappa 1977), oily wastewater (Karakulski et al., 1995) and industrial wastewater (Amenaghawon and Obahiagbon 2014). The application of membrane technology in wastewater treatment has become a good way to treat water since it removes particles, colloids and macromolecules to clean the water (Aziz and Mojiri, 2014). In freshwater production from surface water, membrane technology has also been employed. The cost effectiveness of the membrane technologies is determined by two major factors namely: permeate flow rate maintenance and system reliability.

Membranes available for industrial use include thin film polyamide membrane and ceramic membrane (Cheryan 1998). Charcosset (2009) reported the pressure-driven membrane process. It consists of Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO). These membrane processes have found wide application in water treatment. They operate according to their pore sizes (Pendergast and Hoek 2011) as seen in Table 2.2.

Table 2. 2: Classification of membrane by pore size

Membrane process	**Pore size (µm)**	**Uses**
Microfiltration (MF)	0.1 -3	Suspended solids, turbidity reduction.
Ultrafiltration (UF)	0.01 -0.1	Viruses and colloidal organic removal.
Nanofiltration (NF)	0.001-0.01	Sugar, Salt.
Reverse Osmosis (RO)	< 0.001	Trace organism

The process of pressure driven requires that the feed water is driven through the membrane by the pressure difference that exists across the membrane. The water that permeates through the membrane is referred to as a permeate while the remaining water containing all the rejected species is known as retentate (Peters 2010).

2.5.2 Membrane Materials

The first membrane materials were reported in the late 1950s by Reid and Breton (1959) and also by Loeb and Sourirajan (1963). Numerous membrane materials have been developed since then to improve on the performance and capacity of the existing ones. Membrane materials are typically classified as biological and synthetic (Ladewig et al., 2013; Idris et al., 200) Synthetic is divided into organic membranes (e.g. polymeric and liquid membrane) and inorganic (e.g. ceramic or metal membranes) (Ahmad et al., 2013). Polymer and ceramics are the most important materials in synthetic membranes, though they can be made from different materials. Organic materials are either cellulose-based or made of modified organic polymers (Ladewig et al., 2013). Structural classification is important because it is the structure that determines the separation mechanism and application. The membranes used for wastewater treatment are typically organic materials. Organic (polymeric) membranes are mainly used for commercial application and research development due to their superficial processing into viable membrane structure and multiple polymer availability as well as ability to fabricate novel polymer structures (Peyravi et al., 2012). The membrane used for the treatment of water and wastewater consists of a thin skin having thickness of about 0.20 to 0.25 μm supported by a more porous structure of about 100 μm in thickness (Tchobanoglous et al., 2003). Furthermore, membranes can be categorized into two major groups based on the nature of the materials namely organic and inorganic membrane.

2.5.2.1 Polymeric membranes

Polymer membrane is generally accepted in water treatment industries. Polymeric membrane has economic competitiveness, reasonable processability, and scalability (Kosinov et al., 2016). Most polymeric membranes are made for commercial use and this could be attributed to advantages such as easy fabrication and low cost. They are used in the preparation of MF and UF membranes. The membranes that fall under this category include Poly-vinylidene fluoride (PVDF), Polyacrylonitrile (PAN), Polysulphone (PSF), Polyacrylonitrile (PAN), Cellulose acetate and

Polyethersulphone (PES). The polymeric membrane has limitations which include plasticization and permeability/selectivity (Zhao et al.,2013). They also possess poor chemical properties leading to hydrophobicity and fouling. Improving the chemical properties of polymer membrane has attracted the interest of several researchers because of its costly application in water purification, fuel cell, pervaporation and many separation processes (Hilal et al., 2017). Other factors are the durability and the mechanical strength of the membrane (Deng and Hagg, 2015). Among all those materials, CA, PSF and PES are the most commonly used polymers for UF membranes (Idris and Ahmed, 2007). In this research, PES was used as the backbone of the membrane investigated for water treatment.

PES is a type of polymeric membrane that has widely been used for separation and purification purposes. It is a thermoplastic polymer and is typically amorphous in nature (Kumar et al., 2006; Nair et al., 2001). PES membranes show a high glass transition temperature, good chemical resistance (inertness) to aliphatic hydrocarbons, thermal resistance, physical properties and easy to fabricate in a wide variety of modules and configurations as well as wide range of pore size available from UF and MF from 10 Å to 0.2 μm (Ladewig and Al-Shaeli 2017). It is also increasingly used in many industrial processes such as biomedical fields for blood purification, pharmaceuticals and in water purification (Barzin et al., 2004; Samtleben et al., 2003; Baker, 2012; Bolong et al., 2009). However, the hydrophobic nature of PES membrane has resulted in low membrane flux and fouling thereby affecting its application in water treatment (Luo et al., 2011). This hydrophobic property also prevents spontaneous wetting with aqueous media. Therefore treating PES membrane with a hydrophlic agent will be required (Nunes and Peinemann 2011). There has been some interest in improving low-pressure membrane anti-fouling performance by incorporating nanoparticles into the membranes. Figure 2.5 shows the primary structure of PES. The structure shows that the Polyethersulphone structure is made up of Sulphur Dioxide (SO_2) aromatic rings and Methyl groups (CH_3).

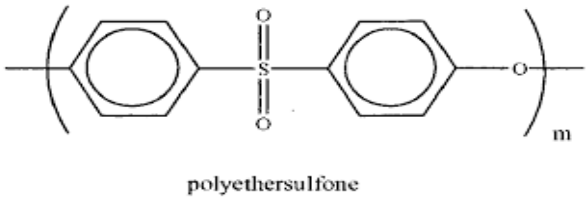


Figure 2. 5: Primary structure of PES (Adapted from Idris et al., 2011).

2.5.2.2 Inorganic Membranes

The inorganic membrane has outstanding thermal and chemical stability when compared to polymeric membranes. It also has higher antifouling property due to hydrophilicity of the inorganic materials (Gallucci et al., 2011). However, the inorganic membrane has some setbacks despite their wide use and application. They are also useful in UF and MF and can withstand high-pressure operations (Kosinov et al., 2016). The inorganic membrane can be made from glass, metal or ceramics that include materials such as silica, zirconia, aluminium carbon, zeolite particles and nanomaterials (Wang and Peng, 2010). Inorganic membranes are highly selective but high cost and reproducibility are a major setback to this membrane.

Ceramic membranes are used in separation technology. They have outstanding properties in separation techniques such as higher chemical, thermal and mechanical stability when compared to the organic membrane (Belfer et al., 2000). The stability of this membrane makes UF and MU membrane suitable in different field of industries such as food, biotechnology and pharmaceutical (Baker, 2004). The membranes are made from aluminium, titanium or silica oxides. Advantage of the ceramic membrane is the ability to withstand high-temperature conditions which polymeric membranes could not attain (Belfer et al., 2000).

Metal membrane especially palladium have been used for hydrogen separation for a long period. Palladium and its alloy is the main material for metallic membrane (Gallucci et al., 2011). The metallic membrane can be acquired through the sintering

of metal powder such as molybdenum or stainless steel or tungsten. The merit of this metallic membrane lies in its mechanical strength and permeating flux (Basile and Gallucci, 2011) while its setback includes high cost due to palladium which is not naturally available and surface poisoning that is more than thin metal membranes. Many researchers have reported about the impact of poisoning on the metallic membrane such as H_2S /CO-based membrane as a major setback (Ladewig et al., 2013).

Different research has been carried out on the zeolite membrane for the past 25 years. Zeolite is a porous crystalline, aluminosilicates of alkaline or alkali earth metals; either on micro, meso, or nanoscale (Aoki et al., 2000). They are porous crystalline aluminosilicates with a uniform pores structure and a controlled channel diameter; this property makes them ideal for membrane materials (Michalkiewicz and Koren, 2015). Zeolite membranes have been used in the last decade not only as a separative membrane but also in a catalytic membrane reactor, chemical reactors, a chemical sensor, open electronic devices, electrodes and insulating materials (Jana et al., 2012). They are also known as molecular sieves that separate the large pore size molecules shape and adsorption properties (Bernardo et al., 2009; Chiang and Chao, 2001). Zeolite membranes are used in many applications such as water separation, gas separation, alcohol separation and pervaporation (Panayotova and Velikov 2002; Kuleyin, 2007; Liu et al., 2014). They possess high thermal and chemical resistance over the polymeric membrane (Khajavi et al., 2007). However, they have some drawbacks that hinder their application. Some of these drawbacks include ease of formation of zeolite pores which are larger than the normal pores. The major setback of inorganic membranes when compared to the polymeric membrane is their ability to stand high chemical, thermal and mechanical stability and wide tolerance to pH (Belfer et al., 2000; Basile and Gallucci, 2011).

To improve on the separation performance of the organic and inorganic membrane, the incorporation of inorganic materials into polymeric membrane arises and this produces mixed matrix membranes.

2.5.2.3 Mixed Matrix Membrane

Mixed Matrix Membranes (MMMs) are the homogeneous incorporation of inorganic fillers or nanoparticles within the polymer matrix (Hilal et al., 2017). MMM are composite membranes having inorganic particle crystals impregnated within the matrix of the polymer membranes (Daramola et al., 2015). The inorganic material present within the polymers enhances thermal stability, separation performance, permeability, high surface area and mechanical strength of the polymeric membranes as seen in Figure 2.6. The advantage of incorporating inorganic fillers or nanoparticles is the ability of the nanoparticles to change the morphological features and structure of the membrane (Hilal et al., 2017; Padaki et al., 2015). One of the major setbacks in MMMs is the ability of the nanoparticles to disperse uniformly in the membrane matrix as seen in Figure 2.6 (Davey et al., 2016).

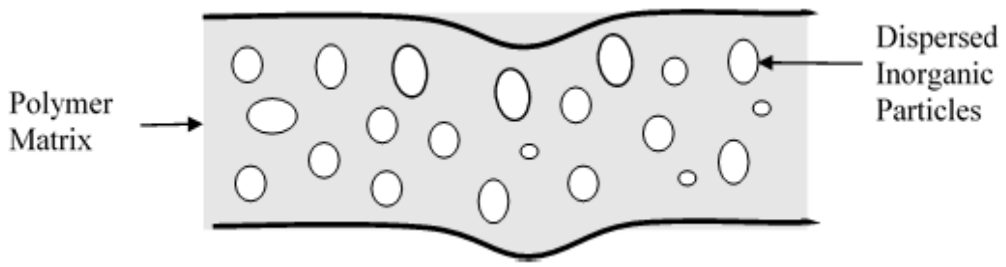


Figure 2.6: Dispersive Mixed Matrix Membrane (Davey et al., 2016)

MMM came to be as a result of the need to overcome the limitations of the inorganic membranes. Vu et a (2003) reported some factors that can hinder high yield of MMM during incorporation of nanomaterial into the membrane these include chemical structure of the inorganic fillers and the surface chemistry. The inherent nature of hydrophobicity of PES has resulted in research to make PES membranes that is more hydrophilic. This can be done by both physical and chemical modification according to literature. Pieracci et al (2002) reported the ultra-irradiation as a method of increasing membrane hydrophilicity. Kim et al (1999) reported graft polymerisation modification as another means of improving hydrophilicity. Using

blending/incorporation of inorganic fillers or nanoparticles as a means of increasing hydrophilicity was reported (Daramola et al., 2015; Jing et al., 2007; Nermen et al., 2009; Padaki et al., 2015). Among all these methods, incorporation with inorganic fillers or nanoparticles has received greater attention from researchers as a result of its availability, thermal stability, and hydrophilicity applicable in water treatment (Luo et al., 2005).

Several studies have been conducted on the MMM . Yuliwati et al (2012) carried out a study on the effect of conditions in submerged UF for oily wastewater treatment using a MMM. The PVDF ultrafiltration membranes were prepared through pore-forming and Lithium Chloride Monohydrate ($LiCl.H_2O$) and Titanium Dioxide (TiO_2) nanoparticles were used as a pore-forming and hydrophilic additives, respectively to enhance the mechanical properties (Luo et al., 2011; Padaki et al., 2015). From literature, many inorganic particles such as TiO_2, Al_2O_3, sodalite, and SiO_2 have been proposed to intensify the mechanical properties of the PES membrane (Arthanareeswaran, et al., 2008). The advantages of MMM is that the desirable mechanical properties; economical propensity of the polymer and the inorganic disperse phases possess unique structure and good surface area but there are some factors that hinder obtaining high quality MMM. These include: the nature of inorganic fillers, surface chemistry and chemical structure (Vu et al., 2003).

2.6 Membrane preparation methods

Production of a polymeric membrane is a complicated process which involves many steps namely; Material selection, drying process, doping solution preparation, casting or spinning, a phase inversion process and post-treatment (Mohanty and Purkait, 2012). Among the various steps mentioned, the dope dissolution process is expensive and time-consuming especially when the membrane is prepared from some glassy amorphous polymers such as PVDF, PSF, PES, PA, PI and Polyether ketones (PEEK) (Gordano and Buonomenna, 2012). In this study, phase inversion method was used as a method for the preparation of novel Fe-NPs /PES composite membrane.

2.6.1 Phase inversion method

Phase inversion method is an exchange process between liquid and solid phase, solvent, and nonsolvent (Scott, 2014; Mohanty and Purkait, 2011). It is used to prepare asymmetric membrane and most of the polymeric membranes of desired symmetric, composition and morphology (Gordano and Buonomenna, 2012). The polymeric membrane forms due to the solidification or precipitation of de-mixing of the solvent and nonsolvent upon the immersion of the polymer solution into the coagulation bath. Water is commonly used as nonsolvent. However, another desirable organic solvent can also be used (Wang et al., 2006). Phase inversion method can be classified as a dry phase inversion, wet phase inversion, and dry/wet phase inversion method.

- Dry phase inversion method occurs when the solution is cast onto the glass plate (using a casting knife for pre-set thickness) or suitable substrate and left to vaporize. Solvent and nonsolvent solutions are vaporised at the same time.
- Wet phase inversion method involves soaking of the membrane into the nonsolvent medium after casting. Here, phase separation occurs because of the reaction between solvent and nonsolvent mixture. This process is widely used to produce asymmetric membrane for UF, MF, RO and gas permeation.
- Dry/ wet inversion method occurs when the membranes are left to vaporize after casting before immersion into the nonsolvent medium.

2.6.2 Nanomaterials for membrane modification

A lot of research has been carried out in recent years on the use of nanomaterials as one of the most advanced processes for wastewater treatment. These nanomaterials are classified into three main categories based on their nature and potential. These include nano-adsorbents, nano-catalysts, and nanomembrane (Padaki et al., 2015b, Anjum et al., 2016). In nano-adsorption, the adsorbent can be produced from atoms of the same elements that are chemically active with high adsorption capacity on the surface areas of the nanomaterials, these materials include silica, activated charcoal (Kyzas et al., 2016; El Saliby et al., 2013). For nano-catalysis, metal oxides and

semiconductors are employed with different types of nano-catalysts like Fenton and electrocatalysts for pollutant decomposition in wastewater (Dutta et al., 2014; Kurian and Nair, 2015). In nano-membrane technology, this system can be produced from nanomaterials such as nano metal particles, carbon nanotubes, and non-metal particles among others. The system uses pressure-driven mechanism for water and wastewater treatment (El Saliby et al., 2008; Rao et al., 2015). The present study focused on the nano-membrane using nano metal particles (iron nanoparticles) for MMM for volatile organic compound (BTEX) removal.

Iron-based nanoparticles (Fe-NPs) have been successfully prepared using plant extract (Kharissova et al., 2013). The natural occurrence of iron and its simple synthesis process make ferric oxide a low-cost material (Huber, 2005). Finely divided iron has been studied for many years. The theory describing magnetic Fe-NPs was fully formed by the early 1960s and has been confirmed by experiment (Huber, 2005).

Over the years, the chemical method of production of nanoparticles using sodium borohydride as a reducing agent has played an important role in the various synthesis of nanoparticles (NPs) (Sun et al., 2016). The disadvantage of this chemical synthesis includes a toxic agent, high cost, energy dissipation and adverse effect on environment. Bio-synthesis of NPs has been acquiring more attention over the chemical synthesis due to its relative advantages (see Figure 2.7). Bio- synthesis are gaining attention in the synthesis of nanomaterial in nanotechnology (Njaqi et al., 2011; Talal et al., 2011). The greatest weakness of iron is its reactivity, especially with respect to water and oxygen. Plant extract was considered for the synthesis of nanoparticles through a biosynthetic method that requires inherent reducing agents and primarily polyphenol (Njaqi et al., 2011; Talal et al., 2011). Xu et al (2011) reported that the final product of Fe-NPs obtained through bio-synthesis contain zero-valent iron (nZVI) and also other nanoparticles (Fe_xO_y and FeOOH or iron(III) hydroxide ($Fe(OH)_3$), in varying degree. It has also been reported that agglomeration

of Fe-NPs tends to be spontaneous under normal conditions as a result of particle interaction (Markova et al., 2014).

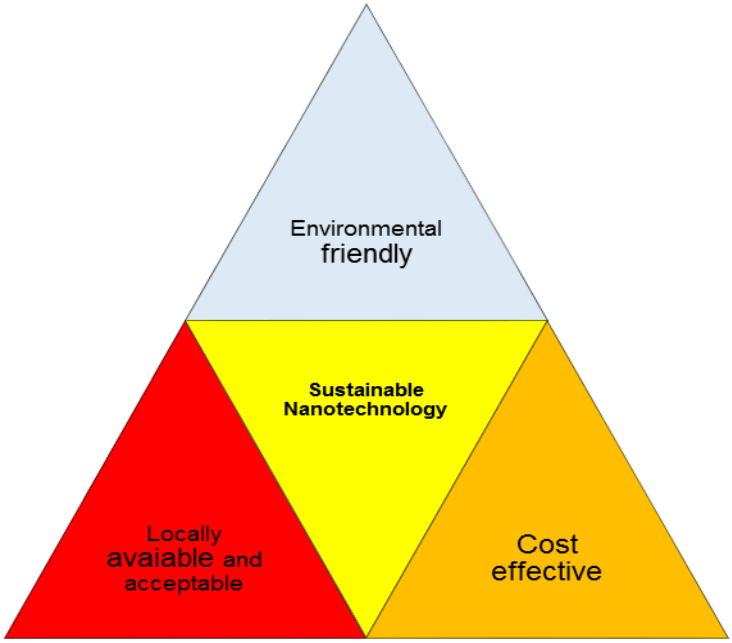


Figure 2.7. Sustainable green nanotechnology (Adapted from Saif et al., 2016)

In this study, the bio-synthesis method was adopted by using plant extract of pomegranate leave to synthesis Fe-NPs. This method is cheap, locally available and environmental friendly (Saif et al., 2016). There are some nanoparticles that have been used to enhance membrane operations and these include: Aluminum oxide (Al_2O_3), silicon oxide (SiO_2) and titaum oxide (TiO_2).

In recent years, material and technology sustainability have come to the highest level of general development. In any society, where nanotechnology is being used to transform the way it develops and dissipates materials, the technology will definitely change the flow, recovery and recycling of valuable resources. The change will be mostly on the use of energy and clean water accessibility (Karn et al., 2003). In the next 30 years, nanotechnology will be penetrating and incorporated into all aspects of daily life (Karn et al., 2003). Nanoscale materials are set of substances where at least

one dimension is approximately less than 100 nanometers. The surface area to volume ratio of a nanoscale is large; this property is responsible for the widespread use of nanomaterials in industries (Saif et al., 2016; Amin et al., 2014). The green synthesis of nanoparticles for sustainable green nanotechnology in the wastewater treatment application is always cost-effective, locally available and socially acceptable and eco-friendly. These nanomaterials have the potential to decontaminate surface water, industrial effluent, groundwater and drinking water (Gupta et al.,2015; Brumfiel, 2007; Karn et al., 2003). Karn et al (2003) reported the application of nanotechnology in water treatment; the ability of application of nanoparticles to remove smallest contaminants from water and to reduce pollutant from the environment. Nanoparticles have the capacity to pierce through and thus can treat water/wastewater and this is not applicable to conventional water treatment technology (Prachi et al., 2013).

2.7 Nanocomposite membranes

Membrane filtration technology fabricated with nanomaterials is one of the most effective methods in wastewater treatment among the current advanced technology (Zhang et al., 2015). The system is used for effective removal of heavy metals, monoaromatic compounds, dyes and other contaminants (Jie et al., 2015). Nanomaterials in novel membrane play an important role in the chemical decomposition of organic foulant separation beside particles separation (Liang et al., 2010). This type of membrane is composed of one-dimensional nanomaterials (comprising organic and inorganic materials) such as nanotubes, nanofibers, and nanoribbons (Liu et al.,2014). The advantages of this treatment technique include removal efficiency, economical and simple to design (Guo et al., 2015; Zhang et al., 2015).

2.7.1 Thin-film composite membrane

A lot of studies have been done on a thin-film composite (TFC) membrane since the 1970s and it has been commercially applied for large-scale separation (Yave et al., 2010a). TFC is composed of three well-defined layers; an ultra-thin top layer,

asymmetric porous sub-layer and a reinforcing non-woven fabric its thickness is in microns (Dalwani, 2011). Some of the methods used in developing TFC are spin coating, dip-coating and interfacial polymerisation (Peyravi et al., 2012). The porous support layer is prepared by a phase inversion method while the active barrier layer is deposited onto the support by the interfacial polymerisation method (Wu, 2012). TFC are mainly used in separation units, optical instrument coating of the membrane and in another field of science and technology such as fuel cell (Daramola et al., 2012; Yave et al., 2010)

TFC membrane has an advantage over asymmetric membrane because of its distinctive layer but asymmetric membrane consists of one homogeneous layer and prepared by single-step phase inversion method (Jeong et al., 2007). This is as a result of the polymers used for the upper selective layer and support layer which can be in dependably selected and optimised in the view to achieving desired composite membrane properties (Jeong et al., 2007a). The results allow the active layer to be optimised separately to obtain a good water permeability and solute rejection. Xu et al. (2011) reported TFC membranes as the most popular choice for RO in water desalination.

Advancement in membrane technology has brought about the use of various nanomaterials for TFC membrane modification to reduce membrane fouling and to obtain a composite membrane with enhanced performance (Anjum et al 2016; Arthanareeswaran et al., 2008).

2.7.2 PES membrane modification with iron nanoparticle for BTEX removal

More effective approach for treating and remediating water for human consumption and other uses are needed. Removing volatile organic compounds from wastewater is a significant challenge. The use of PES membrane modified with iron nanoparticles as MMM is promising and it is presented in this study.

The aim of water treatment is to remove an unwanted component from water for safe use and the membrane provides a physical barrier for such a component based on

their size thereby giving room for unconventional water sources (Baker 2004). Benzene, toluene, ethylbenzene and xylene (BTEX) popularly referred to as BTEX, are monoaromatic hydrocarbons, found in groundwater crest and other water resources due to disposal of effluent from industrial contaminated site and incidents such as leakages of petroleum from pipelines and oil spills (Alberici et al., 2002; Castillo et al., 1998; Costa et al., 2012). These organic compounds are volatile in nature and highly soluble in water; they constitute one of the major pollution problems in the soil and groundwater. They have negative impact on human health when ingested such as nervous system disorder, cancer, they also affect kidney and liver. The Environmental protection Agency classified them as harmful and potential carcinogens under Safe Water Drinking Act (US EPA, 2011; Andersen et al., 2013). They may also have a unforeseen effects on the development of a fetus in the womb (US EPA, 2011; Aguilera et al., 2010). According to Leusch and Bartkow (2010), BTEX compounds have been found in groundwater, surface water and even in drinking water. It has been reported that the wide industrial usage of these compounds has resulted in their persistent presence in the effluents of industries such as rubber and paint industries, petrochemical industries, etc. (Leusch and Bartkow, 2010; Costa et al., 2012). BTEX have been neglected in municipal wastewater despite their negative impact on human health (Fayemiwo et al., 2017).

BTEX compounds are monoaromatic hydrocarbons with 6-carbon benzene ring as their main structure as seen in Figure 2.8. They exist in petroleum products such as refineries, gasoline stations and other contaminated sites like coal hazardous effluent site, paints, rubber and ink industries (Leusch and Bartkow, 2010). These organic compounds are volatile in nature and they constitute one of the major pollution problems in the soil and groundwater. These compounds account for as much as 90 % of the gasoline component found in the water-soluble fraction (Saeed and Al-Mutairi, 1999).

In recent years, BTEX compounds are receiving much awareness as a result of hazardous threats posed to groundwater and contaminated sites (Council et al., 2003).

When compared with other poly-aromatic peers, their solubility in water and low octanol-water partition coefficient (K_{oc}) values favour hydrophilicity dissolution though, they are hydrophobic in nature. These compounds co-exist with one another or with methyl tert-butyl ether (MTBE). Table 2.4 details the physical and chemical properties of BTEX compound as adapted El-Naas et al. (2014). However, the structure of the compounds, its molecular weight, and density affect separation during membrane filtration (El-Naas et al. (2014)

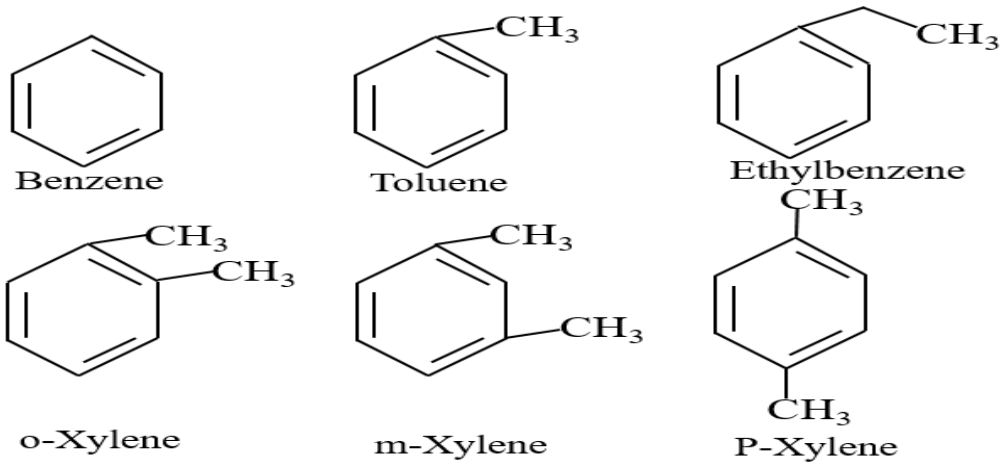


Figure 2. 8: Structure of BTEX compounds (Adapted from El-Naas et.al., 2014).

Table 2. 3: Physical and chemical properties of BTEX compounds (Adapted from El-Naas et.al 2014)

Parameters	**Benzene**	**Toluene**	**Ethylbenzene**	**Xylenes**
Formula	C_6H_6	$C_6H_5CH_3$	$C_6H_5CH_2CH_3$	$C_6H_4(CH_3)_2$
Molar weight	78.12	92.15	106.18	106.18
Density (g/mL)	0.8765	0.8669	0.8670	0.8685
Solubility (mg/ L)	1780	500	150	150
Boiling point (°C)	80.1	110.6	136	138.3°C-144.4
Melting point (°C)	5.5			
Soil-water partitioning co-efficient (K_{oc})	97	242	622	570
Vapour pressure (Nm^{-2})				
A	17.1	6.63	2.86	2.48
B	0.0547	0473	0.0445	0.0442

BTEX compounds are the major source of environmental pollution in ground water; they are frequently found in the hazardous waste site. They are extensively used in many chemical, industrial and commercial processes more than any other solvent (WHO,1993). Its presence in groundwater creates hazard to public health the

environment and also to aquatic bodies (Council et al., 2003; Chi-Hui et al., 2010; Leusch and Bartkow 2010). From the information collected from US Agency for Toxic Substances and Disease Registry (ATSDR) and the World Health Organization, the concentration of BTEX compounds in different water sources are reported in Table 2.4.

Table 2. 4: Concentration of BTEX compound in water (part per billion (ppb))

Water Source	**Benzene**	**Toluene**	**Ethylbenzene**	**Xylene**
Surface water	<0.1 – 2.1	<1 – 15	<0.1 – 1.8	<0.1 – 1.2
Contaminated Surface water	Up to 100	NA	Up to 15	Up to 32
Groundwater	<0.1 – 1.8	<1 – 100	<0.1 – 1.1	<0.1 – 0.5
Contaminated Groundwater	Up to 330	Up to 3500	Up to 2000	Up to 1340
Drinking water	<0.1 – 5	<1 – 27	<1 – 10	<0.1 – 12

NA: Not applicable. All data in this table from ATSDR 2000, 2007; WHO 2008.

It has been reported that the intake of benzene, toluene, ethylbenzene and xylene compounds by human is 10, 43, 20 and 24 micrograms (µg) per day respectively (Leusch and Bartkow, 2010). According to US EPA National Primary Drinking Water Regulations Maximum Contaminant Levels for BTEX in drinking water are 0.005, 1.0, 0.7, and 10.0 mg l^{-1}, respectively (Liang et al., 2008). According to Australian Drinking Water Guidelines (ADWG), the concentration of benzene in drinking water should not exceed 1 µg/L and the other compounds are allowed in the range of 300-800 µg/L in water (NHMRC, 2011; Leusch and Bartkow, 2010). South Africa natural water system has a higher concentration of natural organic matter beyond 10 ppm (Water SA, 2008). Maximum contaminant level (MCL) of benzene is

5 ppb. Chronic exposure to low levels of benzene can lead to anaemia, a decrease in blood platelets, and may increase one's risk of getting cancer (US EPA, 2013). Other effect on exposure of toluene causes skin and eye irritation, electrolyte imbalances and respiratory depression, while ethylbenzene exposure might be associated with hearing loss and neuro behavioural function impairment; xylene in high concentrations acts as narcotic, inducing neuropsychological and neurophysiological dysfunction. Occupational exposure has been associated with anemia, leukopenia, chest pain and ECG abnormalities (Langman, 1994; Schupp et al., 2005; ATSDR 2000).

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CHAPTER 3

EXPERIMENTAL PROCEDURES

This chapter discusses the experimental procedures and materials employed in this study. These include the synthesis and characterization techniques of iron nanoparticles from pomegranate leaf, the fabrication of nanocomposite membrane (Fe-NPs/ PES) membrane. Also, a detailed description of the method used in the performance evaluation of the membrane has been presented.

3.1. Material and equipment used for the study

The pure PES (Mw=58,000 g/mol with density=1000g); solvent (N, N-dimethylacetamide, DMAC 97 %); ammonium ferrous sulphate $(NH_4FeSO_4)_2.6H_2O$); ammonium ferric sulphate $(NH_4SO_4)_2.12H_2O$) and sodium hydroxide (NaOH, 99 %) were purchased from Sigma-Aldrich (Pty), South Africa. De-ionized water and the BTEX-contaminated water used were prepared was prepared in the laboratory. All reagents used in this study were purchased from Sigma-Aldrich (Pty), South Africa. They were used as supplied, without further purification. The Nitrogen gas was supplied from AFROX South Africa. A casting blade was used for membrane fabrication as shown in Figure 3.1.

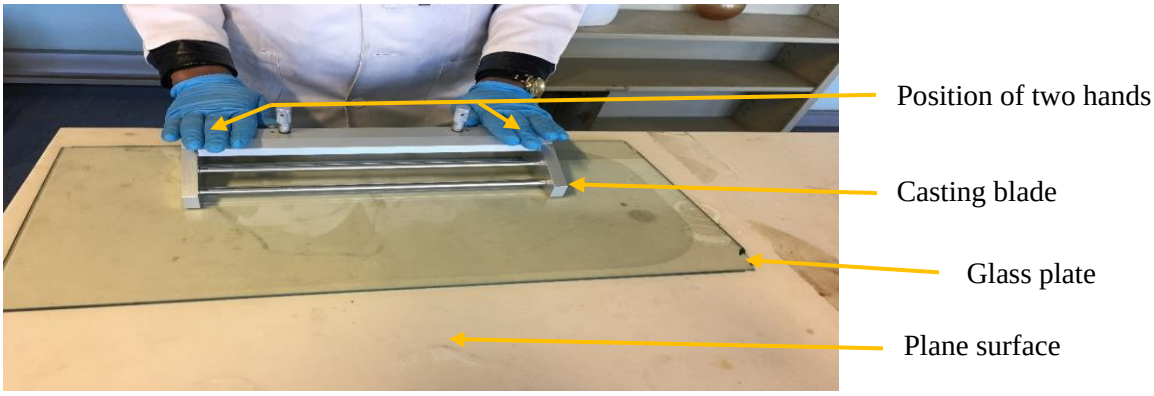


Figure 3.1: Membrane casting blade

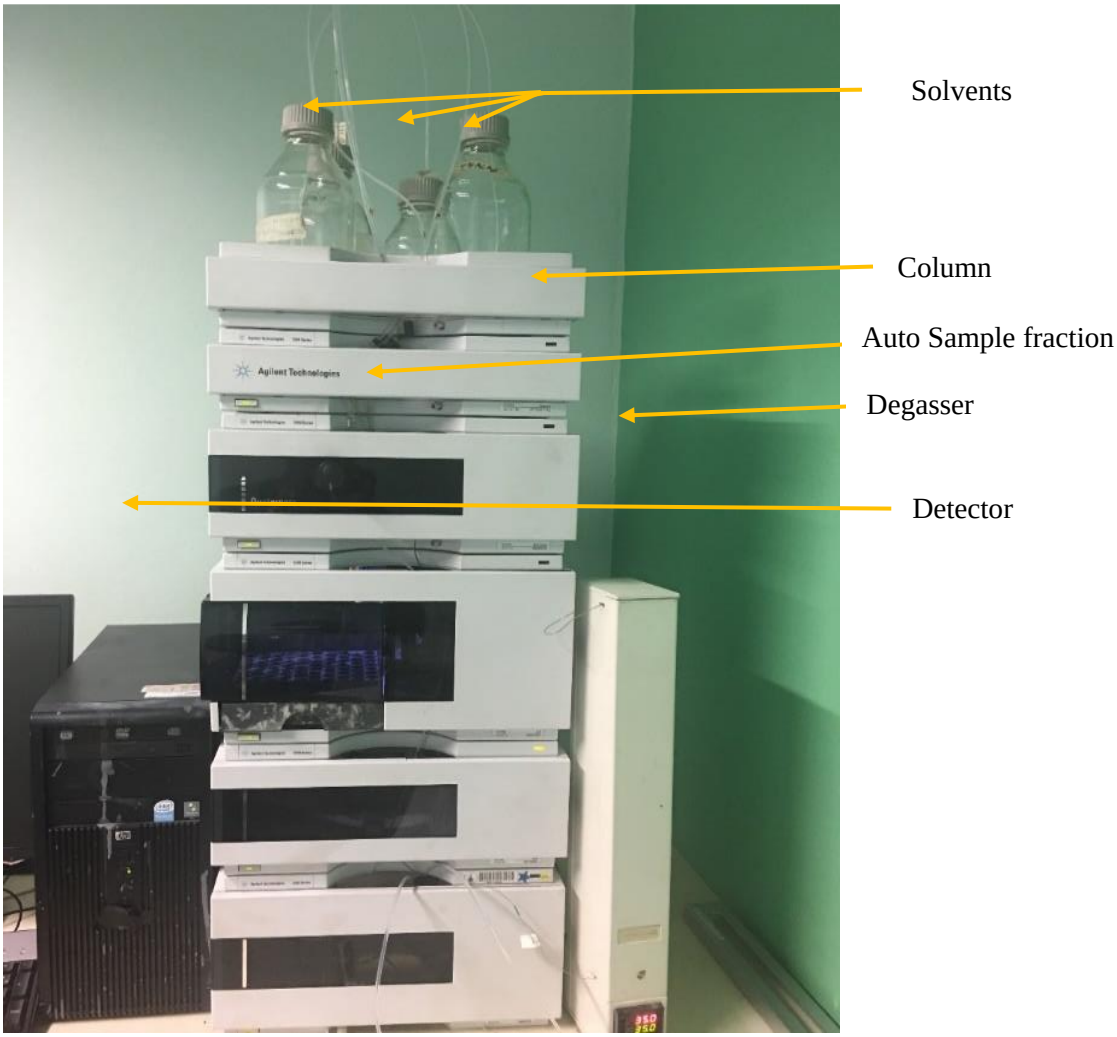


Figure 3. 2: HPLC used for the analysis

3.2 Methodology

The procedures used in this work were divided into four main stages as shown in Figure 3.3.

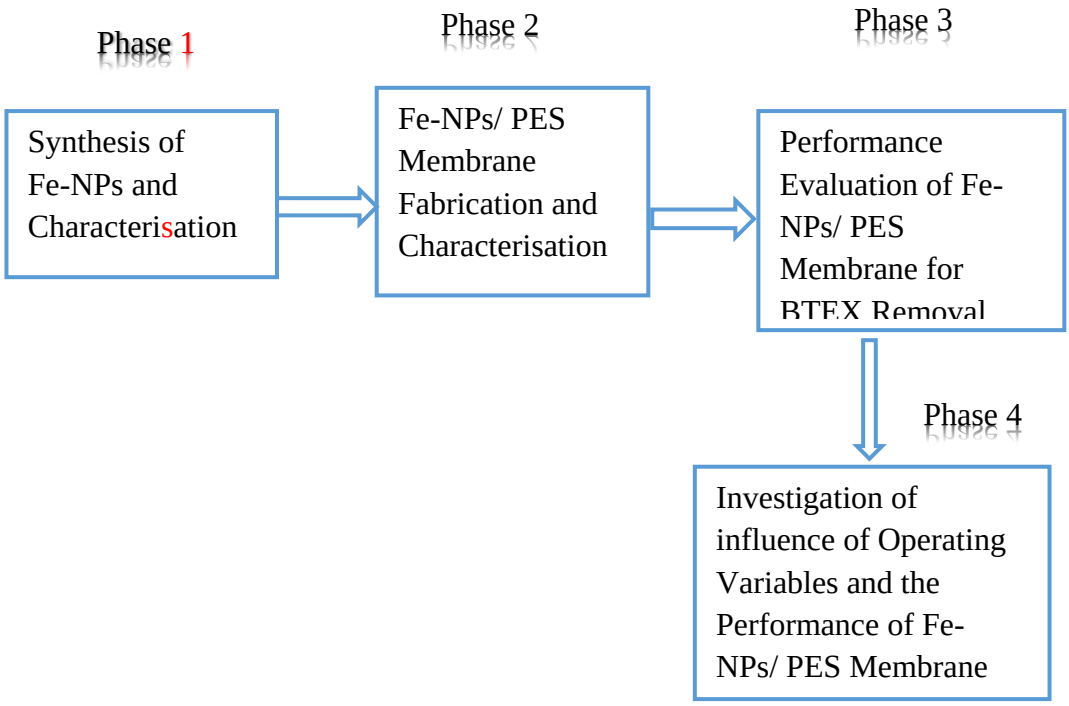


Figure 3.3: Flow diagram of the work phases

3.2.1. Iron nanoparticles

Metallic or zero valent iron (Fe^0) is a reducing agent that can readily react with dissolved oxygen and water to some extent:

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \quad (3.1)$$

$$Fe^0_{(s)} + 2H_2O_{(aq)} \rightarrow Fe^{2+}(aq) + H_{2\,(g)} + 2OH^-_{(aq)} \quad (3.2)$$

Equation 3.1 and 3.2 represents corrosion/ electrochemical reactions by which iron is oxidized from oxygen and water. Iron is oxidised when exposed to oxygen and water (Gillham and Hannesin 1994). The corrosion reaction can be inhibited or accelerated

by manipulating the solution chemistry. Iron corrosion chemistry has been put into productive use in the treatment of hazardous and toxic chemical (Gillham and Hannesin, 1994). Advantages of nanoscale iron particles include an effective transformation of a large variety of environmental contamination. Some iron oxide and their composites have been proved to be effective materials for dye degradation by adsorption and also in water treatment (Zhang, 2003) due to their high surface area.

3.2.2. Preparation of Pomegranate Leaves

In the present study, natural abundant Pomegranate leaves were used for the biosynthesis synthesis of iron nanoparticles. Pomegranate leaves (*Punica granatum*) are found growing in front of the School of Chemical and Metallurgical Engineering Richard Ward's building, University of the Witwatersrand, Johannesburg, South Africa. It is also cultivated throughout South Africa. Its leaves are useful in the treatment of medical conditions such as insomnia, skin problem and digestive problems (Prasad et al., 2017). However, pomegranate leave is reported as a capping and reducing agent in this study. The pomegranate leaves are collected and washed to remove dust particles and were dried at room temperature for 48 hours. It was ground into powder with Kenwood blender as shown in Figure 3.4

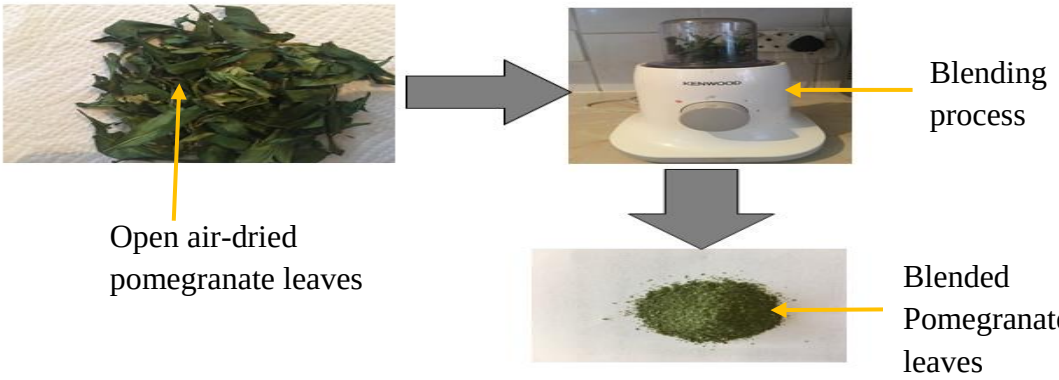


Figure 3. 4: Flow diagram of pomegranate leaves preparation

3.2.3. Synthesis of Iron nanoparticles

In this research, the bio-synthesis which is cost-effective, sustainable and environmentally friendly was employed (Saif et al., 2016) as shown in Figure 3.5

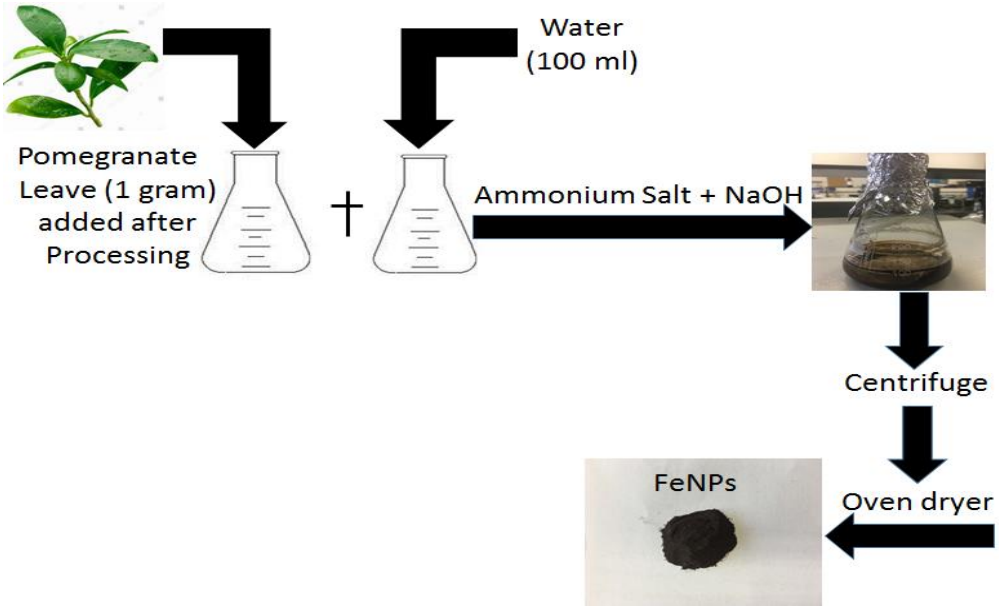


Figure 3.5: Experimental procedure for Fe-NPs synthesis

3.2.4. Characterizations of iron nanoparticles

Pomegranate leave contains polyphenol-rich extract (Prasad et al, 2017). Iron (Fe) especially iron oxide can easily absorb hydroxyl groups (-OH) to become hydrophilic (Zhang et al., 2010). It also possesses high surface area because of its crystal structure (Prasad et al, 2017). A scanning electron microscopy (SEM) was used to characterise the morphology of the synthesised nanoparticles. The elemental composition of the synthesized material was identified by using the energy dispersive X-ray spectroscopy (EDS). The functional group was identified using Fourier transform infrared spectrometer (FTIR) (Perkin Elmer spectrum Two).

3.2.5. Membrane fabrication

Membrane fabrication was done by phase inversion method to obtain a homogeneous mixture of each membrane with Fe-NPs (Prasad et al, 2017; Scott, 1995). This was achieved by measuring PES (20 wt.%) dissolved in N-N dimethylacetamide (80 wt.%) at the ratio of 1:4 and keeping the weight of the PES and solvent constant while varying the weight of the Fe-NPs (Daramola et al., 2015; Arthanareeswaran et al., 2008). The mixture of Fe- NPs and the solvent was first ultrasonicated before adding PES and the solution was stirred on a magnetic stirrer for 24 h (Daramola et al., 2015; Li et al., 2009). Consequently, the percentage weight of the synthesized FeNPs was measured accordingly to be: 5 wt.%, 10 wt. %, 15 wt.% and 20 wt.% using equation 3.3:

$$\frac{NPs\ amount\ (g)}{PES\ (g)+NPs} \times 100\% \qquad (3.3)$$

The component of the casting solution was PES polymer as the base membrane material, dimethylacetamide (DMAC) and FeNPs as the hydrophilic modifier (Table 3.1). The homogenous mixture of the fabricated membrane was hand cast on a glass plate. The thickness of the membrane was controlled by varying the micrometre screw gauge by the sides of the casting blade. The solution was cast to the thickness of 100 µm on a clean glass plate using casting knife. After casting, the glass plate was immediately immersed in the deionized water bath to coagulate the solution to form the composite membrane. Pure PES with 0 % Fe-NPs was also fabricated for comparison. All the fabricated membranes were soaked in deionised water for 24 hours at room temperature to remove the remaining solvent from the membrane. Thereafter, the membrane was air-dried. The steps involved membrane fabrication is shown in Figure 3.6.

Table 3.1 Composition of a casting solution

Membrane	DMAC (ml)	PES (g)	FeNPs (wt.%)
M1	20	5	0.00
M2	20	5	0.26
M3	20	5	0.55
M4	20	5	0.88
M5	20	5	1.00

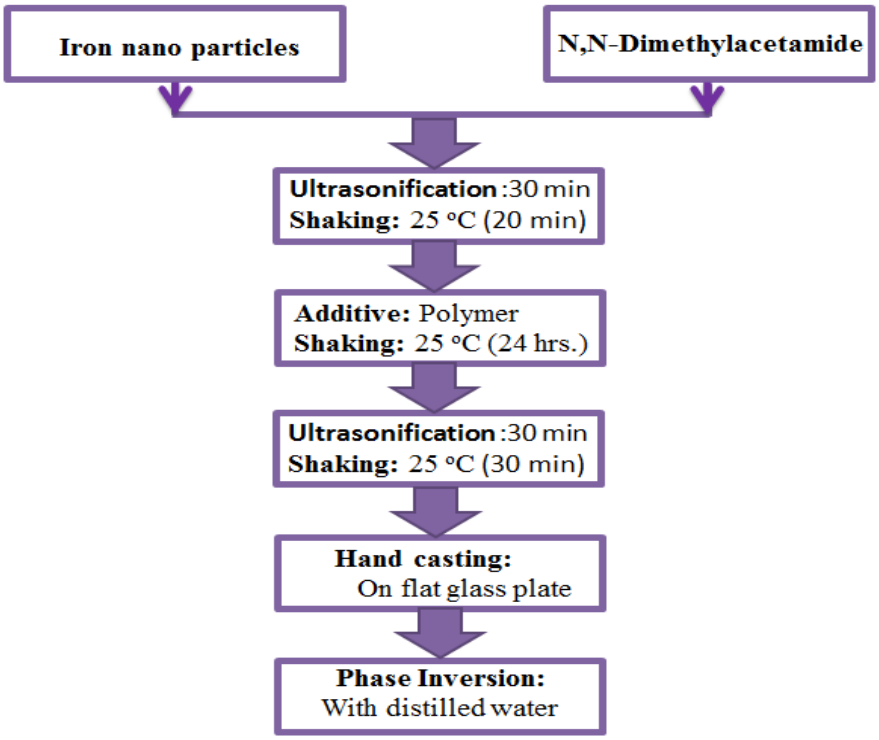


Figure 3.6: Experimental procedure for the fabrication of Fe-NPs / PES mix matrix membrane.

3.2.6. Membrane characterisation

Scanning electron microscopy (SEM), atomic force microscopy (AFM), Thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectrometer, contact angle, mechanical strength were the techniques used to characterise the nanocomposite membrane.

3.2.6.1. Scanning electron microscopy (SEM)

Membrane morphology plays an important role in separation performance by influencing polymer-solvent interaction, the solution viscosity and rate of inter-diffusion of the membrane (Alam et al., 2017). SEM has great magnification that focuses on the beams of energetic electrons to get a visual image of a material (McMullan, 1995). Iron nanoparticles and nanocomposite membrane were examined with SEM to confirm that Fe-NPs were really incorporated within the matrix of the membrane. A portion of the membrane was cut and immersed in liquid nitrogen for the cross-section and another part was cut for the surface and both were coated with carbon and gold-palladium and subjected to the SEM for observation. A Sigma Zeiss model of the SEM located in the School of Chemical and Metallurgical Engineering was used to determine the morphology of the membrane.

3.2.6.2. Thermogravimetric analysis (TGA)

The thermal stability was evaluated using thermogravimetric analysis instrument (Model-SDT Q 600) which is located at the Coal Laboratory in the School of Chemical and Metallurgical Engineering. The temperature range used was from 20 ^{o}C to700 ^{o}C with a heating rate of 20 ^{o}C/min under Nitrogen atmosphere (20 ml/min) to prevent thermo-oxidative degradation. Most organic materials are completely oxidised to volatile species in air (inert atmosphere). Polymeric membrane is thermally stable only up to a certain temperature range of 0 to 160 ^{o}C, as a result of the organic macromolecules within the polymer matrix as well as the molecular weight of the organic molecule (Ravikumar, 2012).

3.2.6.3. Fourier Transform Infrared Spectroscopy (FTIR)

The hydrophilic functional group of the membrane was evaluated using Fourier transform infrared (FTIR). The composite membrane was placed on the diamond surface, attenuated total refection (ATR) was used to hold the sample on the diamond surface and measured in the range of 200 cm^{-1}- 600 cm^{-1} in FTIR spectroscopy (Perkin Elmer- spectrum Two model).

3.2.6.4. Mechanical strength

The mechanical strength of the membrane was carried out by measuring the breaking strain and breaking strength of the membrane and nanocomposite membranes. These were carried out using texture analyser (TA) (model TA. XT. plus) nano tensile tester to investigate the mechanical stability of the membrane.

3.2.6.5. Contact angle

The wetting behaviour of the membrane was investigated using contact angle tester (Data physics Optical Contact angle OCA 15 EC GOP). The measurement of the contact angle is affiliated to three-phase equilibria (solid-liquid interface or liquid-vapour interface) (Kertesz et al., 2014). In this work, the phase equilibria used are the membrane, water and air. Contact angle of the membrane was measured in the sessile drop method where each sample was measured by placing water droplets on the outer surface of the membrane using a micro-syringe at 10 different positions after which, the samples were measured and averaged. The static contact angle between water and the membrane surface was measured to evaluate the hydrophilicity of the membrane (Yu et al., 2005).

3.2.6.7. Atomic force microscopy (AFM)

Membrane surface roughness (R_{RMS}) was measured using atomic force microscopy (AFM) (model Di 3000). This explained membrane surface roughness and its relation to water permeation (Luo et al., 2005).

3.3. Performance evaluation of the membrane

The performance of the nanocomposite membrane was evaluated in dead-end filtration cell. The system is made up of 400 ml filtration glass tube with a maximum operating temperature of 80 ^{0}C and pressure of 10 bar with the effective surface of the membrane of 34 cm^{2} (with other accessories as shown in Figure 3.7).

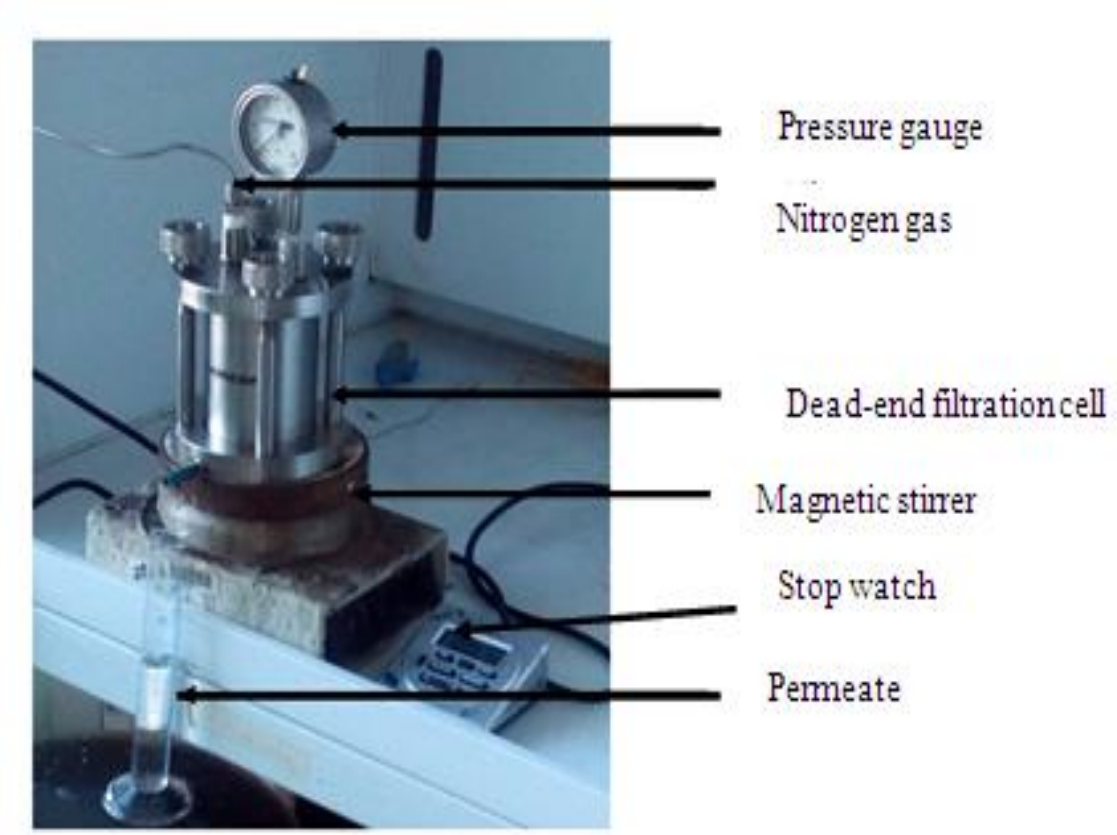


Figure 3.7: Schematic dead-end filtration system for treatment of BTEX-contaminated water.

A fresh membrane was mounted on the filtration cell and the reservoir was first filled with deionized water to check the original flux of the membrane. The system was pressurized until a steady flux was obtained and the filtration was conducted at different pressures 1.1, 1.3 and 1.8 bar. The membrane samples were first pressurised

using de-ionised water at 25 ± 4 ^{o}C for 30 min under pressure 1.8 bar to reach a constant flux. After which, the pressure was reduced to 1.1 bar and the membrane flux test was taking (Vatanpour et al., 2011; Zhao et al., 2014). Equation 3.4 was used to calculate the pure water flux under identical operating condition for all membranes (feed concentration and transmembrane pressure).

$$J_w = \frac{V}{A \times T} \tag{3.4}$$

Where J_w is pure water flux (L/m^{2}h), V is volume of permeate water (m^3), A is the effective area of the membrane (m^2) and T denotes the permeation time (h).

The cell was emptied and refilled with BTEX water. The BTEX water was prepared by measuring 1.25 ml of BTEX compounds each in 500 ml bottle of deionised water. Subsequently, the mixture was stirred for 30 minutes at 60 ^{o}C for homogeneity. The same procedure was used to check for the original flux (Crittenden et al., 2012). 5 mg/L of BTEX with a concentration of 191.29 mg/L and pH of 8.4 was poured in the feed tank and the mixture was continuously stirred. The dead-end filtration cell was run for 2 h to open up the membrane pores. Samples were collected from the permeate at a specified interval of 10 min per sample at different pressures 1.1, 1.5 and 1.8 bar. BTEX removal was tested and the removal percentage was calculated using Equation 3.6. TMP was obtained using equation 3.5:

$$TMP = Pf - Pp \tag{3.5}$$

Where P_f is feed pressure, Pp is permeate pressure

BTEX rejection % was also obtained using Equation 3.6.

$$R = \frac{C_F - C_P}{C_F} \times 100\% \quad (3.6)$$

Where R is the membrane BTEX rejection in %; C_F is the BTEX concentration in the feed to the dead-end mode unit (mg/l); C_P is the BTEX concentration in the permeate (mg/l).

The concentration of BTEX compounds were analysed using high-performance liquid chromatography (HPLC) (Agilent 1200series model, Eclipse XDB C-18 column); 70 % acetonitrile to water (70:30), 10 µL injection volume and flow rate at 1 mL/min.

3.4. Porosity and Mean pore size calculation

The porosity of the membrane ε (%) was determined using the gravimetric method and this is defined as the volume of pores divided by the total volume of the porous membrane (Vantanpour et al., 2012).

$$\varepsilon = \frac{W_w - W_d}{A \times L \times dw} \times 100\ \% \quad (3.7)$$

Where W_w is the weight of the wet membrane; W_d is the weight of the dry membrane; A is the effective membrane area (m^2); dw is the water density (1.00 g cm^{-3}); and L is the membrane thickness (m).

The mean pore size (r_m) was also determined by filtration velocity method according to Guerout -Elford-Ferry Equation and is calculated as:

$$Rm = \sqrt{\frac{(2.9 - 1{\cdot}75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times P}} \quad (3.8)$$

Where η is the viscosity of the water (8.9×10^{-4} Pa); Q is the water flux per unit time (m^3/s) and P is the working pressure (0.18 MPa).

Gravimetric method was used to determine the water uptake analysis of PES and PES/Fe-NPs. Membranes were immersed in deionised water for 24 hours after cutting into small pieces. Membranes were then removed from the water and lightly patted with a dry paper towel to remove some excess water and weighed. The membrane was also allowed to dry for another 24 hours and weighed. The water uptake was calculated using the Equation 3.9:

$$Water\ uptake\ (\%) = \frac{W_w - W_d}{Ww} \times 100 \qquad (3.9)$$

Where W_w is the weight of the wet membrane (g), W_d is the weight of the dry membrane (g).

3.5 Effect of operating variables

The effect of operating variables on the performance of the membrane for BTEX removal was investigated. The operating parameters investigated in the study include: pressure, concentration and pH. To obtain information on influence of pressure, operating pressure was varied within the range of 1.1 bar to 1.8 bar. It is important to know the concentration of the BTEX contaminated water in the retentate to obtain a non-toxic permeate. The concentration of BTEX contaminated water was varied from 191.29 mg/L and 956.45mg/L.

The effect of acidic pH on the membrane performance was investigated also. The pH of the BTEX contaminated water was adjusted to 3.45 at 16.9 ^{o}C by adding 0.5M HCL. The BTEX contaminated water was poured into the dead-end filtration cell and monitored for 1 h. Samples were collected from permeate at a specified interval of 10 min per sample at constant pressure. The samples obtained during this experiment were analysed using HPLC (Agilent 1200series model, Eclipse XDB C-18 column);

70 % acetonitrile to water (70:30), 10 µL injection volume and flow rate at 1 $mLmin^{-1}$.

The results obtained from acidic pH were compared to the studies performed without pH alteration.

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CHAPTER 4

MEMBRANE SYNTHESIS, CHARACTERIZATION AND EVALUATION

This chapter discusses the results obtained from the synthesis and characterization of Fe-NPs and nanocomposite membrane. It presents also the removal efficiency of the membranes during the removal of BTEX contaminated water.

4.1. Characterisation of iron nanoparticles.

The morphology of the synthesised Fe-NPs, and nanocomposite membrane were characterised using SEM. The SEM images and spectra of Fe-NPs are shown in Figure 4.1. The SEM image depicts spherically-shaped, clustered iron nano-particles ranging from 40 nm to 150 nm as reported in the literature (Zhang et al., 2011; Rao, 2012). The aggregated nanoparticles suggest magnetic iron properties. The energy dispersive spectroscopy (EDS) was used to determine the distribution and composition of the Fe-NPs as given in Figure 4.1. The weight percent of carbon in the Fe-NPs is 13.24% which can be assumed to be originated from pomegranate leaf extract that acted as a capping and stabilising agent. In addition, it could also be from the carbon tape used during sample coating. The percentage of oxygen in Fe-NPs is 41.99% which could be attributed to the oxygen present in the functional groups of the pomegranate extract such as phenol besides the oxygen acting as a capping agent. The percentage of sodium is 24.91 % which can be assigned to the presence of sodium hydroxide used in the preparation of the solution to convert the excess iron into Fe_3O_4. The iron percentage in Fe-NPs is 19.81 % which is the Fe produced (Prasad et al., 2017).

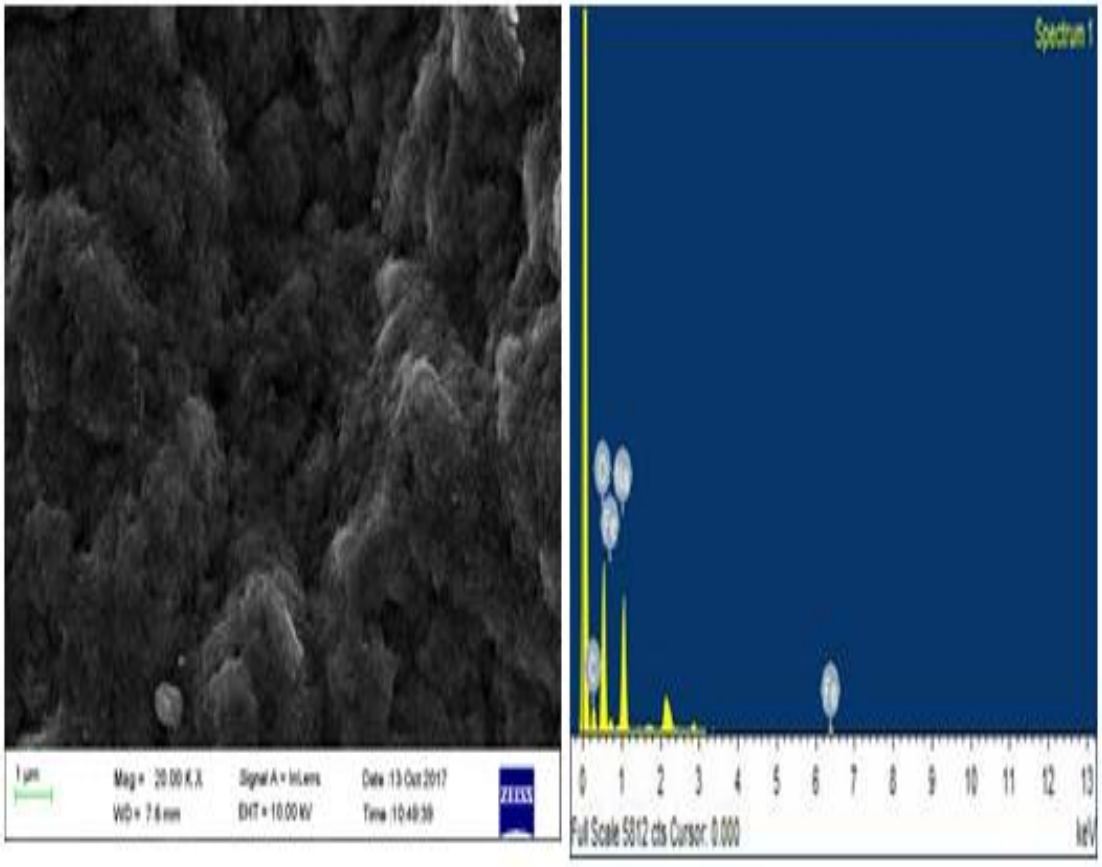


Figure 4.1: (a): SEM image of Fe-NPs (b): Elemental image of Fe-NPs

The FTIR spectroscopy was carried out to identify functional groups of molecules present in the pomegranate leave extract such as punicalin, phoneline, flavones glycosides and luteolin responsible for the reduction and stabilisation of Fe-NPs nanorods (Jasuja et al., 2012; Ismail et al., 2012). As depicted in Figure 4.2, there are strong bonds at 3445 cm^{-1} which indicates hydroxyl group (-OH) group. The peak at 585 cm^{-1} indicates the characteristic band of Fe (Prasad et al., 2017).

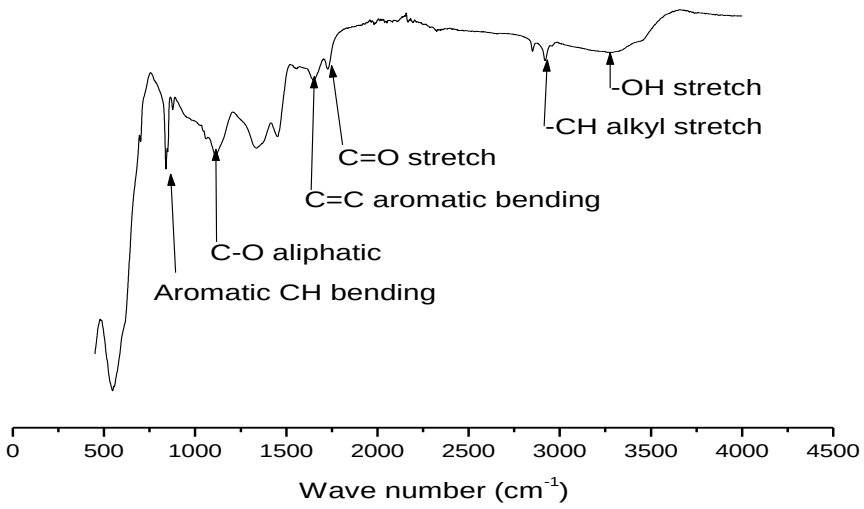


Figure 4.2: FTIR spectra of Fe-NPs

4.2 Membrane characterisation

4.2.1 SEM analysis

The surface morphology of the membranes was examined. Figure 4.3 depicts the surface images of PES and Fe-NPs/PES membranes with their changes. It was observed that Fe-NPs/PES membranes had an improved surface structure, with uniform distribution of pore as seen in 5 wt. % Fe-NPs. According to Boom et al. (1992), the phenomena is known as macro void formation. This could be attributed to the enhanced phase separation caused by the presence of nanomaterials in the polymer matrix (Vatanpour et al., 2011; Boom et al., 1992). The presence of hydrophilic additives in the polymer may increase the membrane porosity due to phase inversion process. From this study, it is observed that the micro-void formation was suppressed at high percentage loading of nanoparticles within the polymer matrix as seen in Figure 4.3 (10 wt. % -20 wt. % Fe-NPs). This result is consistent with the literature (Alam et al., 2017; Ayyaru and Ahn 2016).

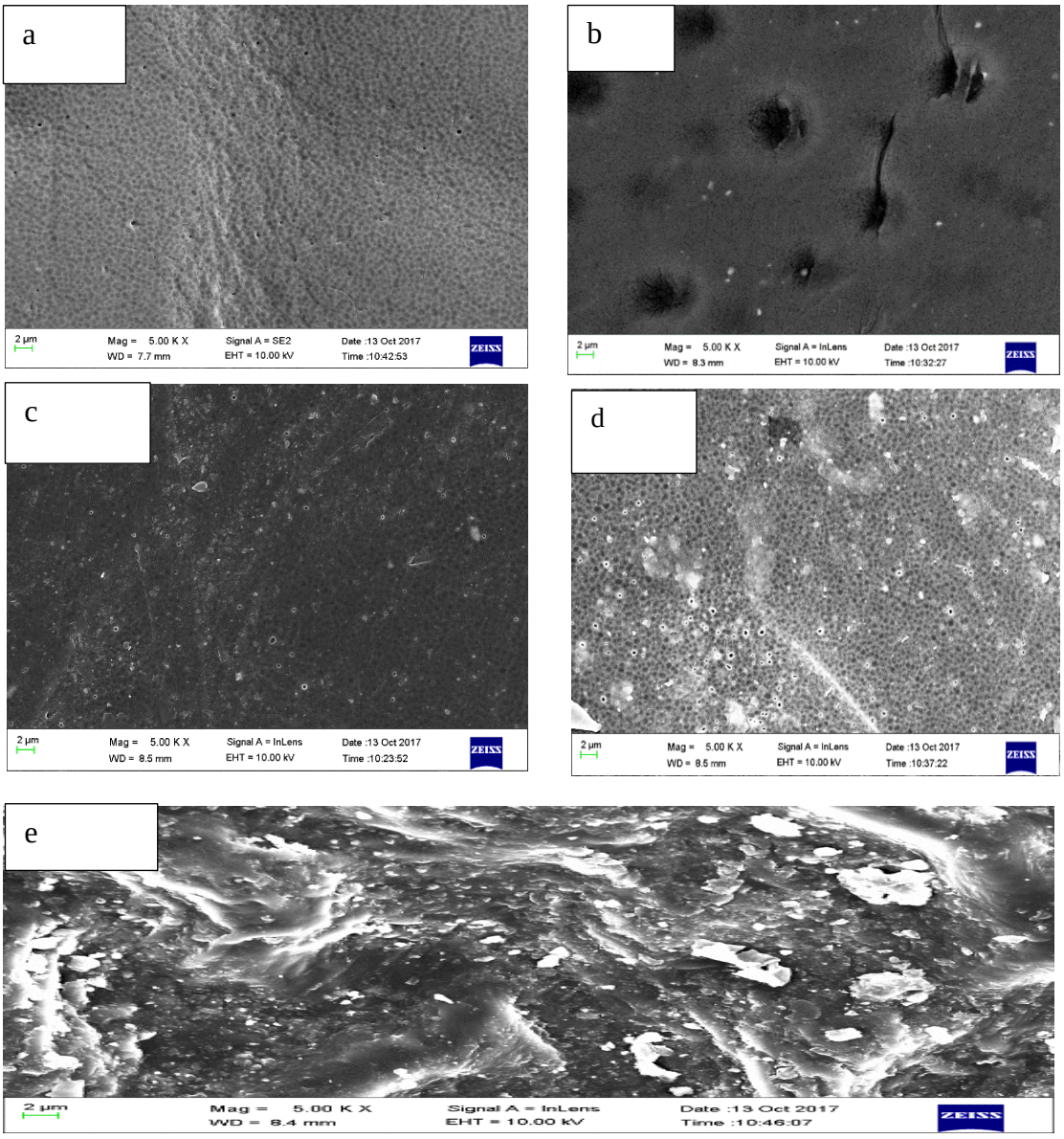


Figure 4.3: Surface morphology of synthesised PES and Fe-NPs/PES membranes. (a) PES (0wt.%), (b) 5wt.% Fe-NPs, (c)10 wt.% Fe-NPs, (d) 15 wt. % Fe-NPs, (e) 20 wt.% Fe-NPs.

The cross-sectional images of the PES and Fe-NPs/PES membranes are shown in Figure 4.4. The image shows that the number of microvoids decreased with an increase in polymer concentration and the spongy-like structure is more pronounced at increase in polymer concentration. Implying, there are more macro voids in the

MMMs. It is suggested that the addition of hydrophilic nanoparticles improves the water penetrating rate using phase inversion method and this contributes to the formation of a macro void in the membrane matrix (Zhang et al., 2008). The cross-sectional structure in Figure 4.4 shows that the FeNPs were successfully dispersed within the matrix of the polymer. The fractional free volume (FFV) ratio of the polymer to the amount of FeNPs within the polymer matrix decreased at increasing loading of FeNPs. From the literature, similar results were observed at higher concentrations of nanomaterials (Javed et al., 2017).

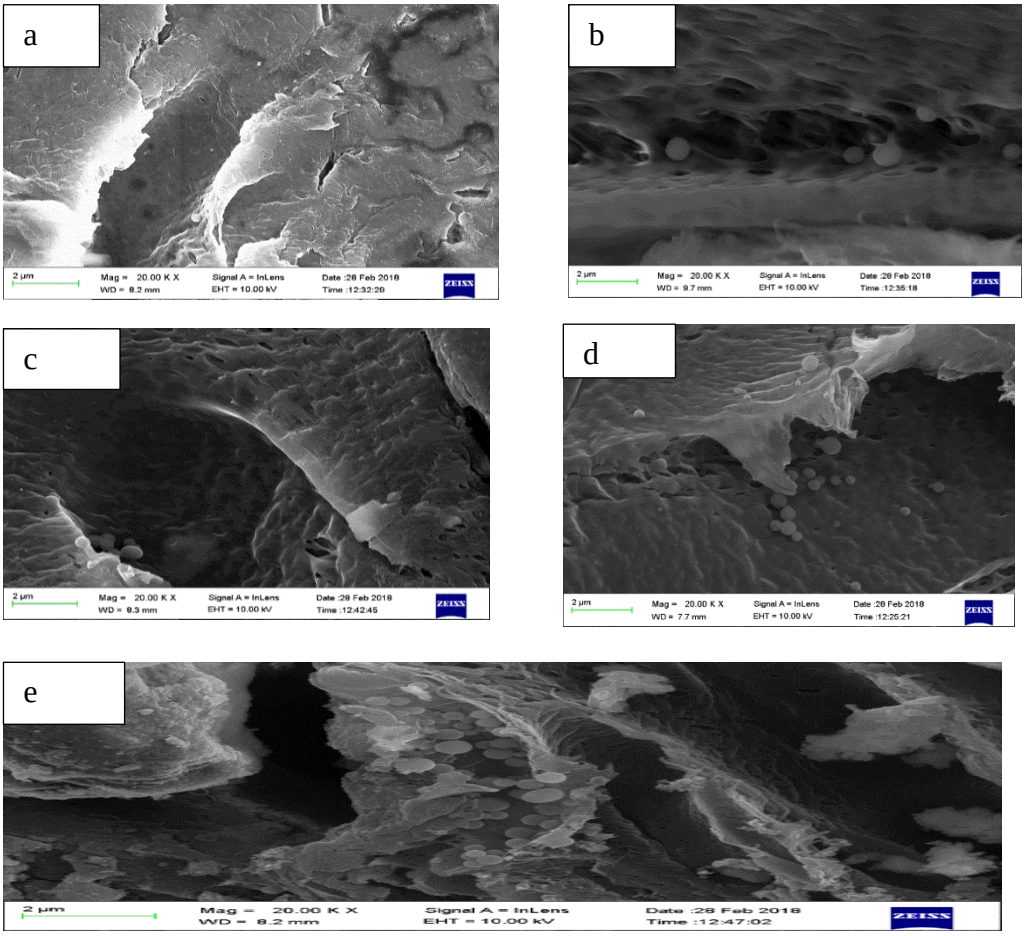


Figure 4.4: Cross-sectional morphology of synthesised PES and Fe-NPs/PES membranes. (a) PES (0wt.%), (b) 5wt.% Fe-NPs, (c)10 wt.% Fe-NPs, (d) 15 wt. % Fe-NPs, (e) 20 wt.% Fe-NPs

4.2.2. Fourier transform infrared spectroscopy (FTIR)

This technique identifies the functional groups present in the membrane (Ayyaru and Ahn 2016). It also uses the infrared absorption bands to identify molecular components and structures (Shockravi et al., 2017).

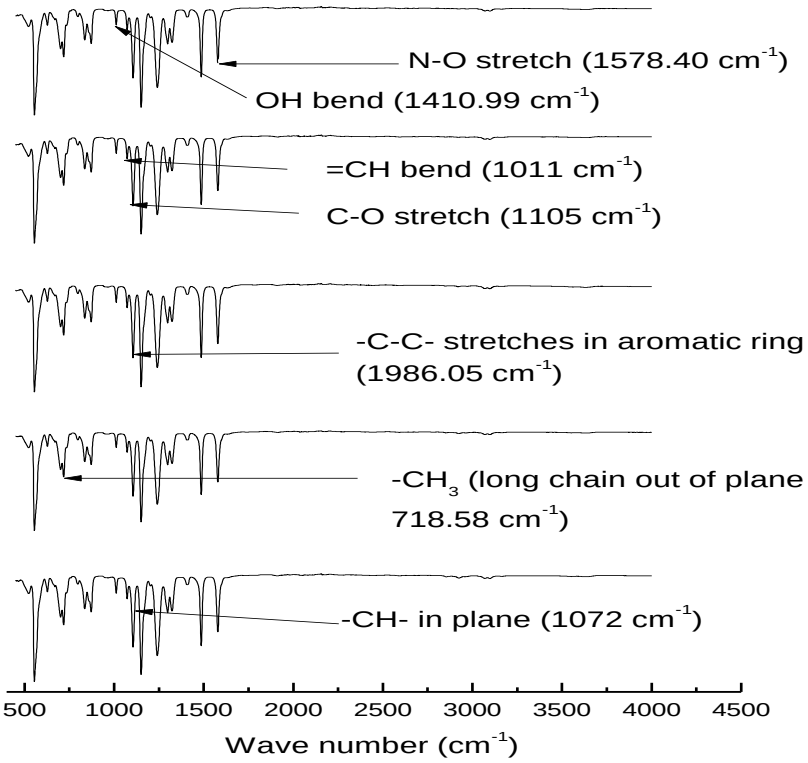


Figure 4.4: FTIR spectra of PES and Fe-NPs/PES membranes at different wt. % of Fe-NPs.

All the membranes manifested typical spectra of polymer (PES) which is the aromatic bands at 1578 and 1486 cm^{-1} from the benzene ring and C = C bond stretch and aromatic ether band around 1240 cm^{-1}. McCurry (2008) reported that adsorption in this region is as a result of a variety of single functional group including C-C, alcohol (C-O) and amine (C-N). From 2000-1740 cm^{-1} is the alkyl group attached to the aromatic ring H-C=C-R where R is the alkyl group (Vatanpour et al., 2012). Methyl

group (CH_3) is detected at the wavelength of 718 cm^{-1} (Jalali et al., 2016). The strong and broad absorbance band at wavelength 1105 cm^{-1} and 1986.05 cm^{-1} could be attributed to C-O stretch and C-C stretches in the aromatic ring, respectively (Shockravi et al 2017). The functional groups are consistent in all the membranes and confirms the presence of additives in the polymer matrix (Qu et al., 2010).

4.2.3. Thermogravimetric analysis

The results of the TGA of PES and Fe-NPs/ PES membranes are shown in Figure 4.6

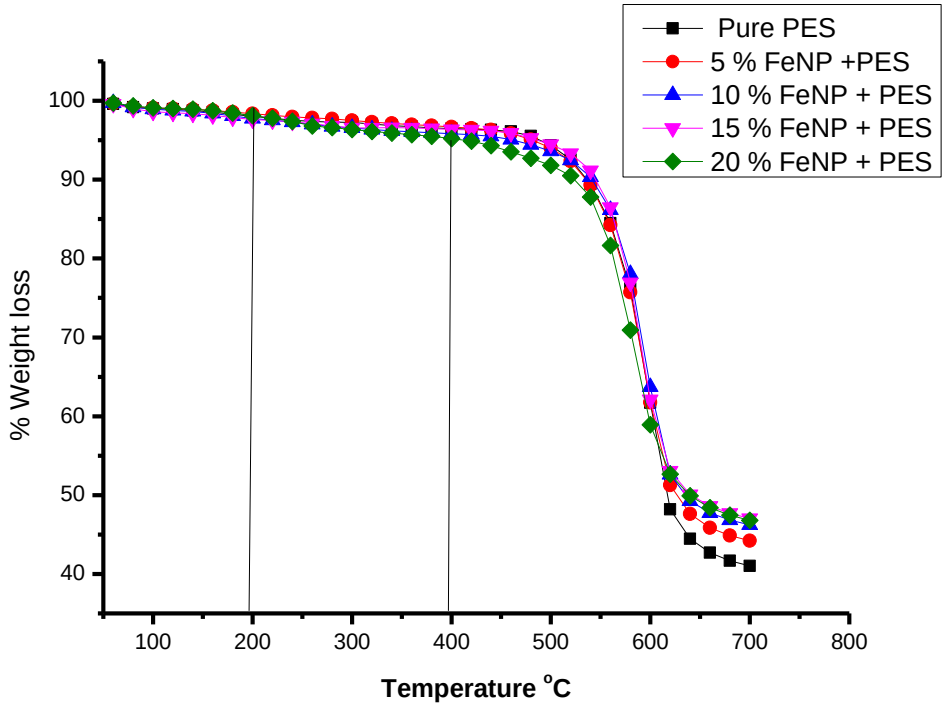


Figure 4.5**:** TGA curves of PES and Fe-NP/PES membranes

The curves of pure PES and Fe-NPs membranes showed two zones of weight loss. The first weight loss between 160-250 ^oC, is due to the removal of moisture content in the membrane (Ravikumar, 2012). The second weight loss from 250-500 ^oC indicates loss of solvent in the membrane after fabrication. From 500 ^oC upwards

indicates decomposition at onset temperature of the membranes (Qu et al., 2010). The pure PES membrane (0 wt. % Fe-NPs loading) shows weight loss between 450-500 ^{o}C. It is observed that 5 wt.% Fe-NPs loaded membrane is thermally stable up to 417.70 ^{o}C, with a weight-loss of 52.55% between 418 to 692.17 ^{o} C when compared to thermal stability of pure PES (422.43 ^{o}C). It is clear that the addition of nanoparticles to the membrane enhances thermal stability. Membrane with 10 wt. % Fe-NPs loading displays a higher thermal stability than membranes with 0 wt. % and 5 wt.% loading. The thermal stability of 10 wt.% Fe-NPs loading is 434.84 ^{o}C with 49.62 % weight loss. From the trend, increasing nanoparticles results in an increase in thermal stability but membrane with 15 and 20 wt.% Fe-NPs loading does not follow the trend. As for membrane with 15 wt. % Fe- NPs loaded, the thermal stability was 450 ^{o}C and this could be as a result of some impurities in the sample. The fact that the membrane can be stable at higher temperature makes it cost competitive on energy.

4.2.4. Mechanical strength

The mechanical property of the membrane was evaluated using texture analyser at room temperature. Figure 4.7 (a) depicts the graph of tensile strength against % Fe-NPs while (b) depicts the graph of Young Modulus against % Fe-NPs.

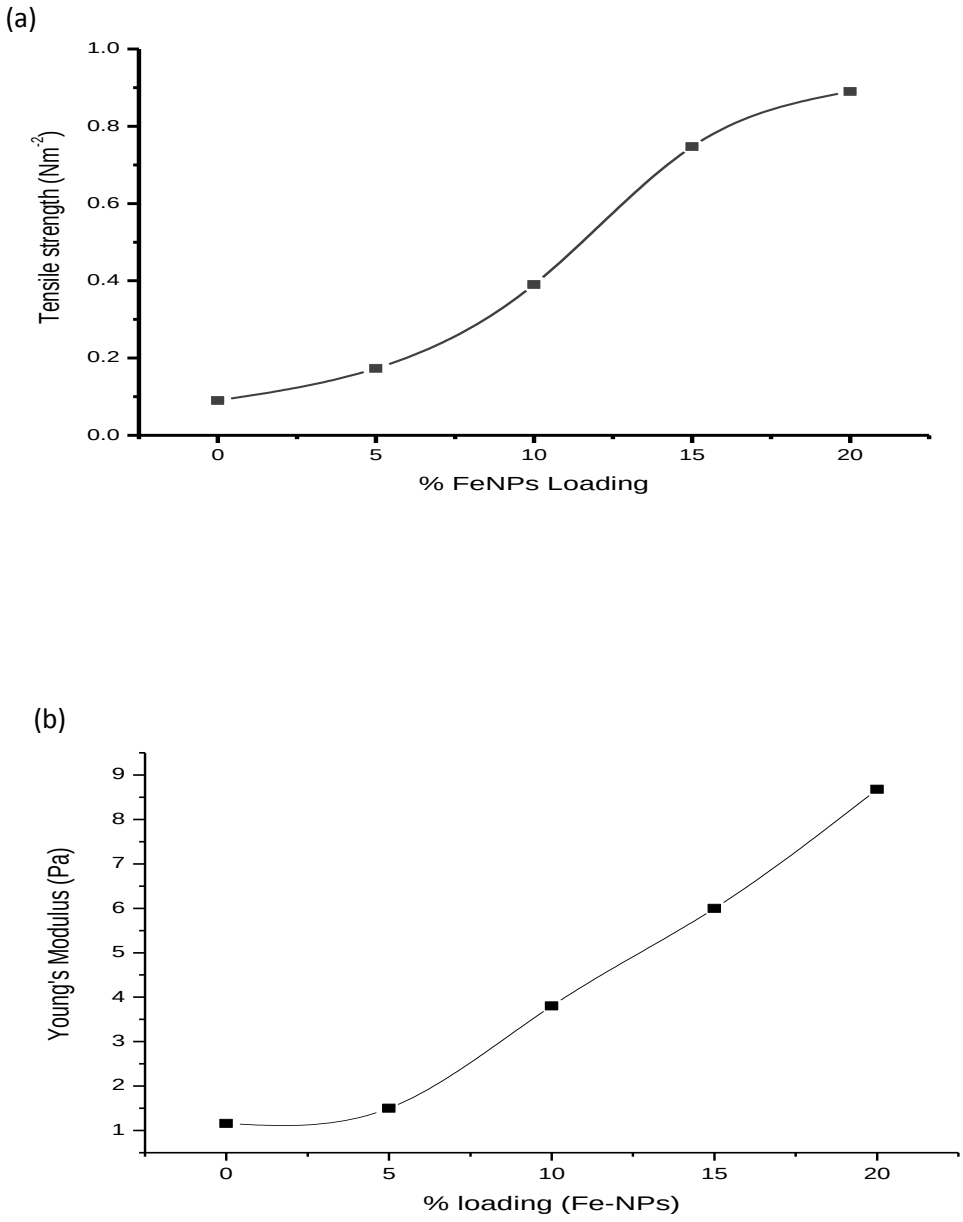


Figure 4. 6: (a) and (b) Mechanical strength of synthesized Fe-NPs/ PES membrane.

The mechanical strength as indicated by tensile strength and Young modulus of the synthesised membranes increased with increasing nanoparticles loading. This observation agrees with literature (Shen and Lua 2012; Daramola et al., 2015). Figure

4.7 (a) shows that the breaking point of 0 wt.% of Fe-NPs was 0.1 Nm^2 while the breaking point 20 wt.% Fe-NPs was 0.95 Nm^2 (b) 20wt. % FeNPs loading displayed the highest tensile strength of 8.94 Pa compared to 0 wt. % loading which gave 1.2 Pa. This confirms the enhanced mechanical strength with increase in nanoparticles loading (Xu et al., 2014; Daramola et al., 2015)

4.2.5. Contact angle

Hydrophilicity and wettability of the membrane were evaluated by measuring the water contact angle. Hydrophobic surface of a membrane correlates with higher contact angle while a small contact angle corresponds with the hydrophilic (Sun et al., 2009). The results of the contact angle evaluated are shown in Table 4.1. The contact angle of PES and Fe-NPs/ PES decreased on the incorporation of 5 wt.% Fe-NPs loading. The decrease in the trend of contact angle reveals enhancement of hydrophilicity of the membrane. As shown by the FTIR spectra in Figure 4.6, -OH groups were generated in large amounts and these -OH groups may be responsible for increase in hydrophilicity. Also, the hydrophilic Fe-NPs are migrated towards the membrane surface during the phase inversion process, thereby enhancing membrane hydrophilicity and decreasing water interface energy (Jeong et al., 2007; Wu et al., 2008). However, there is a possibility for hydrophilic material water droplet on the millimeter scale to penetrate into the bulk through large pores resulting in the increase (Yu et al., 2005). It was noticed that there was no further enhancement in membrane surface hydrophilicity at 15 wt. % Fe-NPs loading such that the measured contact angle increased with the increase of Fe-NPs. This increase could be attributed to the reduced penetration of the test water droplet in the millimeter scale. Addition of Fe-NPs into the membrane reduces the pore size of the membrane thereby making the top surface of the membrane smoother, leading to relatively high-water contact angle. It could also be as a result of irregular dispersion of Fe-NPs within the polymer matrix. Dong et al (2012) reported an increase in contact angle with increasing Mg $(OH)_2$ nanoparticles at 10 wt. % of PEG contents. Yu et al., (2005) also reported a similar behaviour.

Table 4.1: The average contact angle of Fe-NPs/PES

Membrane	Contact angle (^{o})
M1	69.09 ± 0.6
M2	65.79 ± 0.9
M3	63.02 ± 0.7
M4	71.06 ± 1.5
M5	66.48 ± 0.8

4.2.6. Membrane surface Roughness (R_{RMS})

The surface roughness of the membrane was evaluated, the AFM image of PES and Fe-NPs/PES membranes are shown in Figure 4.8. This described the surface roughness in relation to water permeation. Rougher surface of the membrane has a higher value of R_{RMS} and this explains that the membrane is more hydrophilic, pore volume and density that are connected to membrane filtration performance (Luo et al., 2005). The roughness (R_q) of the PES and composite membranes were compared and the results are shown in Table 4.2. The results show that the membrane surface roughness increased with the increase in nanoparticles, thereby enhancing the separation performance of the membrane.

Table 4.2 Results of AFM analysis

List	Membrane (wt.% Fe-NPs)	Ra (nm)	Rq (nm)
(a)	0	7.09	11.66
(b)	5	11.50	15.95
(c)	10	24.99	30.34
(d)	15	29.85	40.10
(e)	20	40.49	52.72

Where R_a is the average roughness

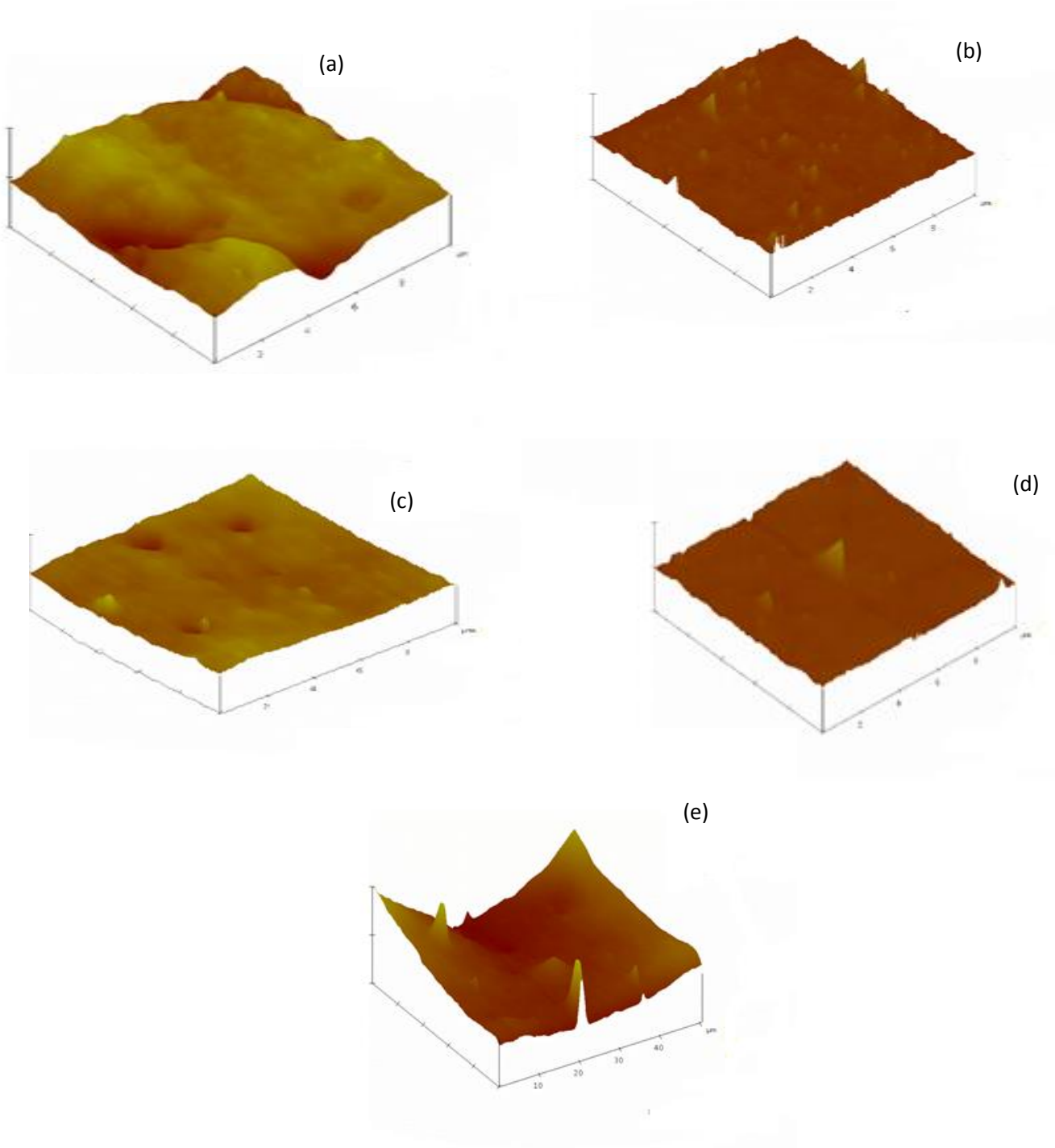


Figure 4. 7: (a)- (e) Surface roughness of the membrane. (a) PES (0 wt.%), (b) 5 wt.% Fe-NPs, (c)10 wt.% Fe-NPs, (d) 15 wt. % Fe-NPs, (e) 20 wt.% Fe-NPs.

4.3. Membrane performance evaluation

4.3.1 Pure water permeation

Pure water flux of 0 wt. % Fe-NPs and fabricated MMMs was evaluated as a function of applied pressure as shown in Figure 4.9. Figure 4.9 depicts that water flux increases linearly with the applied pressure. Water flux increased from 17.58 $L/m^2 h^{-1}$ to 90.00 $L/m^2 h^{-1}$ for the 10 wt. % Fe-NPs loading at pressure 1.8 bars. Moreover, the pure water flux of the membrane with 0 wt.% Fe-NPs was found to be lower than that of the membrane with 10 wt. % Fe-NPs at the same pressure. The improvement in the pure water flux can be attributed to the enhanced hydrophilicity of the membrane with iron nanoparticles (Ayyaru and Ahn 2016).

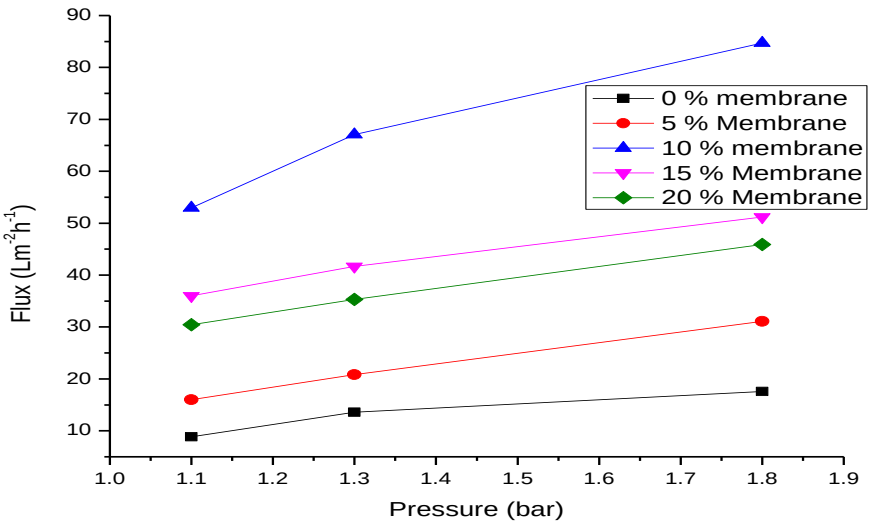


Figure 4.8: Pure water flux against pressure.

Figure 4.10 show the water flux variation at various Fe-NPs loading. It was observed that the flux increased until the loading got to 10 wt. % but decreased as it reached 20 wt. % solution. This could be because of high viscosity of the PES during 20 wt. % Fe-NPs membrane fabrication having an adverse effect on the membrane structure or

due to the pore structure of the membrane (Ayyaru and Ahn 2016; Alam et al., 2017). However, water molecules could accumulate on the membrane with larger surface roughness and large pore size thereby reducing the membrane flux.

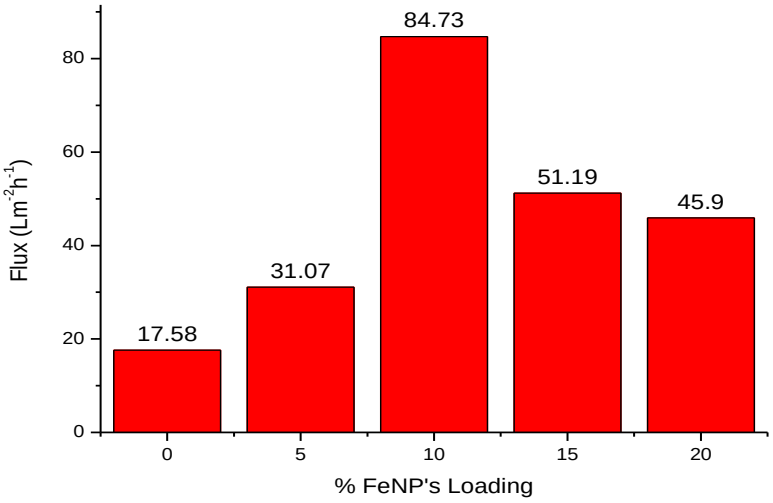


Figure 4.9: Membrane flux as a function of Fe-NPs loading

4.3.2. Percentage Rejection

The rejection of 5 wt. % Fe-NPs loading was slightly lower than that of 0 wt. % Fe-NPs (see Figure 4.11). This could be attributed to the increase in mesopores from the MMMs in 5 wt. % Fe-NPs resulting in some BTEX molecules having penetrated through the membrane, lowering BTEX rejection in 5 wt. % Fe-NPs. A similar result has been reported by Su et al., (2016).

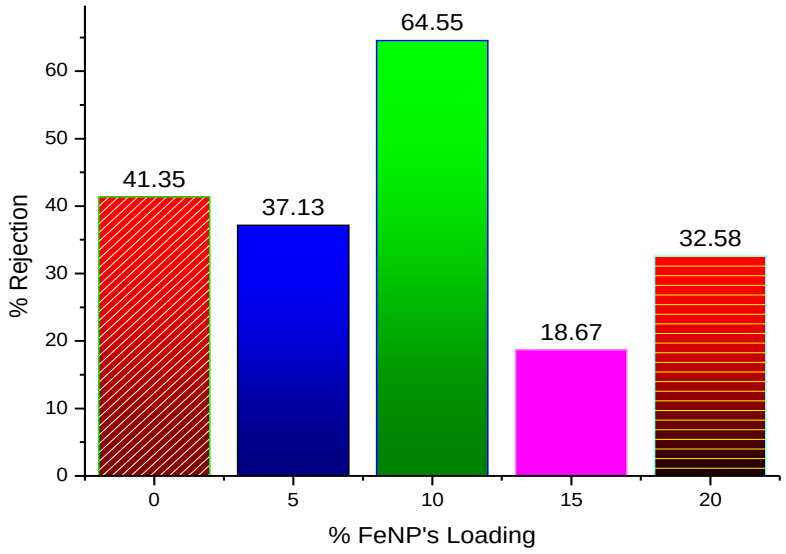


Figure 4. 10: Percentage rejection as function of Fe-NPs

Table 4.3 Results of BTEX rejection as a function of Fe-NPs loading.

Feed	Rejection (%)	Rejection (%)	Rejection (%)	Rejection (%)	Rejection (%)
	0 wt.%	5 wt.%	10 wt.%	15 wt.%	20 wt.%
Benzene	30.99	31.24	53.19	29.19	23.65
Toluene	42.83	44.27	49.38	22.79	29.69
Ethylbenzene	73.90	41.71	53.42	22.72	61.59
Xylene	8.84	31.29	84.12	0	15.38

The performance of the Fe-NPs/ PES membrane was further evaluated in terms of selectivity of the membrane to each BTEX component. Table 4.3 depicts the percentage rejection of BTEX as a function of Fe-NPs loading. Rejection of Ethylbenzene was the highest using membrane 0 wt. % Fe-NPs with maximum rejection of 73.90%. This could be attributed to the pore size of the membrane, the molecular shape of the ethylbenzene, and its molecular diameter. The molecular diameters of BTEX are 0.58, 0.6, 0.63, 0.63 nm respectively (Kim and Lee, 2001). The retention of ethylbenzene by 0 wt.% Fe-NPs loading makes the membrane highly selective for ethylbenzene. At 5 wt. % Fe-NPs loading, the ethylbenzene decreased with about 32 %. Rejection of xylene increased with 38 % with increase in Fe-NPs loading (Table 4.3).

Membrane selectivity is based on the type with the highest number of pores with the smallest size (Wang et al., 1994). Smaller pore size will always favour effective retention and higher number of pores will favour higher permeate flux. However, bigger pore size will favour higher permeate flux, but the solute rejection will collapse; 10 wt. % FeNPs gave higher permeate flux with BTEX retention.

4.4 Summary

In this chapter, nanocomposite PES/FeNPs was successfully synthesised using phase inversion method. Five different weight per cent loading of PES/FeNPs, ranging from (0 wt. % - 20 wt. % Fe-NPs loading) were adopted during the synthesis of MMMs. The membranes were characterized using SEM, FTIR, TGA, contact angle, AFM and mechanical strength. The SEM images confirm the successful synthesis of PES/FeNPs within the polymer matrix. The membrane was evaluated using pure water to check for the original pores and BTEX compounds for the flux, permeability and percentage rejection. From the result, it was noticed that membrane incorporated with nanoparticles was enhanced.

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CHAPTER 5

EFFECT OF OPERATING VARIABLES

This chapter presents the results of operating variables such as pressure, concentration and pH on the performance of mixed matrix membrane during the treatment of BTEX contaminated water.

5.1. Nanocomposite membranes: Effect of operating variables.

The effect of pressure, BTEX concentration and pH were evaluated by varying each of the operating parameters.

5.2 Effect of operating pressure and the feed BTEX concentration on the permeate flux

The effect of the operating pressure and feed BTEX concentration of 191.29 mg/L on the permeate flux are represented in Figure 5.1. The Figure 5.1 shows that the permeate flux decreases with concentration at a fixed operating pressure. At pressure of 1.1 bar, flux decreases from 14.12 $L/m^2\ h^{-1}$ to 7.06 $L/m^2\ h^{-1}$ with feed BTEX concentration at a fixed operating pressure when BTEX concentration increases. Flux increases with pressure at BTEX concentration from 7.06 $L/m^2\ h^{-1}$ to 11.3 $L/m^2\ h^{-1}$ while the pressure increases from 1.1 bar to 1.8 bar. This could be as a result of effective driving force (Purkait et al., 2004).

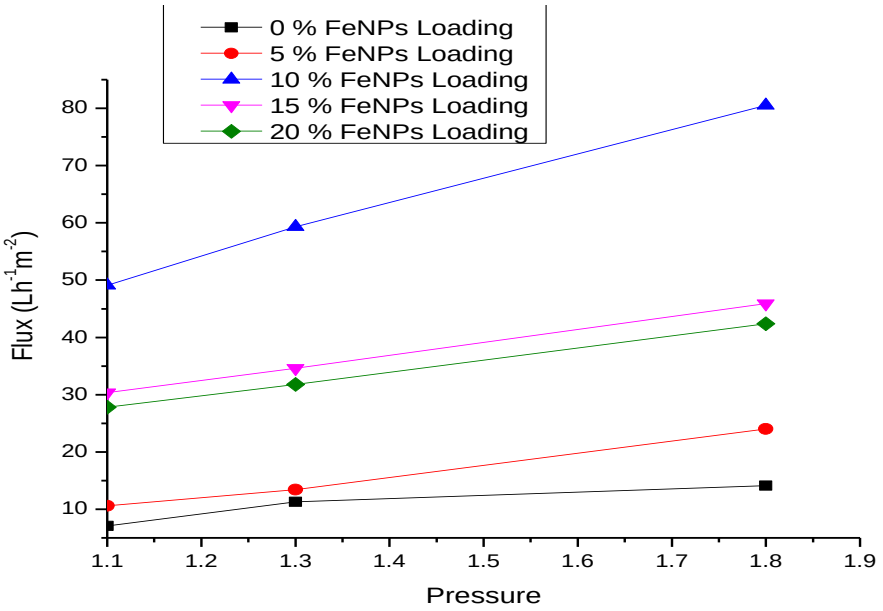
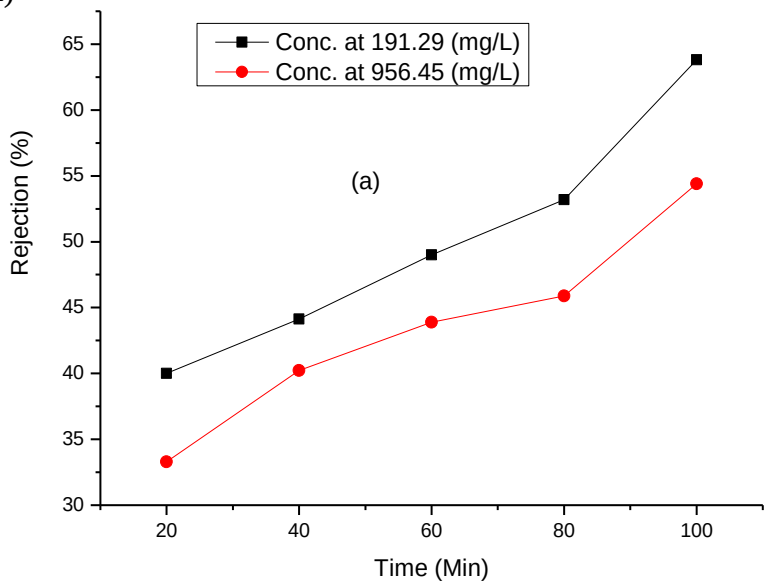


Figure 5.1: Variation of permeate flux at different pressures.

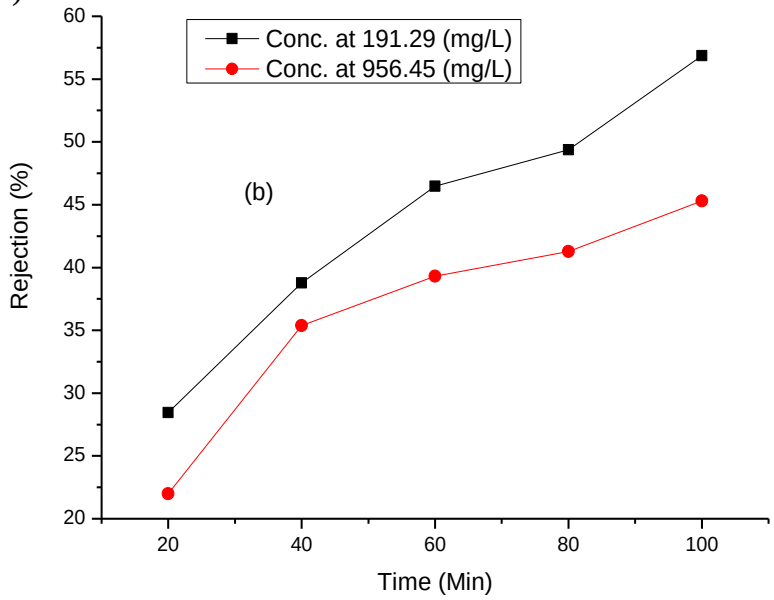
5.3. Effect of Variation of Feed BTEX Concentrations

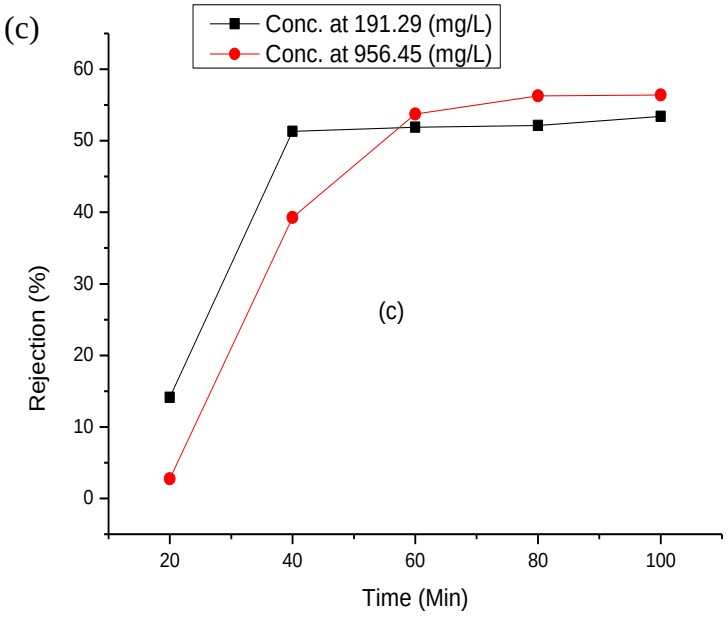
The effect of the solution concentration was evaluated by performing rejection experiments in the concentration range of 191.29 mg/L and 956.45 mg/L with membrane 10 wt.% Fe-NPs on 1.8 bar. The results of BTEX concentration are shown in Figure 5.2 (a-d) (a. Benzene, b. Toluene, c. Ethylbenzene and d. Xylene). BTEX rejection was 63.81 % and 54.40% for benzene, 56.86% and 45.38% for toluene, 53.42% and 57.88% for ethylbenzene and 84.12% and 2.48% for xylene.

(a)


Conc. at 191.29 (mg/L)
Conc. at 956.45 (mg/L)
(a)
Rejection (%)
Time (Min)
65
60
55
50
45
40
35
30
20
40
60
80
100

(b)


Conc. at 191.29 (mg/L)
Conc. at 956.45 (mg/L)
(b)
Rejection (%)
Time (Min)
60
55
50
45
40
35
30
25
20
20
40
60
80
100



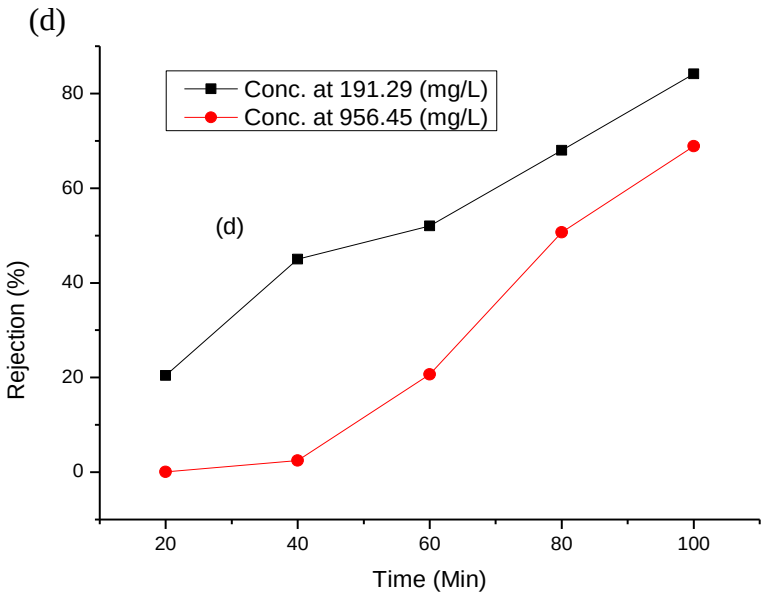


Figure 5.1: (a-d) Effect of variation of feed BTEX concentration.

From the results, increasing feed BTEX concentration decreased with BTEX rejection. The reason is as a result of diffusion force (Su., et al., 2016). Higher concentration can enhance the diffusion force and cause the molecules of BTEX to diffuse into the membrane. Decrease in BTEX rejection with time was noticed also and this could be as a result of accumulation of concentration of the retentate. Benzene and toluene have significant decrease in rejection compared with ethylbenzene and xylene and these are particularly due to the molecular size differences of BTEX. The molecular diameters of BTEX are 0.58, 0.6, 0.63 and 0.63 nm respectively (Kim and Lee, 2001). The smaller molecular-sized particles diffused easily into the membrane.

Figure 5.2 depicts the rejection on different membrane at different concentration. The concentration ratio to BTEX was varied by changing concentration at a fixed membrane.

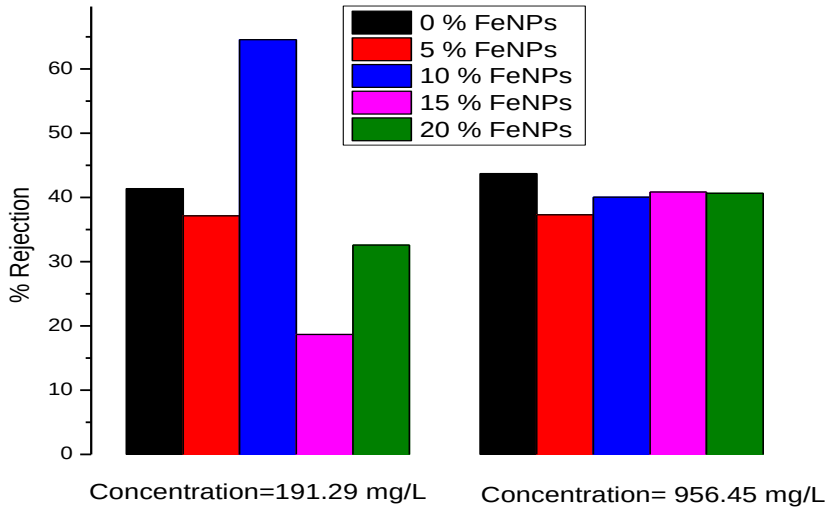
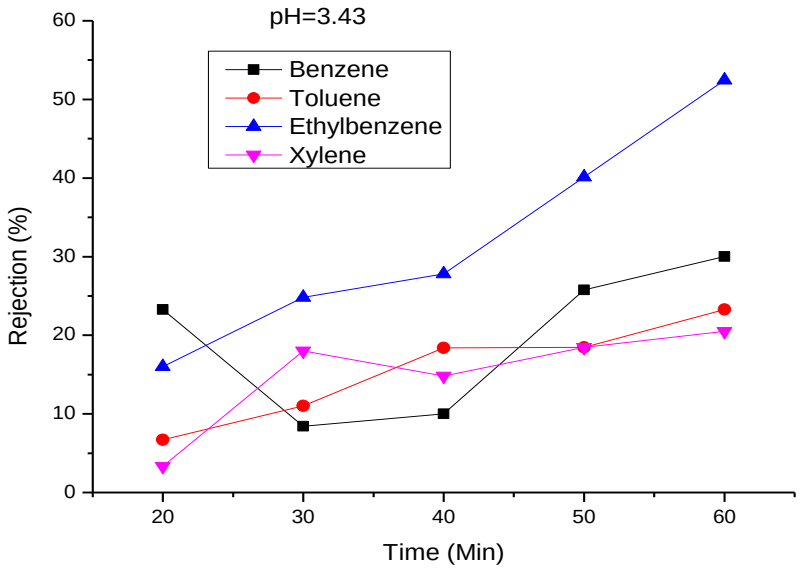


Figure 5. 2: Effect of feed BTEX concentration on different membranes.

5.4 Effect of Hydrogen ion concentration (pH)

The pH solution is an important factor that influences membrane charge and the rejection property of a membrane (Karanikol et al., 2017). Figure 5.4 shows the effect of pH on the BTEX rejection with time. At low pH value of 3.43 using 10 wt. % FeNPs at a concentration of 191.29 mg/L, the results show that after treatment, the pH moved from 3.43 to 5.40. The percentage rejection was increasing with time when 30 % for benzene, 23.28 % for toluene, 52.45 % for ethylbenzene and 20.52 % for xylene were respectively fed.

(a)



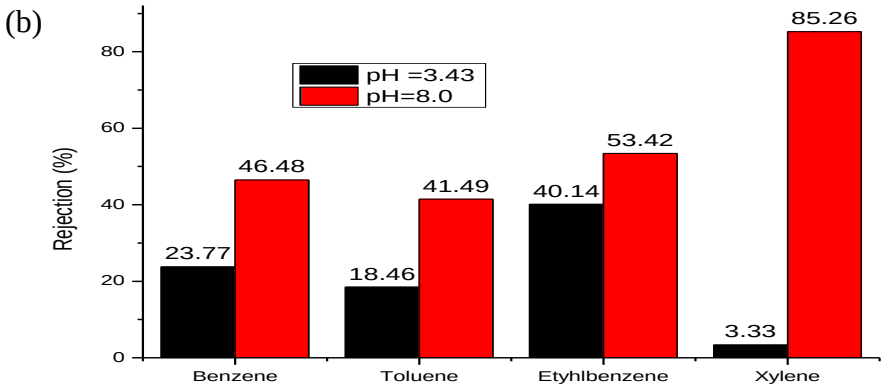


Figure 5. 3:(a) and (b) Effect of solution pH on BTEX rejection.

Additional results of effect of the solution pH and concentration are depicted on the appendix 1.

5.5 Results of this study compared to literature are presented in Table 5.1.

Results of this study compared with literature are presented in Table 2. Notwithstanding the difference in the preparation methods and operating conditions employed in the previous studies as documented in Table 2, the experimental results obtained from the membrane prepared in this study are comparable to literature. The BTEX rejection in this study is higher than the one reported by Bilsted (1996).

Table 5.1: Results compared with literature.

Membrane	Materials Treated	Filler	BTEX rejection (%)	References
CNT/ PVDF /PSF	BTEX	CNTs	> 80.00	Su et al. (2016)
CNT/PSF	BTEX	CNT	54.00	Bilsted (1996)
MWCNTs	BTEX	CNTs	98.99	Hamidreza et al. (2012)
Fe-NPs/PES	BTEX	Fe-NPs	64.55	This study

References

Kim, J.H., Lee, S.H., 2002. Molecular Dynamics Simulation Studies of Benzene, Toluene, and p-Xylene in a Canonical Ensemble. J. Kor. Chem. Soc. 23 (3), 441-446.

Karanikola, V., Corral, A., F., Jiang, H., Saez, E., A., Ela, W.P., Arnold, R., G., 20017. Effects of membrane structure and operational variables on membrane distillation performance. *J.* Membr. Sci. 524,87-96.

Purkait, M.K., Chandan, D., 2004. Removal of dye from wastewater using micellar-enhanced ultrafiltration and recovery of surfactant. Sep. Purif. Technol. 37, 81–92.

Su, F., Lu, C., Tai, J, 2016. Separation of Benzene, Toluene, Ethylbenzene and P-Xylene from Aqueous Solutions by Carbon Nanotubes/Polyvinylidene Fluoride Nanocomposite Membrane. J. Water Resource. Prot. 08, 913–928.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

Global demand for water has increased exponentially as a result of an increasing population and this is a serious problem facing the world today. The global decline in water quality and treatment has brought about the incorporation of nanofillers within the membrane matrix, and this treatment technique will effectively remove BTEX compounds from BTEX-contaminated water. Several methods have been proposed, but the application of nanotechnology and membrane technology have been demonstrated to be effective in removing BTEX compounds from the contaminated water.

Considering the objectives mapped out from the beginning of this study, the underlisted conclusions have been drawn from this work:

- Iron nanoparticles were successfully synthesized using pomegranate leaves via green synthesis route. The characterization of the synthesized Fe-NPs shows that iron nanoparticles can be produced from plant extract.

- Novel Fe-NPs/PES hybrid membrane containing different weight percentage (0 wt.%, 5 wt. %, 10 wt.%, 15 wt.% and 20 wt.%) of Fe-NPs were successfully fabricated using the phase inversion method. The quality of the synthesized membranes was evaluated using the characterization methods such as SEM-EDS, contact angle, mechanical strength, TGA, AFM and FTIR.

The surface images of the SEM confirmed the presence of well-distributed nanoparticles within the membrane matrix confirming that nanoparticles are compatible with PES membranes even though there were physical changes in the properties and structures of the nanocomposite membranes. The structure of the membranes also confirmed that increase in addition of Fe-NPs affected the casting solution and membranes pore structure. The chemical composition of the iron nanoparticles and the membranes were achieved using FTIR. The hydrophilicity, thermal stability, and mechanical strength were enhanced with the addition of Fe-NPs but later, resulted in a decrease in mechanical strength at the higher content of Fe-NPs.

- The membrane performance evaluation indicated that addition of Fe-NPs increases the flux and percentage rejection. Water flux of a composite membrane increased with increasing weight percent loading of nanoparticles, it got to the maximum of 80.50 $L.m^{-2}h^{-1}$ at 10 wt.% Fe-NPs loaded with lowest contact angle showing better hydrophilicity properties. The results for the percentage BTEX rejection show that membrane blended with Fe-NPs loaded exhibited the best average removal performance at 10 wt. % Fe-NPs loaded with uniformly distributed pores density.

- The operating parameters were influenced during evaluation of the effect of the operating variable. It was also noticed that increasing the feed BTEX concentration decreased its rejection. The flux increases with the pressure at BTEX concentration of 7.06 L/m^2 h^{-1} to 11.3 L/m^2 h^{-1} while the pressure increases from 1.1 bar to 1.8 bar at low pH value of 3.43 using 10 wt. % Fe-NPs loading when the concentration was 191.29 mg/L. The results showed that after treatment, the pH increased to 5.40 while the percentage rejection increased with time.

From this study, volatile organic compounds can be effectively removed by using Fe-NPS/PES mixed matrix membranes. The results from this study have shown the potential for practical application of Fe NPs/PES membranes in the treatment of BTEX-contaminated water. The best separation performance displayed by membrane with 10 wt.% Fe-NPs loaded have shown that this membrane performed very efficiently in BTEX removal from contaminated water. This membrane can suitably be applied in wastewater treatment plants to reclaim wastewater from BTEX-contaminated water.

6.2. Recommendations

To the best of knowledge, filtration of BTEX from wastewater using mixed matrix membrane is limited in the literature. Therefore, further research is needed to improve on the quality of the membrane via optimisation of the synthesis method. This could enhance the quality of the membrane further and reduce the time of synthesis. The yield of synthesised nanoparticles was quite low and consumed a lot of time. This could also be improved through optimising the synthesis procedure to reduce time, improve purity and high yield.

Furthermore, the evaluation of the membrane could be expanded using cross-flow filtration system to achieve comparative performance in behaviour of Fe-NPs / PES membrane. Investigation on the quantity of Fe-NPs loading within the membrane matrix should be investigated in future.

APPENDIX

Appendix A: Effect of feed BTEX concentration on Rejection

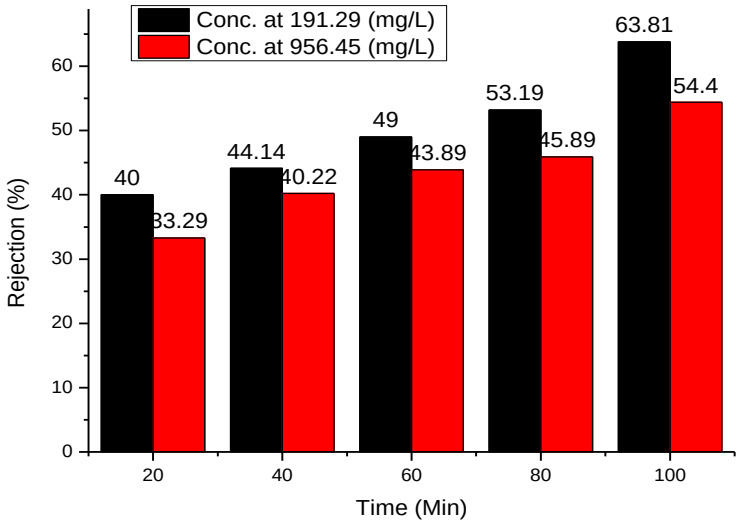


Figure A1: Effect of concentration on rejection (benzene)

TOLUENE

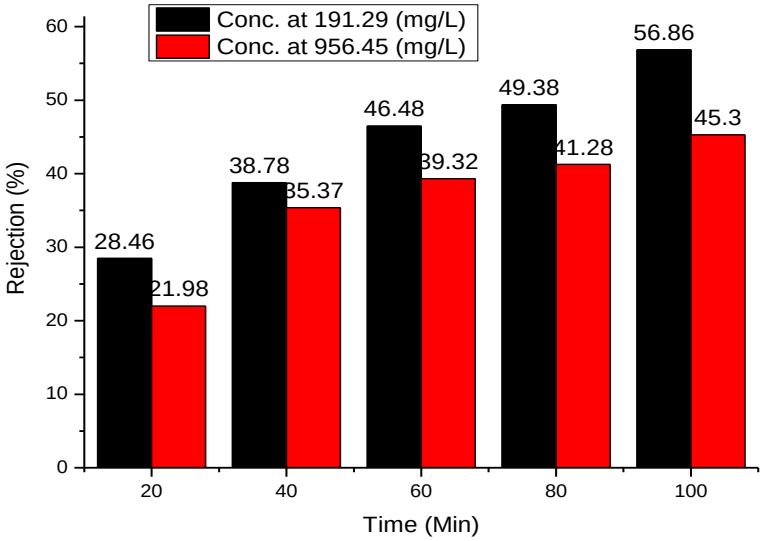


Figure A2: Effect of concentration on rejection (toluene)

ETHYLBENZENE

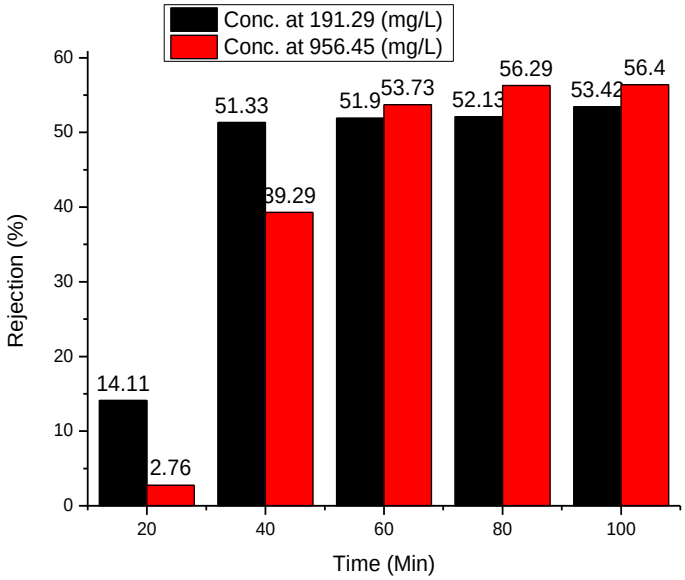


Figure A3: Effect of concentration on rejection (ethyl benzene)

XYLENE

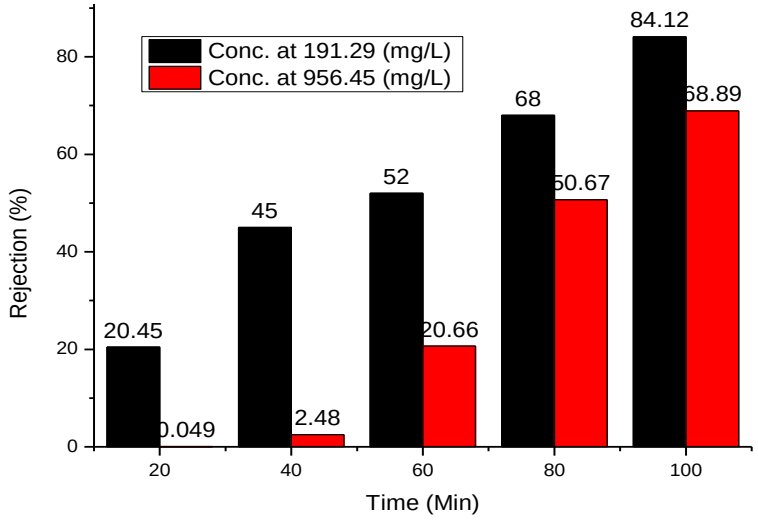


Figure A4: Effect of concentration on rejection (xylene)

Appendix B: Effect of pH on rejection (10 wt. % Fe-NPs)

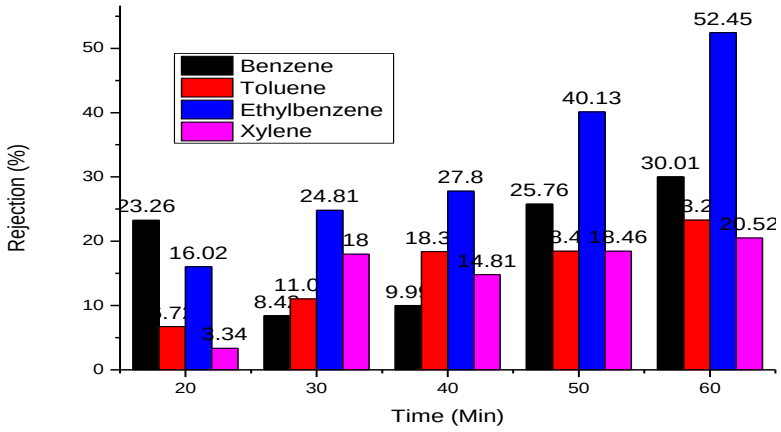


Figure B1: Effect of pH on BTEX rejection with 10 wt.% Fe-NPs

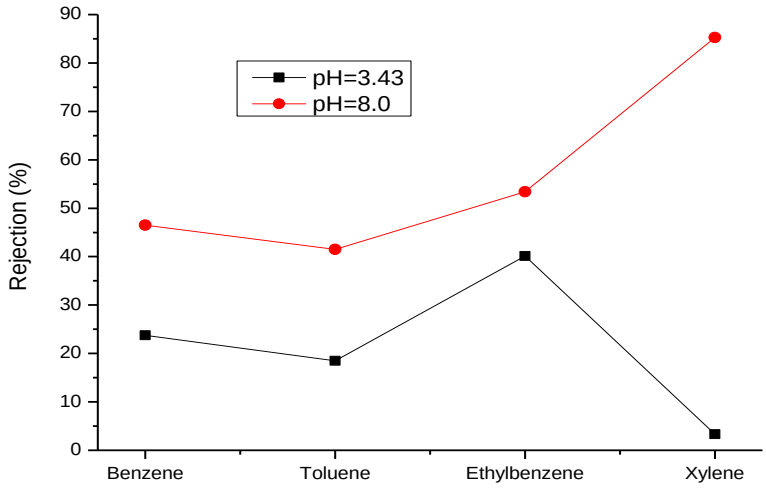


Figure B2: Effect of pH on BTEX Rejection