

**TiO₂ NANOPARTICLES-FUNCTIONALIZED POLYMERIC
MEMBRANES FOR WATER TREATMENT**

MS in Biomedical Sciences



By

MARYAM HINA

NUST201260461MSMME62412F

Supervisor: DR. NASIR M. AHMAD

Co-supervisor: DR. MUHAMMAD NABEEL ANWAR

Department of Biomedical Engineering & Sciences
School of Mechanical & Manufacturing Engineering, SMME
National University of Sciences and Technology, NUST
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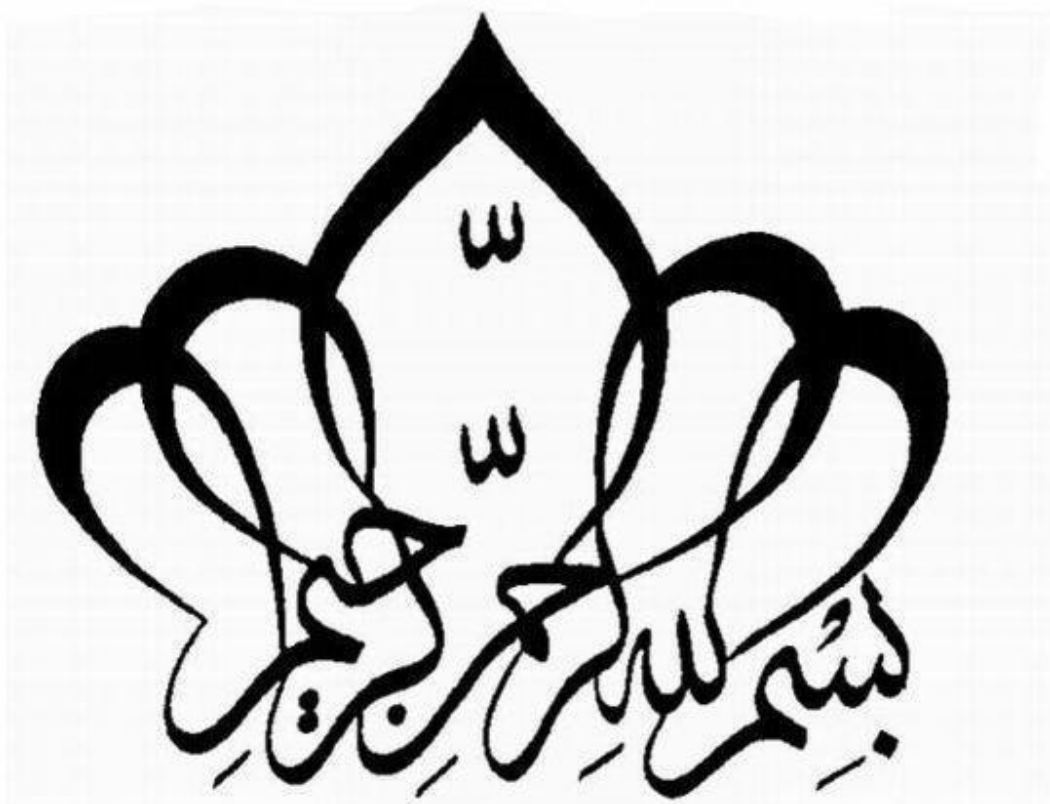
A thesis submitted in partial fulfilment of the requirements for the degree of
Master of Science in Biomedical Sciences

Supervisor: **DR. NASIR M. AHMAD**

Co-supervisor: **DR. MUHAMMAD NABEEL ANWAR**

Department of Biomedical Engineering & Sciences
School of Mechanical & Manufacturing Engineering, SMME
National University of Sciences and Technology, NUST
Islamabad, Pakistan

December, 2014





CERTIFICATE OF APPROVAL

Form TH-4

We hereby recommend that the dissertation prepared under our supervision by: Miss Maryam Hina (NUST201260461MSMME62412F) Titled: **TiO₂ Nanoparticles-Functionalized Polymeric Membranes for Water Treatment** be accepted in partial fulfillment of the requirements for the award of **MS** degree

Examination Committee Members

Name: Dr. Syed Omer Gillani

Department: SMME

Signature: _____

Name: Dr. Umar Ansari

Department: SMME

Signature: _____

Name: Dr. Muhammad Bilal Khan

Department: CES

Signature: _____

Supervisor: Dr. Nasir M. Ahmad

Signature: _____

Co-Supervisor: Dr. Muhammad Nabeel Anwar

Signature: _____

Head of Department

Date

COUNTERSIGNED

Date: _____

Dean/Principal

DEDICATION

This thesis is dedicated to my parents, my siblings and fiancé.

For their unconditional support, heed, affection, endurance and
reassurance

DECLARATION

It is hereby declared that this research study has been done for partial fulfillment of requirements for the degree of Master of Science in Biomedical Sciences. This work has not been taken from any publication. I hereby also declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Maryam Hina

ACKNOWLEDGEMENT

“And if you would count the favors of Allah, never could you be able to count them. Truly, Allah is Oft-Forgiving, Most Merciful” [16:18]

I would like to thank Allah, the most Glorified, all the praise is for Allah, He is the Most Great and There is no power and no might except by Allah. All praises and thanks to Allah Almighty who gave me unbelievable strength to complete this research.

I am very thankful to my supervisor Dr. Nasir M. Ahmed and co supervisor Dr. Muhammad Nabeel Anwar for their tremendous supervision. Their support and encouragement during whole project help to overcome the complications of the project. Their guidance was really very supportive for me.

I am also very grateful to Sir Tahir (ASAB), Dr. Asim laeeq and Dr. Asad ul Khan from Comsats, for providing me opportunity to work in their lab, to utilize their resources during membrane work.

I would like to thank Dr. Syed Omer Gillani (SMME), Dr. Umar Ansari (SMME) and Dr. Muhammad Bilal Khan (CES) for serving as my committee members.

I am also very thankful to the Dr. Amir Habib (SCME), MS student Mr Tanveer (SCME) and Miss Zahra (IESE) for guiding me during nanoparticles synthesis. This project is completed because of the great cooperation of staff of Synthesis lab (SCME), Water lab (SCME) and ASAB labs.

Beside all these a very special and great thanks to my parents Zahida Perveen and Muhammad Zaman, I am here just because of their support, their day and night efforts for my higher studies are priceless. I would also like to admire my siblings Areeja, Junaid, Alishba and my fiancé Farhan, without their support and prayers I wouldn't be able to complete this degree.

Maryam Hina

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LIST OF ABBREVIATIONS

MMMs: Mixed Matrix Membranes

SEM: Scanning Electron Microscopy

UV: Ultra Violet

kJ: Kilo joule

PES: Poly Ether Sulfone

PVDF: Poly Vinylidene Fluoride

APTMS: 3-Amino Propyl Trimethoxy Silane

FTIR: Fourier Transform Infrared Spectroscopy

NMP: n-methyl-2-pyrrolidone

rpm: revolutions per minute

nm: nanometer

ml: milli liter

gm: gram

eV: electron Volt

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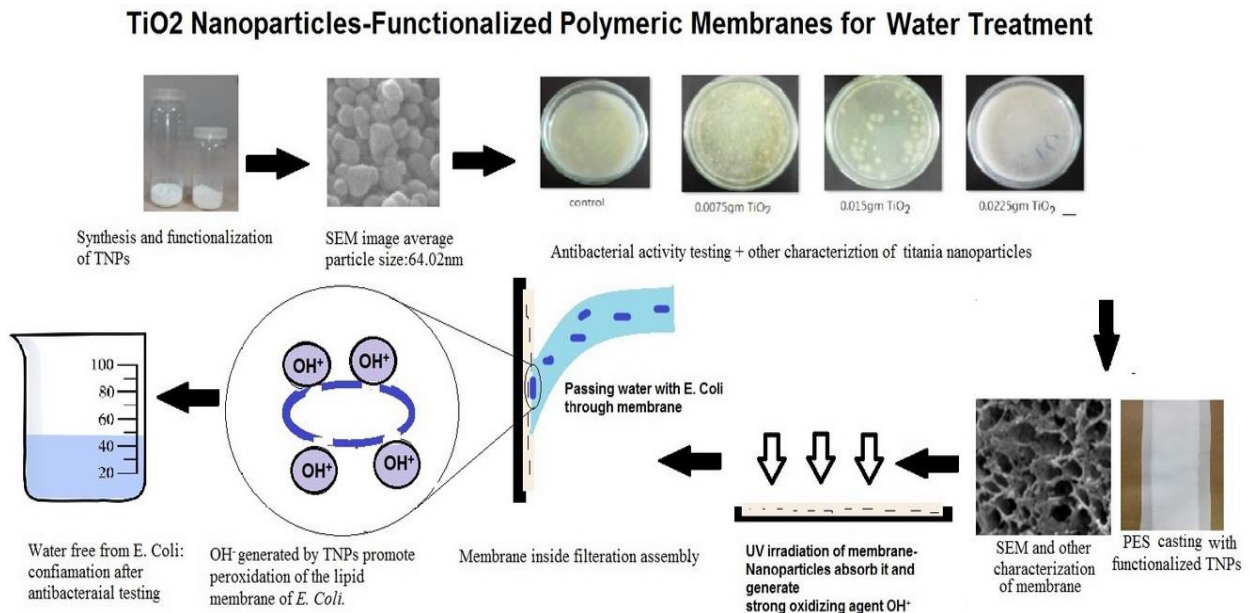
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ABSTRACT

One of the major challenges to public health in world is water pollution. In many developing countries the access to safe drinking water falls below acceptable levels. Bacterial contamination is one of the main causes of water pollution. Considering such important challenges, in the present study, antibacterial functionalized TiO_2 nanoparticles were prepared and incorporated into the polymeric membranes to enhance their water treatment capability. The morphology, surface chemistry as well as other important performance of membranes for water treatment such as antibacterial activity against *E. coli* and *MRSA* were investigated. TiO_2 nanoparticles were prepared and UV irradiated to activate their photo catalytic activity against bacteria. The phase inversion method was used to develop TiO_2 nanoparticles incorporated polyethersulfone (PES) flat-sheet mixed matrix membranes (MMMs). The antibacterial drug Ceftriaxone was also incorporated in selective membranes to evaluate its activity. The membranes were also exposed to UV light at intensity: 300W and wavelength: 320nm. The characterization of nanoparticles and membranes was done using different techniques like SEM, XRD, FTIR, TGA and DTA. By increasing the concentration of nanoparticles the membrane performance such as hydrophilicity, thermal stability, and water flow were enhanced while decrease in roughness and mechanical strength were observed. Both nanoparticles antibacterial activity as well as prepared membranes indicated that antibacterial activity is enhanced with the increase in nanoparticles concentration and UV exposure duration.



CHAPTER 1: INTRODUCTION

¹ A part of this chapter is submitted for publication in Journal of Membrane Science

1.1 Background

The safe drinking water is not available to about 1.2 billion people, 2.6 billion have slight or no sanitation while 3,900 children a day and millions of people die per annum from diseases spread through impure water (Shannon et al., 2008). Different issues related to water quality are the cause of water borne diseases. Along with chemicals, pesticides and other impurities, more than 100 types of pathogenic bacteria, protozoa and viruses are major cause of water contamination. As a result different diseases are spreading among the people. According to World Health Organization and UNICEF the increased unsafe water supply is mainly causing diarrhoeal diseases (Brewis, Gartin, Wutich, & Young, 2013). Different types of contaminants present in water can be categorized in the following table (Cartwright, 2013)

Table 1.1: Different types of contaminants present in water

Water contaminants	Examples
Suspended solids	Dirt, clay, colloidal materials, silt, dust, insoluble metal oxides, and hydroxides
Dissolved organics	Trihalomethanes, synthetic organic chemicals, humic acids, fulvic acids
Dissolved ionics (salts)	Heavy metals, silica, arsenic, chlorides, sulfates
Gases	Hydrogen sulfide, methane, radon, carbon dioxide
Microorganisms	Bacteria, viruses, protozoan cysts, fungi, algae, molds, yeast cells

1.2 Water pollution in Pakistan

One of the major threats to public health in Pakistan is water pollution. Pakistan is also included in those developing countries where safe drinking water access drops below acceptable levels. A study reported that quality drinking water is accessible to only 25% of the population (Sehar, Naz, Ali, & Ahmed). The rank of Pakistan concerning drinking water quality is at 80 among 122

nations. This is mainly because of poor management and monitoring of drinking water quality. The ground and surface water which are the main sources of water are contaminated by different sources mentioned in table 1. Human activities are also cause of these sources, like improper dispose of industrial, municipal, agrochemical wastes. Such wastes cause microbial and chemical pollutants to ride in the water and affect human health (Azizullah, Khattak, Richter, & Häder, 2011).

1.3 Traditional ways of water treatment

The removal of organic contaminants and micro-organisms can be done using different drinking water treatment processes (DWTP). Traditional water treatments employ various techniques including flocculation, coagulation, sand filtration, sedimentation, and chemical oxidation to remove contaminants, organic carbon microbes and other particles (Zeng et al., 2013).

1.4 Present study

Water treatment and water recycling play a steadily increasing role, with membrane technology constantly gaining market share, being applicable from small to large scales and to retain compounds with a variety of sizes (Jacangelo, Rhodes Trussell, & Watson, 1997). It has some inherent advantages such as porosity, pore size and hydrophilicity. The performance of polymeric membranes can be further enhanced by the incorporation of tasks specific nanoparticles. TiO_2 are one of the particles, that if added to membrane, increase hydrophilicity, permeability and antifouling properties of the membrane. These nanoparticles are preferred because of their super-hydrophilic and photo catalytic effects. (Blake et al., 1999; Rahimpour, Jahanshahi, Mollahosseini, & Rajaeian, 2012; Yan, Wang, Yao, & Yao, 2013). The TiO_2 nanoparticles can be used in killing of bacteria or degradation of chemicals utilizing their photo catalytic behavior with UV light. (Rahimpour et al., 2012; Tsuang et al., 2008). The photo catalysis provide hygienic environment for water disinfection process (BHATI, TAK, SHARMA, & AMETA, 2013).

The influence of TiO_2 particles in altering the membrane properties was studied by several researchers (Kwak, Kim, & Kim, 2001; J. B. Li, Zhu, & Zheng, 2007; María Arsuaga et al., 2013; Rahimpour et al., 2012). Rahimpour et al prepared PVDF membrane using sulfonated polyethersulfone (SPES), TiO_2 nanoparticles and polyvinylpyrrolidone (PVP) in the casting solution. The long term stability of flux, antibacterial and antifouling properties were enhanced

in the membrane. The membrane showed good antibacterial results when exposed to UV light because of photo catalytic property of TiO_2 nanoparticles (Rahimpour, Jahanshahi, Rajaeian, & Rahimnejad, 2011). In another study the antifouling properties of membranes were enhanced by adding TiO_2 nanoparticles onto the sulfonated polyethersulfone membrane surface by self-assembly. The contact angle analysis indicated increased hydrophilicity of the membrane because of nanoparticles addition in it. It was also observed that this membrane prevent its fouling from hydrophobic substances (Luo, Wen, Liu, Liu, & Jia, 2011).

In this study, polyethersulfone (PES) was chosen as the polymer for membrane synthesis because of its specific properties such as high heat distortion temperature and high mechanical properties. It has good heat and environment resistance capacity. The hydrophobic nature of this membrane decreases the membrane flux and increases the fouling of membrane (Luo et al., 2011; Shariatmadar & Mohsen-Nia).

1.5 Objectives of the study

The objectives of the present study are

- To prepare TiO_2 nanoparticles incorporated antibacterial PES membranes with hydrophilic nature that can also eliminate bacteria present in water.
- To explore the morphology, surface chemistry as well as other important performance of membranes for water treatment.

To achieve this objective, TiO_2 nanoparticles were prepared and added in the PES matrix. In the first step synthesis, characterization and antibacterial testing of TiO_2 nanoparticles were carried out. The functionalized TiO_2 nanoparticles were then incorporated into PES to prepare TiO_2 nanoparticles functionalized polymeric membranes for water treatment.

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CHAPTER 2

TITANIUM DIOXIDE NANOPARTICLES: Synthesis and Characterization

² A part of this chapter is submitted for publication in Journal of Membrane Science

2.1 Literature review

Nanotechnology has a great impact on world. This technology embraces macromolecular entities, quantum dots, macromolecules, molecules and atoms. Every aspect of human life is renovated by nanotechnology by enhancing quality of products and improving research and development area (Davies, 2008). This technology has impact on commercial and consumer industries like clothing, food, cosmetics and water purification processes. There has been a marvelous growth of nanoparticles in different applications like drug delivery, antibacterial materials and electronics (Jones & Ogden, 2013). According to the National Science Foundation, within next decade the nanotechnology is most likely to become a \$1 trillion industry.(Wiesenthal, Hunter, Wang, Wickliffe, & Wilkerson, 2011).

In October 2011 the European Union defined nanomaterial's as "a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or agglomerate; where 50% or more of the particles exhibited, one or more external dimensions in the size range 1–100 nm" (Gogos, Knauer, & Bucheli, 2012). Nanoparticles are mostly well-defined as particle whose one dimension is less than 100nm (Christian, Kammer, Baalousha, & Hofmann, 2008). The fine particles and NPs of same composition have usually different physicochemical properties. The number of atoms on particle surface increases with decrease in size of NPs. Since surface properties of such particles are different from interior, such as energy level, reactivity and electronic structure (Shi, Magaye, Castranova, & Zhao, 2013).

2.1.1 Titanium

Titanium (Ti) is widely distributed, ninth utmost abundant element on the earth's crust. Earth contain about 4400 mg/kg average concentration of Ti on its crust (0.63% of the Earth's crust). The Ti is not found in metallic state because of its higher affinity for different elements especially oxygen and other elements(S. M. Gupta & Tripathi, 2011; Shi et al., 2013). The British clergyman William Gregor discovered Titanium in 1791. It was produced from mineral menachanite. Titanium word was given to this oxide of metallic element by Klaproth. In 1946 the metal was commercially prepared by Kroll (Christie & Brathwaite, 1998). Some of its properties are listed in Table 2.1.

Table 2.1: Properties of Titanium (Christie & Brathwaite, 1998).

Low density
Corrosion resistance
Good strength
Very low thermal conductivity
very low electrical conductivity
Strong like steel
45% lighter than steel and 60% heavyweight than aluminum
Coefficient of expansion is lower than aluminum and steel alloys
Ductile and malleable
Brittle upon addition of other elements

2.1.2 Titanium dioxide nanoparticles

Naturally occurring oxide of Ti is TiO₂ also known as titanium oxide, titania, titanian anhydride. It is odorless and noncombustible powder. It has melting point of 1843°C, boiling point of 2972°C, molecular weight of 79.9 g/mol. The density of these particles is 4.26 g/cm³ at 25°C (Shi et al., 2013). TiO₂ belongs to transition metal oxides family. The four most common polymorphs of TiO₂ present in nature are: tetragonal anatase, orthorhombic brookite, tetragonal rutile, and monoclinic TiO₂ (S. M. Gupta & Tripathi, 2011; Wiesenthal et al., 2011).

2.1.3 Phases of TiO₂ nanoparticles

The three most common phases anatase, brookite and rutile have different properties. In bulk material the rutile is more stable phase; however, when TiO₂ is prepared using solution-phase preparation methods the anatase structure is more stable. It has been found that rutile and brookite have surface energy higher than anatase. (Reyes-Coronado et al., 2008) Reactants used during synthesis also determine the phase formed. The precursor chemistry determines the growth and nucleation of different polymorphs, all of this ultimately contribute in the crystal structure stability. Another complicated factor is the experimental conditions used in synthesis of different phases (Cheng, Ma, Zhao, & Qi, 1995)

2.1.3.1 Rutile

The most stable form of titanium dioxide is rutile. It is one of the major ore of titanium discovered in 1803 by Werner in Spain. The word rutile is derived from the Latin rutilus which means red. The color of this phase is reddish brown but also sometimes bluish, yellowish or violet. It is slightly transparent to opaque. Rutile may encompass iron (up to 10%), and also other impurities such as niobium, tantalum, vanadium, chromium and tin. Distinguished countries in which it is present are African countries, Swiss Alps, Brazil and the USA (Carp, Huisman, & Reller, 2004).

Rutile TiO₂ has 6 atoms per unit cell, a tetragonal structure. At most temperatures and pressures up to 60 kbar this phase is stable. The brookite and anatase structures transformed into the rutile phase after attaining a definite particle size, for particle sizes greater than 14 nm the rutile phase become more stable than anatase. When the rutile phase is attained, it grew much rapidly than the anatase. It can be active or inactive depending on its preparation. The rutile phase is a poor as photocatalyst. (S. M. Gupta & Tripathi, 2011).

This phase is important for powder or polycrystalline materials because of the low surface energy of its three main crystal faces. These are (110) (100) and (001). The face 110 is mostly studied as it is the most thermally stable form. It has rows of bridging oxygen in it, associated with only two Ti atoms. This phase is the most stable phase for particles above 35 nm in size (Fujishima, Zhang, & Tryk, 2008).

2.1.3.2 Brookite

It was discovered in 1825 at Snowen (Pays de Gales, England) by A. Levy. It was named as Brookite in honor of the H.J. Brooke an English mineralogist. The crystals of this phase are dark brown to greenish black opaque. Crystals have pseudo hexagonal outline with tabular to platy shape. Minerals associated with this phase are anatase, quartz, rutile, chalcopyrite, feldspar, sphene and hematite. Distinguished countries in which it is present are Austria, Russia, Switzerland and USA (Carp et al., 2004).

Brookite TiO₂ belongs to the crystal system which is orthorhombic. Its unit cell is shaped by edge-sharing of TiO₆ octahedra, single unit is composed of 8 TiO₂ formula units (S. M. Gupta & Tripathi, 2011). This form is most stable for 11–35 nm nanoparticles. In recent times, the

brookite phase, most difficult to prepare and rare form, is investigated as a photocatalyst. The crystal faces in order of stability are (010) < (110) < (100) (Fujishima et al., 2008)

2.1.3.3 Anatase

It was discovered in 1801 was named by R.J. Haüy. It was initially called as octahedrite. The word anatase is derived from the Greek word ‘anatisis’ that means ‘extension’, owing to its longer vertical axis as compared to rutile. It is associated with feldspar, rock crystal and axinite in crevices (Carp et al., 2004)

Anatase TiO₂ also has a tetragonal structure but the distortion of the TiO₆ octahedron is slightly larger for the anatase phase. The energy difference between anatase and rutile phases is small (~2 to 10 kJ/mol) and at 0 K the anatase phase is more stable than the rutile. This phase has lower density, higher electron mobility but low dielectric constant, these properties make this phase superior over other phases so ultimately it is preferred for solar cell applications. The higher degree of hydroxylation in the anatase phase, slightly higher Fermi level and lower capacity to adsorb oxygen increases its photoreactivity (S. M. Gupta & Tripathi, 2011).

Anatase is the most stable phase for 11 nm below nanoparticles. Anatase are similar with natural crystals because of two low energy surfaces, (101) and (001). The (100) surface is less common on typical nanocrystals but is observed on rod-like anatase grown hydrothermally under basic conditions (Fujishima et al., 2008)

2.1.4 Synthesis of TiO₂ nanoparticles

Mostly TiO₂ nanoparticles synthesis is through titanium salt hydrolysis in acidic solution. The nucleation from sol-gel or chemical vapor condensation can control the shape size and structure of the TiO₂ nanoparticles. TiO₂ nanomaterials (tubes wires and particles, tubes, wires) are usually coated with silicon, aluminum and polymers to prevent aggregation and increase photostability (Weir, Westerhoff, Fabricius, Hristovski, & von Goetz, 2012). The synthesis of TiO₂ nanoparticles using low-valent organometallic precursors has been reported at low-temperature reaction. Reaction of bis- (cyclooctatetraene) titanium with dimethyl sulfoxide in organic solution produced TiO₂ at room temperature. Amorphous titania powder was precipitated in the absence of any supporting ligand (Tang et al., 2005). The hydrothermal treatment using CTAB can also be utilized to prepare these nanoparticles. The 17.6 nm diameter and 2.1 nm

mean pore size of particles was obtained in this experiment. Calcination temperature was 400 °C (Peng, Zhao, Dai, Shi, & Hirao, 2005). In another research spherical nanometer-size nanoparticles with average diameter of about 683 to 50 nm were obtained using glycolated precursors in the synthesis (Pal, García Serrano, Santiago, & Pal, 2006). The production of amorphous titania can be done by adding titanium (IV) isopropoxide in water (low concentration) and ethanol. The hydrothermal heating of amorphous titania with water and NaOH for 48hours at 200 °C. XRD pattern showed particle radius of pure brookite >30 nm. The radius of these anatase particles was 3.5 nm (Oskam & Poot, 2006). The drop wise addition of Titanium isopropoxide (1.5-15 mmol) in mixed water solution and ethanol (150ml) was carried out in another experiment. The nitric acid was then used to adjust solution pH in the range of 0.7. The clear Ti precursor because of acidic environment is then subjected to glass-lined hydrothermal bomb for 4hours at 240 °C, the crystallized TiO₂ nanoparticles were formed after hydrothermal reaction in the colloidal suspension form. The particle size obtained after this reaction was 7-25 nm. The vacuum-drying of sample at room temperature was then performed to get powdered TiO₂ nanoparticles (Chae et al., 2003). In another similar experiment titanium tetraisopropoxide controlled hydrolysis was performed for TiO₂ nanoparticles synthesis. The Ti(OCH(CH₃)₂)₄ (1.25ml) + absolute ethanol (25 ml) was added dropwise in distilled water (250 ml), whose pH is adjusted by nitric acid to 1.5. Stirring of solution was done overnight until transparent and clear colloidal solution was formed. The evaporation of solution in rotavapor at 358 °C was carried out and finally TiO₂ in powdered form was obtained after oven drying TiO₂ nanoparticles prepared via sol-gel synthesis of titanium isopropoxide. The mean diameter of the TiO₂ powder is less than 10 nm (Kim, Kwak, & Suzuki, 2006). Amusingly TiO₂ NPs can be formed by anodization Ti wire in a KCl aqueous solution. In a 1 M KCl aqueous solution + Ethylene glycol (99.2 wt. %) + NH₄F (0.5 wt. %) + de ionized water (.3 wt. %) anodization of Ti was conducted. First step involves cleaning of Ti sheets and wires was performed by their sonication in isopropyl alcohol, acetone and methanol. Sonication duration was 10min for each solution. Then rinsing with distilled water and drying with nitrogen gas was performed. Two electrode system was established using anode of Ti wire and cathode of platinum plate for anodization. The 12 to 15 V voltage range was set and kept constant using a DC power source. The particles formed were collected using centrifuge and washed with DI water. At 450 °C annealing was carried out for 2 hours at about 3 °C/min heating rate. Then finally at room

temperature the particles were cooled down. The TiO₂ NPs are spherical in shape and the average diameter of the particles calculated from the HRTEM images is ~7 nm. (Ali, Kim, Kum, & Cho, 2013).

2.1.5 Photoactivity of TiO₂ nanoparticles

One of the most attractive property of TiO₂ is its photoactivity (Fujishima & Zhang, 2006). The electron hole pair created through irradiation of light, in the TiO₂ itself or adsorbed molecules and then the resulting electron transfer or chemical reaction form the basis of many TiO₂ based photodevices and other properties dependent on it. This passionate research was commenced by Fujishima and Honda's discovery that water can be split into oxygen and hydrogen through photo catalytic reaction (Diebold, 2003).

An energy band gap of 3.2 eV is present in Anatase with 86 nm an absorption edge, this is present in the near UV range. While rutile has energy band gap of 3.02 eV slightly narrower than anatase and it has an absorption edge of 416 nm in the visible range. These forms of TiO₂ are photocatalytic (Lan, Lu, & Ren, 2013). The UV light is absorbed by TiO₂ when it is exposed to UV light of 280–400 nm (3.10 – 4.43 eV) wavelength as a result from a valence band an electron is raised up to the conduction band of TiO₂, as a result a hole is formed in the valence band, as shown in Figure, and electron–hole pairs are generated. So in chemical reactions and other applications like photovoltaic solar cells for electricity generation used this property of TiO₂ which is called photocatalysis. Mostly for enhanced photo-induced performances, TiO₂ surfaces are utilized and reactive species are adsorbed over them in these photo-activated applications. The photo activated performances are lowered when e⁻ and h⁺ usually recombine on TiO₂ clean surfaces. This can be blocked by adsorbed species present on TiO₂ surfaces, active radicals are formed when electrons e⁻ and holes h⁺ are transferred to the adsorbed species (O₂, OH⁻, etc.) (Lan et al., 2013; Yan et al., 2013)

The heterogeneous photocatalysis (photocatalyst is in close contact with liquid or gaseous reaction medium, the photocatalyst is then exposed to light excited state, as a result redox reaction or molecular transformations are initiated) with TiO₂ is preferred over other processes oxidizing contaminants because of following reasons:

- Photocatalyst is a low-cost material

- Mild operating conditions (room temperature, atmospheric pressure) are sufficient for fast reaction.
- A wide-ranging spectrum of organic contaminants can be converted to CO₂ and water.
- Chemical reactants are not required and there will be no resulting side reactions (Benedix, Dehn, Quaas, & Orgass, 2000).

2.1.6 TiO₂ nanoparticles applications

TiO₂ nanoparticles have been applied in photocatalytic water splitting (Ni, Leung, Leung, & Sumathy, 2007), photocatalytic self-cleaning (Benedix et al., 2000), purification of pollutants (McCullagh, Robertson, Bahnemann, & Robertson, 2007), photo-induced super hydrophilicity (Fujishima & Zhang, 2006), photocatalytic antibacterial as well as in photolithography and photochromism applications (Fujishima et al., 2008; Tsuang et al., 2008).

2.1.6.1 Self-cleaning

After discovery of soap, the low contact angles form the base for cleaning procedures. Mostly the surface tension of water is lowered by detergents which then lowered the contact angles. Another option to create low contact angle is to form active thin films on materials surfaces. The active thin films can be formed using active metal oxides or sulfides. TiO₂ coated materials can be used for this purpose. Very low contact angle <1 degree can be obtained when anatase TiO₂ is exposed to UV light. The unique water attracting property instead of water repelling make TiO₂ beneficial over other materials. Instead of staying over the surface in form of droplet, the water spread over the surface in form of sheets (Benedix et al., 2000).

This photo induced hydrophilicity has also increased the TiO₂ -coated materials application range. For example TiO₂ surface with adsorbed stains can be clean easily because of soaking of water between highly hydrophilic TiO₂ surface and stain. So TiO₂ -coated materials are used “photocatalytic building materials” mostly outdoors where they are bare to rainfall show a very efficient self-cleaning purpose, i.e., stains are washed by rainwater as well as partially decomposed by the conventional photocatalytic reaction. The materials in which this property is commercialized are glass, exterior tiles, and PVC fabric and aluminum walls. For example, on Chubu International Airport terminal building, in 2005 the photocatalytic exterior glass with an area of 20,000m² was installed (Hashimoto, Irie, & Fujishima, 2005).

2.1.6.2 Antifogging surfaces

The humid air condenses on the surface of glasses and mirrors, which forms water droplets over the surface results into fogging. To prevent this problem superhydrophilic surfaces are used, these surfaces spread water over them in form of flat sheets and no water droplets of fog can stay over the surface, this will then prevent the scattering of light from surface. In case of less humidity the layer formed on water surface will be thin which may evaporate from the surface quickly. If normal mirror is compared to mirror with TiO₂ superhydrophilic coatings it was observed that normal mirror will fog much quickly as compare to other one, in which clarity level retains for more time (Fujishima, Rao, & Tryk, 2000).

2.1.6.3 Air cleaning

Indoor air pollutants which mostly cause health problems are Volatile organic compounds (VOCs) which human breath (WHO, 1989; USEPA, 1990). These are mostly the cause of sick building syndrome (SBS) including headache, fatigue and irritation of mucous membrane. One of the advanced technology for the economical and quick removal of VOCs is photocatalytic oxidation (PCO). This technique of PCO mostly utilizes ultraviolet (UV) light and nano-semiconductor catalysts, to convert indoor organic compounds into odorless and benign components— carbon dioxide (CO₂) and water vapor (H₂O). The nano-titania (TiO₂) catalyst is mostly used in PCO that is stimulated by UV light (Mo, Zhang, Xu, Lamson, & Zhao, 2009). In another experiment hydrothermal method was used to prepare TiO₂ photocatalyst using titanium isopropoxide as a precursor. Decomposition of organic material and killing of germs occur because of photocatalyst film on the filter of the air purification device. the free germs in the air were sterilized when device was installed in hospitals (J.-H. Kim et al., 2006).

2.1.6.4 Self-sterilizing surfaces

In 1995, Fujishima and co-workers observed that TiO₂ surfaces upon UV light illumination showed a manifest change in the water wettability of the TiO₂ surface. When exposed to UV light the TiO₂ surface becomes hydrophilic which originally shows contact angle of quite a few tens of degrees is decreased and finally reached to zero. Now the surface reaches the level of superhydrophilicity which can be used in formation if antifogging glasses and mirrors. This property when combine with oxidative property of TiO₂ help in self-cleaning of walls and mirrors (Nakata, Ochiai, Murakami, & Fujishima, 2012). This effect can also be utilized in

medical area like surface modification of this catalyst by sulfuric acid solution help in its coating on silicone catheters. Then UV illumination can also kill bacteria present inside or outside silicone catheters. These self-cleaning and self-sterilizing TiO₂ coated silicone catheter can be used practically (Ohko et al., 2001). This was also confirmed in another study in which TiO₂ - coated silicone catheters were simply disinfected under certain light sources and were revealed to be harmless in an trial using cultured cells and in animal testing (Sekiguchi et al., 2007).

2.1.6.5 Heat transfer and heat dissipation

In a heat transfer system CHF (Critical Heat Factor) cause limitation in the heat transfer and thus its enhancement is openly associated to the system performance. One solution to this limitation has been researched. The superhydrophilicity caused by coating of surface by TiO₂ increases the wettability which causes CHF enhancement by two factor (Jeong, Chang, & Chang, 2008). This was also observed by Kim and Kim that nanofluids like titania or alumina-water can be used for CHF enhancement (Kwark, Moreno, Kumar, Moon, & You, 2010). In another experiment comparison study was carried out comparing hydrophilicity of surface with and without titania. The contact angle decrease upon UV illumination was observed in titania coated surface. The relation of heat transfer and high wettability was confirmed using experiment on single water droplet evaporation and pool boiling. Both surface mentioned above were studied in each experiment. It was concluded that critical heat flux and Leiden- frost temperature was higher in TiO₂ coated surface (Takata et al., 2005; Takata, Hidaka, Masuda, & Ito, 2003). The critical heat flux (CHF) and nucleate boiling of FC-72 dielectric liquid and water were also investigated on surface modified with FC-72 dielectric liquid. 50.4% CHF enhancement was observed for water while for FC-72 it was 38.2% and consequently designated that enhancement in boiling performance is determined by the improvement in wettability (Wu et al., 2010).

2.1.6.6 Anti-corrosion applications

Novel silane/TiO₂ bifunctional hybrid films were prepared in an experiment; these films provide protection against metal corrosion in presence and absence of UV irradiation. On stainless steel substrates, the protective bis-[triethoxysilylpropyl]-tetrasulfide silane was prepared, silane help in proper and good dispersion of TiO₂ particles on substrate surface. Noteworthy improvement in the photocathodic protection under ultraviolet irradiation was observed (Liang Liu, Hu, Leng, Zhang, & Cao, 2007). TiO₂ -based photoelectrochemical system can also be used for anti-

corrosion purpose. Cathode protection is provided by a TiO₂ electrode which act as photoanode and a steel cathode. In a hole scavenging medium a TiO₂ electrode provide conduction band electrons to an electrode of steel, this will cause potential shifting towards negative values. This help assembly is also dependent on UV irradiation for proper working (Park, Kim, & Choi, 2002). In another experiment corrosion resistance was observed in steel coated with TiO₂ nanoparticle in dark because of ceramic protective barrier and under UV illumination a photo-generated cathodic protection current was seen (Shen, Chen, & Lin, 2005).

2.1.6.7 Photo catalytic lithography

This application utilizes the remote oxidation property of TiO₂. For remote oxidation of organic film it is placed in front of TiO₂ -coated glass plate. The irradiation with UV light will form active oxygen species (HO•) on TiO₂ surface that causes decomposition of aliphatic and aromatic substances into CO₂. This can be used for etching, modification, and patterning of solid surfaces. A solid surface needed to be modified is placed in front of thin TiO₂ film, through a photomask the film is irradiated only irradiated region is excited while the other region remain unexcited ("Patterning of Solid Surfaces by Photocatalytic Lithography Based on the Remote Oxidation Effect of TiO₂," 2002). In another experiment the small gap between TiO₂ coated film mask and organic or inorganic substrate was 12.5-100 μm to achieve resolution of 10 μm and patterning time observed was 10 min. The patterning could be done on methyltriethoxysilane-, Heptadecafluorodecyltrimethoxysilane-, and octadecyltriethoxysilane- coated glass plates, copper plate and silicon plate (Kubo, Tatsuma, Fujishima, & Kobayashi, 2004). The well-defined micropatterns can also be constructed by using a combine approach in first step self-assembled and electrochemical techniques were used to fabricate superhydrophobic TiO₂ nano- tube film then in second step the film is exposed to UV light through photomask, it will photocatalyse the organic monolayer assembled on the surface of TiO₂ nanotube (Lai et al., 2008).

2.1.6.8 Photochromism

Under UV light on the nanoporous TiO₂ films the reduction of Ag⁺ to Ag nanoparticles can done through photoelectrochemical reduction. Multicolor photochromism can be seen in these Ag-TiO₂ films. The film color changes from brownish-gray to the color of light in visible light while this color is reverted back into brownish-gray upon UV irradiation. The multicolor photochromic

behavior can be control by irradiation conditions regulating as well as matrix materials and geometry of nanopores (Naai, Ohko, & Tatsuma, 2004).

TiO₂ when combine with WO₃ colloids can improve their photochromism. This will increase the total electron number generated in the system because of photo responsive behavior of TiO₂. This will also help in higher accumulation of electrons in WO₃. The photogenerated electrons increase so coloration process enhanced and eventually improved photochromism can be seen (He et al., 2002).

2.1.7 Different forms of TiO₂ used in water treatment

Photocatalysis of titania is proved to be an efficient way for removing variety of microbes and chemicals from drinking water. TiO₂ photocatalyst aqueous suspensions can be used for this purpose. The stirring is recommended to avoid the settlement of catalyst as well as proper contact between target specie and titania can be ensured. Sonication is also used which increase bacterial destruction by increasing intracellular damage (McCullagh et al., 2007). In another experiment complete killing of an Escherichia coli suspension (150 microliter) when place on TiO₂ coated glass plate was observed when illuminated for one hour. The endocrine-disrupter chemicals (EDCs) in water can also be photocatalytically decomposed. Natural estrogens of 17 β-estradiol (E2) and estron (E1) are elementary female sex hormones and even at very low concentrations ($\sim 10^{-9}$ M) they exhibit potent estrogenic activity, it has a great effect on wildlife propagation. Under weak illumination TiO₂ photocatalysts can decompose these two compounds (E1 and E2). In this experiment photocatalytic reactor was designed using photocatalyst TiO₂-modified- PTFE mesh sheets, and this was used to treat the water discharged from the sewage treatment plant 'Kitano' of the Tama River near Tokyo. The discharged water contained concentrations 140 and 15 ngL⁻¹ of E1 and E2, respectively. Under UV illumination (1.2mWcm⁻²), decomposition of E1 occur in very short time, so for water treatment TiO₂ photocatalysis can be useful as an innovative method for eliminating synthetic and natural estrogens efficiently, devoid of producing biologically active intermediates (Fujishima, Zhang, & Tryk, 2007)

Doping of TiO₂ with different metals and nonmetals can be done to increase region of photoactive wavelength. TiO₂ nanoparticles co doped with Fe and N showed increase wavelength

and photocatalytic activity that help in more degradation of methylene blue (Fan, Liu, Hong, & Zhang, 2009).

Organic pollutants can be degraded using heterogeneous photocatalysis. The Ag@ TiO₂ core-shell structured nanoparticles can be used for purification of dyeing waste water. The AY-17 dye can be degraded by solar photocatalysis. Ag core stores electrons in it which prevent the recombinations of holes and electrons (Khanna & Shetty, 2013). When the surface of TiO₂ is doped with gold/ gold ions the electron/holes recombination is eliminated as a result MB photooxidation increased. (X. Z. Li & Li, 2001)

The TiO₂ microsphere can also be used for water purification, then can be reused more than 50 times. They can conduct efficient photo oxidation in water suspension and then can be removed easily from treated water (X. Z. Li, Liu, Cheng, & Tong, 2003).

In another study, an innovative E-H₂O₂/TiO₂ (E-H₂O₂) electrogenerated hydrogen peroxide) photoelectrocatalytic (PEC) oxidation system was efficaciously developed for treatment (X. Z. Li & Liu, 2005).

Another system developed for water treatment consists of a photocatalytic and an electrochemical oxidation unit, with TiO₂ photocatalyst and a boron-doped diamond (BDD) electrode respectively. This system can purify 12 L/day water (Ochiai et al., 2010). TiO₂ nano rod spheres prepared using non-hydrothermal method can be used for photocatalytic killing of bacteria and elimination of contaminants. TiO₂ nanorod spheres that showed maximum antibacterial activity were obtained after calcination at 500°C (Bai, Liu, Liu, & Sun, 2013).

A chemical vapour deposition (CVD) approach can be used for synthesis of composite TiO₂ nanofiltration (NF) membranes they can be used to degrade methyl orange. These membranes also showed high water permeability (Romanos et al., 2012)

In polyester fiber production plant the low cost polyester filter cloth (22 mm) can be coated with TiO₂/polyvinyl alcohol (PVA) that can form a composite membrane that can be used to remove nitrate and ammonium for water reusing purpose. The interaction between polyester and PVA was enhanced because of the nano-TiO₂ that could be helpful in decreasing fouling (L. Liu, Zhao, & Yang, 2012).

The lower band-gap energy TiO₂ can be produced by doping it with nitrogen. This TiO₂ can respond to visible light and absorbance can extend up to 600nm in visible region. Doping can be done at molecular level for enhanced nitrogen concentration (21.8%). This nitrogen doped TiO₂ showed good properties when compared with commercially available Degussa P25. Antibacterial activity and degradation of chemical compound (Acid Orange 7 (AO7)) was enhanced in case of doped TiO₂, so this form of these particles is good for disinfection and waste water treatments (Y. Liu, Li, Qiu, & Burda, 2006). The nitrogen doped titania nanoparticles is used for photocatalytic degradation of three azo dyes in another experiment. The dyes were reactive black 5 (RB5), procion red MX-5B (MX-5B) and acid orange 7 (AO7). The results obtained were consistent with above study (Y. Liu, Chen, Li, & Burda, 2005).

Another use of these nanoparticles is their immobilization on silica surface that can be helpful in catalyst separation in aqueous environment after the photocatalytic reactions. The amorphous silica support used in this study was compared with the mesostructured silica SBA-15 that forms a well-organized structure in which the mesoporous channels contain TiO₂ crystals of alike sizes in the support. This modified structure has increased activity up to eight times as compared to the Degussa P25 TiO₂. This means that the textural properties of the silica support have great impact on the catalytic activity of immobilized TiO₂ photocatalysts (López-Muñoz, Grieken, Aguado, & Marugán, 2005)

The interior free spaces of TiO₂ nanotube can be filled with different useful materials such as enzymes, chemical compounds and noble metals. TiO₂ nanotube photocatalyst with p-n junction has been prepared by this research group. The photocatalyst particle with two separate reduction and oxidation surfaces was coated on HEPA filters. The destruction rate of toluene in air was determined. The much higher photocatalytic destruction rate by the p-n junction nanotube catalyst was observed as compared to the commercially available, non-nanotube and nanotube structured material (Chen, Crittenden, Hackney, Sutter, & Hand, 2005).

2.2 EXPERIMENTAL WORK

For TiO₂ nanoparticles synthesis the titanium oxide anatase (general purpose reagent) was obtained from 'Daejung'. APTMS used to functionalized titania nanoparticles was acquired from Aldrich. Deionized water was used throughout experiment. All chemical were used without further purification unless specified.

2.2.1 Synthesis of TiO₂ nanoparticles

Liquid impregnation method was used for synthesis of TiO₂ nanoparticles.

2.2.1.1 Protocol 1:

1. 3 grams of TiO₂ precursor were added in 100ml deionized water. The solution was stirred using magnetic stirring for 48 hours with 5 times sonication of 30min during this duration
2. The solution was placed for 12 hours for settling down
3. It was then placed in oven for 12hours at 105 °C
4. The calcination of the resultant material was carried out in the furnace at 400 °C for 6 hours

2.2.1.2 Protocol 2:

1. 5gm were added in 150 ml deionized water. The solution was stirred using magnetic stirring for 36 hours with sonication of 30min during this duration
2. The solution was placed for 12 hours for settling down.
3. After that washing was done using ethanol and distilled water (50ml:50ml) at 45000 rpm for 30min.
4. The supernatant was kept in another beaker
5. It was then placed in oven for 24 hours at 105 °C
6. The calcination of the resultant material was carried out in the furnace at 400°C for 6 hours

2.2.1.3 Functionalization of nanoparticles

1. Functionalization of particles was done to prevent their agglomeration in the membrane, this technique ensures the proper distribution of particles in the membrane. Following steps were followed to functionalize the above prepared particles.

2. The 2 grams of nanoparticles were added in 100ml chloroform
3. Sonication of solution was then carried out for 30min
4. 6ml APTMS was added in this solution and again sonication was done for 5 hours
5. Magnetic stirring was then done for 1hour at 70°C to properly disperse nanoparticles
6. Centrifugation was also carried out for 30min at 400 rpm to disperse particles and remove solvent from solution
7. The resulting solution was then oven dried for 12 hours at 80°C
8. FTIR was performed to confirm presence of amine group over the particles surface

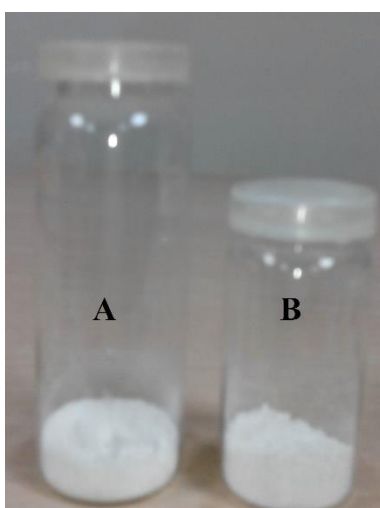


Figure 2.1: A)TiO₂ nanoparticles B)Functionalized TiO₂ nanoparticles.

2.2.2 Characterization of nanoparticles

2.2.2.1 SEM analysis

SEM (Scanning Electron Microscopy) Joel JSM 6490A was used to analyze surface, shape and size of nanoparticles.

2.2.2.2 XRD analysis

The XRD (Model Theta Theta STOE Germany) was done to determine the purity and phase of nanoparticles. It was done to check out purity of samples, means how much percentage of titania nanoparticles are present in the sample. This test identify crystal phase of nanoparticles and also provide the size estimate of crystallite. This technique also provides the peaks and values in percentage of other impurities present in the sample. Nanoparticles sample was directly used for analysis.

2.2.2.3 FTIR analysis

FTIR (FT-IR Perkin Elmer Spectrometer, spectrum 100) was performed before and after functionalization of particles to confirm the presence of amine group over them. The spectrum was recorded by a Perkin Elmer instrument. KBr pellets were prepared with very minute amount of nanoparticles in them. This technique provides information of molecules/ functional groups bonded to the surface of solid.

2.2.2.4 UV VIS spectrometry

UV spectrophotometer (BMS Biotechnology Medical Services UV-2800) was used for absorption studies. The nanoparticles samples were prepared by dispersing particles in distilled water and were sonicated for UV visible absorption spectrum.

2.3 RESULTS AND DISCUSSION

2.3.1 CHARACTERIZATION OF NANOPARTICLES

2.3.1.1 SEM analysis

The powder of nanoparticles when observed in SEM showed proper synthesis of nanoparticles. The size was almost uniform however they were joined together or in agglomerated form at certain places. This is may be because of the fact that the nanoparticles were not dispersed in liquid before analysis and were used in powdered form. The average size of nanoparticles obtained was around 64 nm at 30,000X which means they are in nanoscale and can be used further to embed them inside polymer membrane.

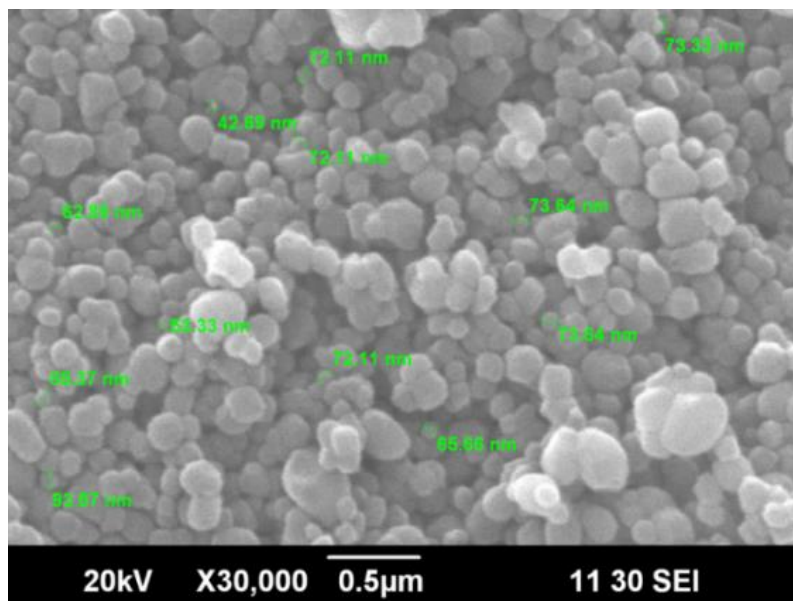


Figure 2.2: Average size of TiO₂ nanoparticles

2.3.1.2 XRD analysis

It was employed to determine the crystal phase of TiO₂ nanoparticles. The crystallite size of nanoparticles obtained in this sample was 41nm. 91% anatase phase was detected while only 12 % brookite was present. The X-ray diffraction pattern of the synthesized Titania nanoparticles is shown in Figure. It can be seen that no spurious diffraction is present which is indicative of crystallographic purity (Varshney, Bhadauria, & Gaur, 2010). The TiO₂ anatase structure is confirmed by the peak at 25° (Ba-Abbad, Kadhum, Mohamad, Takriff, & Sopian, 2012). The

strong diffraction patterns at 25° and 48° also confirmed the anatase structure of these nanoparticles (Thamaphat, Limsuwan, & Ngotawornchai, 2008). Crystalline structure of particles is confirmed by intensity of XRD peaks while broad diffraction peaks are also indicative of small crystallite size. This XRD pattern agrees with JCPDS card no. 21-1272 (anatase TiO₂) and with other literature too (Theivasanthi & Alagar, 2013). The XRD the peaks at 25.316°, 36.932°, 37.802°, 38.530°, 48.047°, 53.870°, 55.040°, 62.128°, 68.808°, 70.335° and 75.021° can be attributed to the 101, 103, 004, 112, 200, 105, 211, 204, 116, 220 and 215 crystalline structures of anatase synthesized TNPs, respectively (Anatase XRD JCPDS Card no. 78-2486) (Bagheri, Shameli, & Abd Hamid, 2013)

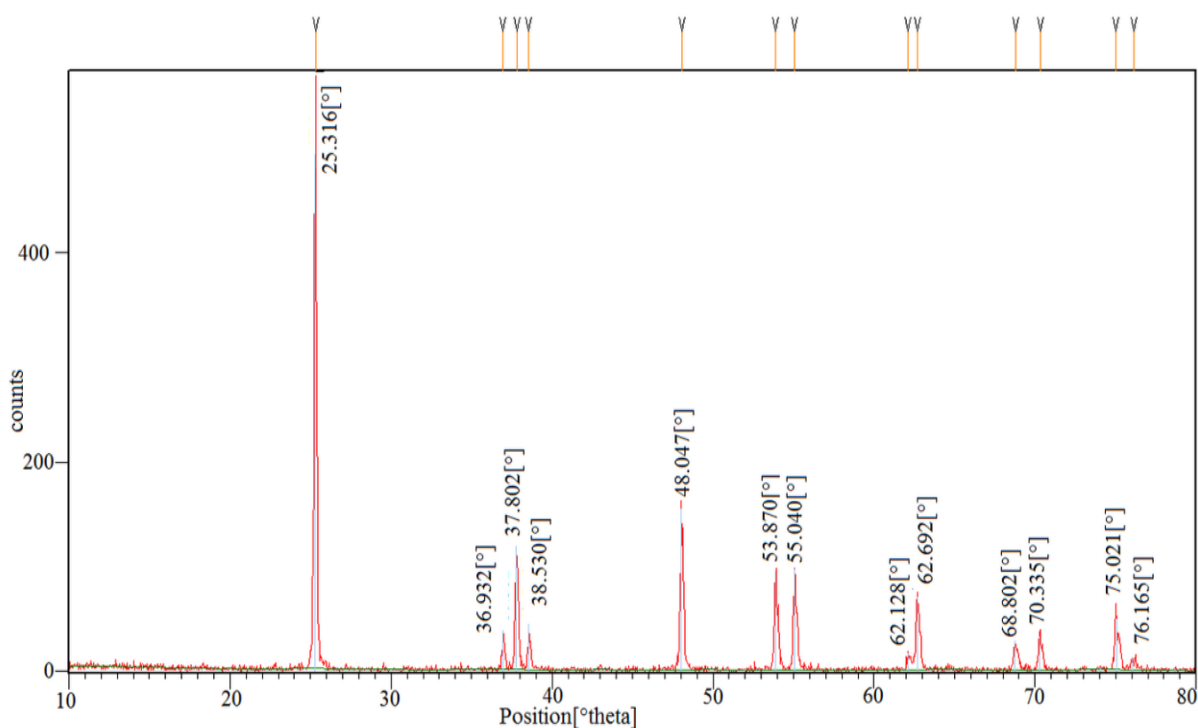


Figure 2.3: XRD results of TiO₂ nanoparticles

2.3.1.3 FTIR analysis

The peak at 1591 cm⁻¹ indicated the presence of amine group over the surface of nanoparticles, while no such peak was observed in non-functionalized nanoparticles.

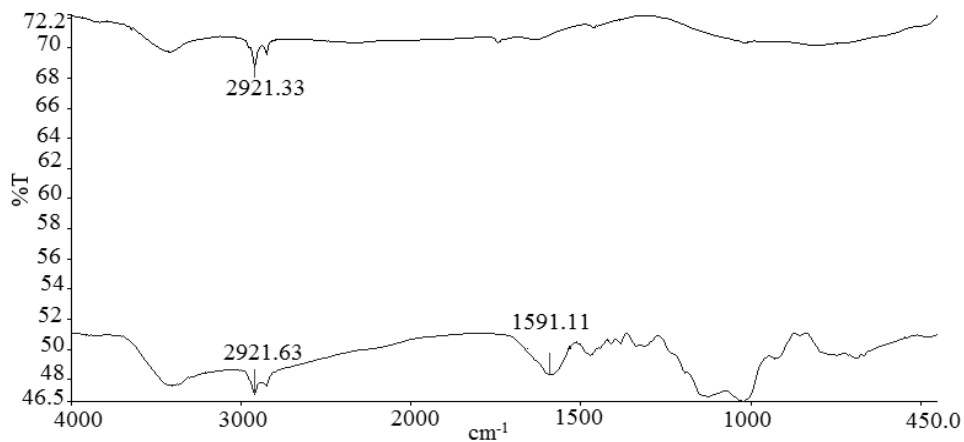


Figure 2.4: FTIR comparison of functionalized and non-functionalized TiO₂ nanoparticles

2.3.1.4 UV VIS Spectrometry

The UV-VIS absorption spectra was measured and shown in figure 4. The sample has got a peak at 380nm. These results are consistent with literature (Bagheri, Shameli, & Abd Hamid, 2012; K. Gupta, Singh, Pandey, & Pandey, 2013; Jwo et al., 2005). These results also confirm the synthesis of titania nanoparticles

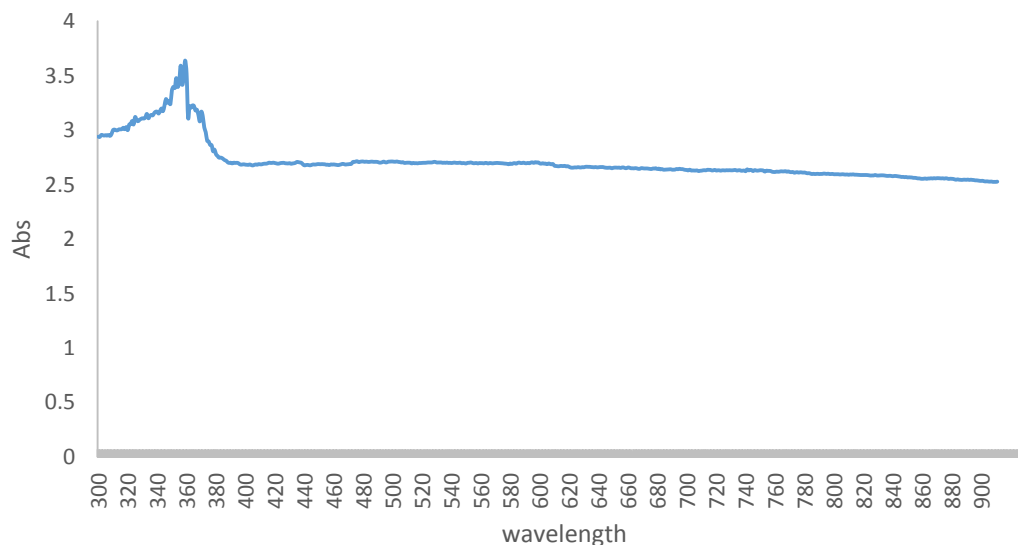


Figure 2.5: UV-VIS of TiO₂ nanoparticles

2.4 CONCLUSIONS

Titanium oxide anatase (general purpose reagent) can be used effectively to prepare TiO₂ nanoparticles. This method of TiO₂ nanoparticles preparation utilizes single source and it is efficient, quick and easy. The synthesis protocol selected can also be used to prepare nanoparticles at large scale. The SEM results confirmed that the size of nanoparticles is in nanometer range (64nm). The recorded spectra of UV absorption also accompany the proficient synthesis of the TiO₂ nanoparticles. The XRD results are indicating the higher purity level of sample by showing 91% anatase phase of these nanoparticles.

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CHAPTER 3: MIXED MATRIX POLYETHER SULFONE MEMBRANE Fabrication and Characterization

³ A part of this chapter is submitted for publication in Journal of Membrane Science

3.1 LITERATURE REVIEW

3.1.1 Membranes in water treatment:

Membranes are used for water treatment from a very long time. These are used in World War 2 by Germans. Muller designed a membrane based method in 1947 for water analysis. The American Water Works Association and United States Public Health Service in 1957 acknowledged the use of membranes for coliform bacteria (Madaeni, 1999).

3.1.2 Membrane technology

In this process feed stream is divided into permeate and retentate with the help of membrane. The solvent is passed through the membrane using the pressure difference between permeate and feed side (Van Der Bruggen, Vandecasteele, Van Gestel, Doyen, & Leysen, 2003).

One of the drinking water treatments is ‘pressure-driven membrane process’ which is very common now a day. This process is further divided into different categories subject on the membrane type, and water quality which is under process. They can be used to remove number of contaminants which cannot be achieved by traditional purification treatments because of this their acceptance in whole world is increasing day by day (Jacangelo et al., 1997). These processes can effectively retain bacteria particulates and viruses. Low-pressure membrane technologies such as microfiltration (MF) and ultrafiltration (UF) are recognized as very attractive processes for producing drinking water (Zheng et al., 2012). They follow cross filtration process in which continuous processing is carried out for purifying water. The water passes through the membrane surface in parallel direction. Water act as permeate and passes through the membrane because of pressure given in the system. This turbulent flow decreases the buildup of particulate matter over the membrane surface. This technology is different to conventional filtration. Some advantages of Crossflow filtration over traditional filtration technologies are:

- Automatic and continuous operation.
- Can remove submicron size contaminants.
- Commonly entails no chemical.
- Can be operated in turbulent flows (Cartwright, 2013)
- Pore size can be changed and selected according to impurities size range

- The waste obtained after membrane separation process contain impurities only.
- Membrane processes can also be combined with other processes used in water treatment, this will enhance the purification process
- Chemical substances if added will be in smaller quantity
- Less energy consumption (Bodzek & Konieczny, 1998)
- Water produced is of good quality
- Sludge produced is very small in quantity
- Compact process
- easy and quick automation of process (Zheng et al., 2012).

3.1.3 Different types of membranes:

Pressure driven membrane processes are divided into different types depending upon the function they perform which is mostly the by diameter size of particle that they can separate (micrometers, μm). These properties of membranes are summarized in the table 3.1 (Bodzek & Konieczny, 1998; Muro, Riera, & del Carmen Díaz, 2012).

Table 3.1: Different properties of membranes.

	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Permeability (l/h.m².bar)	> 1,000	10 - 1,000	1.5 - 30	0.05 – 1.5
Particle diameter they can retain (μm)	10^{-1} -10	10^{-3} -1	10^{-3} - 10^{-2}	10^{-4} - 10^{-3}
Pore size (nm)	100-10000	2-100	0.5-2	<0.5
Retained solutes	Bacteria, fat, oil, grease, colloids, organics microparticles, reject particles	Proteins, pigments, oils, sugar, organics rejection of macromolecules and	Pigments, sulfates, divalent cations, divalent anions, lactose, sucrose,	Salts, sodium chloride and inorganic ions. rejection of macromolecules, micromolecules

	only.	microparticles too	Sodium chloride, rejection of macromolecules, microparticles and multivalent ions too.	mono/multivalent ions and microparticles too
Applications	removal of bacteria and clarification	Removal of viruses bacteria and Macromolecules.	Removal of small organics and multivalent ions	Desalination and Ultrapure water

In microfiltration (MF) membranes adequate amount of water can be passed at low pressure because of the pore size that range from 0.1 μm to 10 μm (largest pore size so higher permeability). Different viruses and germs that are larger than this pore size cannot pass through these pores hence they are removed using sieving mechanism (Lerch et al., 2005; Van Der Bruggen et al., 2003). The permeability of Ultrafiltration (UF) membranes is lower than microfiltration (MF) because of smaller pore size that range from 2 to 100 nm. Because of this pore size these membranes are operated at lower pressures. The NOM (natural organic material) which is constituted by large dissolved molecules are removed using these membranes (Paronen, 2013; Van Der Bruggen et al., 2003). The pore size is further reduced in nanofiltration (NF) that is around 1 nm. This pore size is suitable for removing very small size organic micropollutants, effluents and colors from the treated water` (Mondal & Wickramasinghe, 2008; Van Der Bruggen et al., 2003). Reverse osmosis membranes follow a little different mechanism as these membranes are without predefined pores so they are less permeable and require high pressure so high energy consumption for proper operation. These membranes follow solution diffusion mechanism. The dissolved constituents are rejected and water is allowed to pass through the membrane (Kang & Cao, 2012; Van Der Bruggen et al., 2003).

3.1.4 Different polymer membranes used in water treatment:

Traditionally non cellulose polymers and other cellulose derivatives with greater chemical strength and high thermal resistance were used in the manufacturing of semi permeable polymeric membranes. Different polymer membranes that can be used in water treatment are: polysulfone, poly acrylonitrile (Bodzek & Konieczny, 1998), polyvinylidene fluoride, polyethersulfone, polytetrafluoroethylene, polyethylene, cellulose acetate, polypropylene, and polyvinyl-pyrrolidone (Cartwright, 2013), polyester (L. Liu et al., 2012) .

3.1.4.1 Polyether sulfone membrane:

Polyethersulfone (PES) is a distinct engineering polymer. It holds many worthy properties such as high heat distortion temperature and good mechanical properties. It has high heat-aging resistance, environmental durability as well as easy handling. These properties make it an important membrane material, but the PES structure make it more hydrophobic which causes decrease in membrane flux and also increases fouling issues (Luo et al., 2011).

3.1.5 The polymer membrane properties altered after adding TiO₂ nanoparticles.

Membrane technology can be modified by entrapping metal oxides to form a membrane with more porous or open structure, long term flux stability and antifouling properties can also be enhanced. Strong correlations can also be seen between some physico-chemical properties of modified membranes such as hydrophilicity, porosity, and permeability with the membrane structure having spatial particle distribution. In the modified membranes another parameter that can be improved is the fouling, that can be reduce to a considerable level, the main condition that effect membrane fouling resistance is improper distribution of particles (María Arsuaga et al., 2013). Here is the review of some studies utilizing TiO₂ nanoparticles in different polymer membranes ultimately affecting their properties

The Poly (phthalazine ether sulfone ketone) (PPESK) membrane has good properties and high thermal stability. Li et al in 2007 carried out a study in which PPESK ultrafiltration (UF) membranes with Titanium dioxide (TiO₂)-entrapped particles were made. This improved the surface wettability and hydrophilicity because of addition of hydrophilic TiO₂ particles. Pure water flux was studied through permeability experiment while solute rejection was confirmed by

rejection experiments both showed the membrane with increased pure water flux and solute rejection, the main parameter for controlling these two properties is the amount of TiO_2 added; the preferable amount is mostly very low. Improvement in hydrophilicity and antifouling of membrane was confirmed Protein filtration experiments. Considerably, the membrane's tensile mechanical strength was also improved by TiO_2 addition. (J. B. Li et al., 2007)

Polyethersulfone (PES)-type membranes are ultrafiltration membranes, their performance is affected by fouling from hydrophobic substances. The sulfonated-PES membrane with incorporated TiO_2 nanoparticles can form a composite membrane with better properties. Addition of these particles can lower contact angle of surface i.e. increase its hydrophilicity. Prevention of fouling in these membranes is also imperative, signifying a likely use as a new type of antifouling composite membrane(Luo et al., 2011)

In 2012 Rahimpour et al. prepared PVDF/SPES nano-composite membranes with self-assembled TiO_2 nanoparticles incorporated in membranes along with UV irradiation. The OH functional groups present over the membrane surface form a bond with particles and help in proper deposition of TiO_2 nanoparticles on the surface of PVDF/SPES membrane. The TiO_2 deposition decreased surface contact angle of PVDF/SPES membrane very intensely. The BSA (Bovin Serum Albumin powder) solution flux and initial pure water flux was measured, both of these were lower in TiO_2 deposited membranes as compared to the neat PVDF/SPES membrane. The long-term flux stability and the antifouling property was also increased. The rejection experiments showed the good level of BSA rejection. The antibacterial study results showed that the PVDF/SPES membranes with UV irradiated TiO_2 own high antibacterial activity (Rahimpour et al., 2012)

Similar study was conducted by above group in which they prepared a PVDF membrane using sulfonated polyethersulfone (SPES) and TiO_2 nanoparticles in the presence of polyvinyl pyrrolidone (PVP) in the casting solution. Membrane was prepared by immersion precipitation technique that induced phase inversion. Increase in surface hydrophilicity was confirmed by contact angle analysis. Just like the above mentioned study the antifouling properties, long-term flux stability and antibacterial activity of membrane was confirmed (Rahimpour et al., 2011).

Polymeric nanocomposite membranes can be prepared through anatase TiO_2 coated multiwalled carbon nanotube, by phase inversion method in which polyethersulfone (PES) polymer may act

as host matrix. The TiO_2 coated MWCNTs demonstrated appropriate compatibility with polymeric components showing low agglomeration. The increase in membrane hydrophilicity causes the pure water flux to be higher in mixed matrix membranes as compare to bare PES membrane. The decreased membrane surface roughness and increased hydrophilicity also causes the fouling resistance. It was also observed that coating of MWCNTs with TiO_2 is more beneficial as compare to bare TiO_2 as there photocatalytic activity was also enhanced showing synergistic effect of coating. This effect also enhances antibiofouling property of particles. The MWCNTs coated with TiO_2 particles also form good antibiofouling microporous PES nanofiltration membrane with higher reproducibility level (Vatanpour, Madaeni, Moradian, Zinadini, & Astinchap, 2012).

-effect on thermo mechanical properties of nano composites

New organic–inorganic PS (Polysulphone)/ TiO_2 hybrid membranes can be prepared by a phase inversion and sol–gel process. The microstructure, hydrophilicity, porosity, thermal stability and UF performance of hybrid membrane are upgraded speciously by any suitable TiO_2 concentration. The foremost outcomes can be listed as following:

1. The restriction and elimination of macrovoids, it will affect the membrane's topical asymmetric structure of membrane convert macrovoids to network pores, as a result the compact resistance of membrane is improved.
2. The excellent thermal properties and morphology of hybrid membranes can be improved because of impenetration of inorganic network with polymeric network. The interaction of coordinate bonds and OH bonds also enhance this process.
3. The hybrid membranes display astonishing permeability , increased porosity and hydrophilicity, with unaffected retention properties when compared with polymeric membranes (Yang & Wang, 2006).

3.2 EXPERIMENTAL

For polymer membrane synthesis the PES (polymer) was obtained from (PES Ultrasonex Germany). NMP solvent (N-methyl-2-pyrrolidone) was brought from Sigma Aldrich. Functionalized titania nanoparticles synthesized were used for incorporation in polymer membrane. Deionized water was used throughout experiment. All chemical were used without further purification unless specified.

3.2.1 Polymeric membrane synthesis

Typical fabrication procedure involves mixing 2g of polymer in 18g of NMP solvent (10 wt. % membrane). Magnetic stirring was done for 3 hours at 55°C until polymer completely dissolved. The solution was left for magnetic stirring overnight at room temperature followed by casting of the membrane.

For synthesis of nanoparticles entrapped mixed matrix membranes TiO₂ nanoparticles in three different concentrations (0.4%, 0.75% and 1.5% wt. %) were added in NMP solvent (solution A). **10%** polymer was also added in NMP solvent (solution B). In case of mixed matrix membranes with drug (Ceftriaxone), 1.5% of drug was also added in the filler solution. Both solutions were mechanical stirred on 300 rpm at room temperature for 24 hours. The polymer solution and nanoparticles solutions both were stirred and sonicated separately for 3 times and then mixed with each other. Stirring of mixed solution was done again and then membrane casting was performed. The membranes were prepared using phase inversion using thin film applicator and custom design tray. The membrane casting was done by pouring the above prepared solution over the polyester support which was wetted with NMP before casting to prevent the polymer solution to enter in the support. When the solution was spread over support using thin film applicator, the membrane was immersed in distilled water for precipitation and removal of solvent. Finally, air drying was done under ambient conditions to obtain the membranes.



Figure 3.1: Thin film applicator used for membrane casting.

3.2.2 Characterization of membrane

3.2.2.1 SEM and Energy Dispersive Spectroscopy (EDS)

SEM (Scanning Electron Microscopy) Joel JSM 6490A was used to analyze morphology and membranes structure. Samples were cut into 0.25 cm^2 pieces, mounted on blocks, gold coated and then analyzed.

3.2.2.2 Contact angle analysis

A custom made contact angle device was used to measure surface wettability of membranes. In all measurements de-ionized water was used and on average at least 5-different measurements taken to calculate average contact angle. Experimental error was minimized by taking measurements at different locations and then calculating the average. The main purpose of this technique is used to determine hydrophilicity of membrane.

3.2.2.3 Optical profilometry

Thickness and topography of membranes was measured using NOVEA PS 50.

3.2.2.4 FTIR

FTIR (Fourier transform Infrared) spectra was obtained by a Perkin Elmer Instrument. The membranes samples were cut in small squares of about 2 cm^2 , they were then placed inside the machine and spectra were recorded.

3.2.2.5 Thermo gravimetric Analysis (TGA) and differential thermal analysis (DTA)

Thermo gravimetric Analysis (TGA) and differential thermal analysis (DTA) of membranes were carried out using Perkin Elmer instruments SDT Q600 with simultaneous analyzer at a heating rate of 10 °C with nitrogen gas.

3.2.2.6 Mechanical testing

A SHIMADZU AG-X plus Series Universal Testing Machine was used to measure tensile strength of membrane. The length and width of samples between the jaws was 45mm and 25mm respectively. The crosshead speed was 3 or 1mm/min. All the measurements were taken at room temperature.

3.2.2.7 Water retention

To check water retention capacity of all membranes, they were soaked in water (1gm) for 24 hours. Wet weight was calculated. The membranes were then oven dried (12hrs) and dry weight was calculated. Water retention was calculated using this formula. $[(\text{wet weight}-\text{dry weight})/\text{wet weight}]\times 100$

3.2.2.8 XRF Test

The XRF test was carried out using Joel JSK- 3202M Element Analyzer Japan to find out if there is any TiO₂ nanoparticle present in filtered water or not.

3.2.2.9 Membrane flux

The membrane flux was measured by passing water at three different known pressures. The time taken by each membrane to pass water at each pressure was measured by employing following relation $J=V/ (A.t) = L/ (m^2.h)$ where J is the membrane flux ($L\cdot m^{-2}\cdot h^{-1}$), V is the volume of permeate in (L=liter), A is the membrane area (m^2), and t is ultrafiltration time (h=hour).

3.3 RESULTS AND DISCUSSION

3.3.1 Characterization of membrane

3.3.1.1 Scanning Electron Microscopy

3.3.1.1.1 Top of membranes:

The SEM images of all membranes (figure 6) showed difference in pores and over all morphology of membranes when observed from the top. PES membrane contains uniformly distributed pores. While in other images with increase of nanoparticles concentrations membrane formed is less porous as compare to original polymer membrane especially in the membrane with maximum concentration (1.5% TiO₂ nanoparticles). The interconnectivity of large macro voids also increased at higher concentrations (Rahimpour et al., 2011). The higher concentration of nanoparticles in membranes results in agglomeration of particles over the membrane.

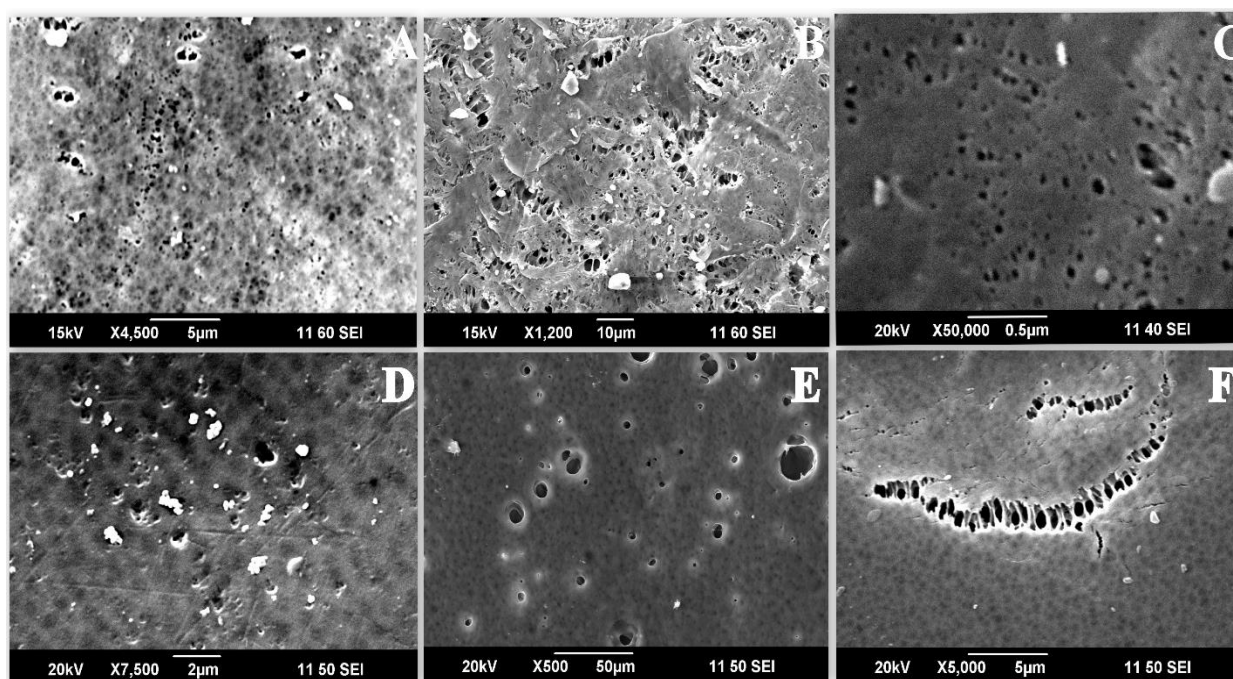


Figure 3.2 : The top of fabricated membranes obtained from SEM (A) PES membrane (MT-1) (B): 0.4% TiO₂ nanoparticles + PES membrane (MT-3) (C) 0.75% TiO₂ nanoparticles + PES membrane (MT-4) (D)1.5% TiO₂ nanoparticles + PES membrane (MT-5) (E) 1.5 % Drug + PES membrane (MT-2) (F) 1.5% Drug + 1.5% TiO₂ + PES (MT-6).

3.3.1.1.2 Average pore size of membranes

Multiple pores were measured and average size was calculated as in figure 7. The membrane with 0.4% TiO₂ nanoparticles showed higher pore size this is may be because of inclusion of particles in polymer membranes. During synthesis the nanoparticles in the casting solution may give more time to non-solvent and solvent solution to be separated this may result in increase of membrane pore size [13]. While pore size was not calculated in membrane with 1.5% nanoparticles because of interconnected macro voids and thick layer type morphology of membrane (J. B. Li et al., 2007; María Arsuaga et al., 2013). The average pores sizes of PES membrane, 0.4% TiO₂ nanoparticles + PES membrane, 0.75% TiO₂ nanoparticles + PES membrane and 1.5% Drug + 1.5% TiO₂ PES membrane calculated through SEM were 651nm/0.651 μ m, 708nm/0.7 μ m, 33.15 μ m and 164.73 μ m respectively. The PES membrane with 1.5% TiO₂ nanoparticles was not porous and it was not able to calculate average pore size of this membrane.

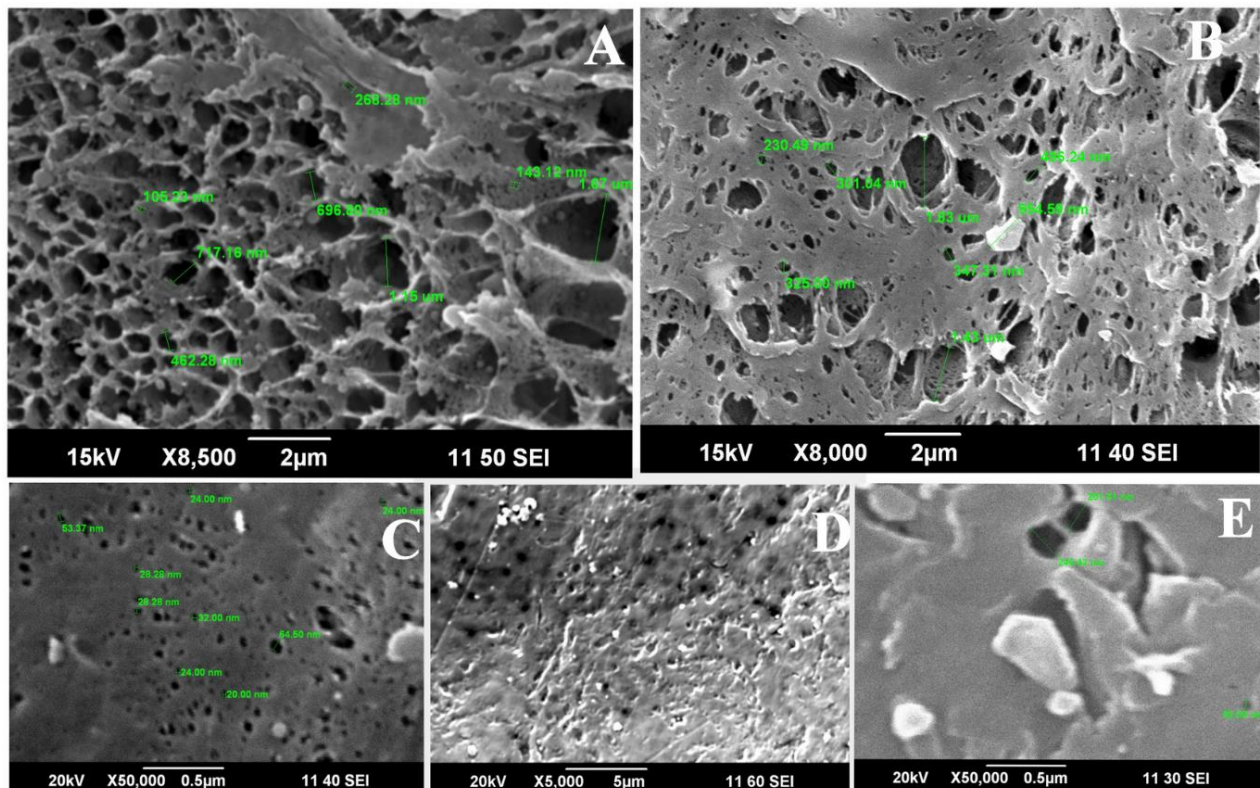


Figure 3.3: The average pores sizes of fabricated membranes obtained from SEM (A) MT-1: 651nm/0.651 μ m, (B) MT-3: 708nm/0.7 μ m, (C) MT-4: 33.15 μ m (D) MT-5 (cannot be determined) (E) MT-6: 164.73 μ m.

3.3.1.1.3 Average width of membranes

Width of the fabricated membranes was found to be approximately similar in case of PES and 0.4% TiO₂ PES membrane. However, the membranes with higher concentration of particles (0.75% and 1.5%) were denser as compare to other membranes and width was also higher (figure 7). Another difference observed between control and other membranes was the finger like structure of microvoids. They were elongated across the width of membranes with nanoparticles. The average width of PES membrane, 0.4% TiO₂ nanoparticles + PES membrane, 0.75% TiO₂ nanoparticles + PES membrane, 1.5% TiO₂ nanoparticles + PES membrane, 1.5 % Drug + PES membrane and 1.5% Drug + 1.5% TiO₂ + PES: 27.92μm were 28.99μm, 28.49μm, 63 μm, 70 μm, 28.28μm and 27.92μm respectively.

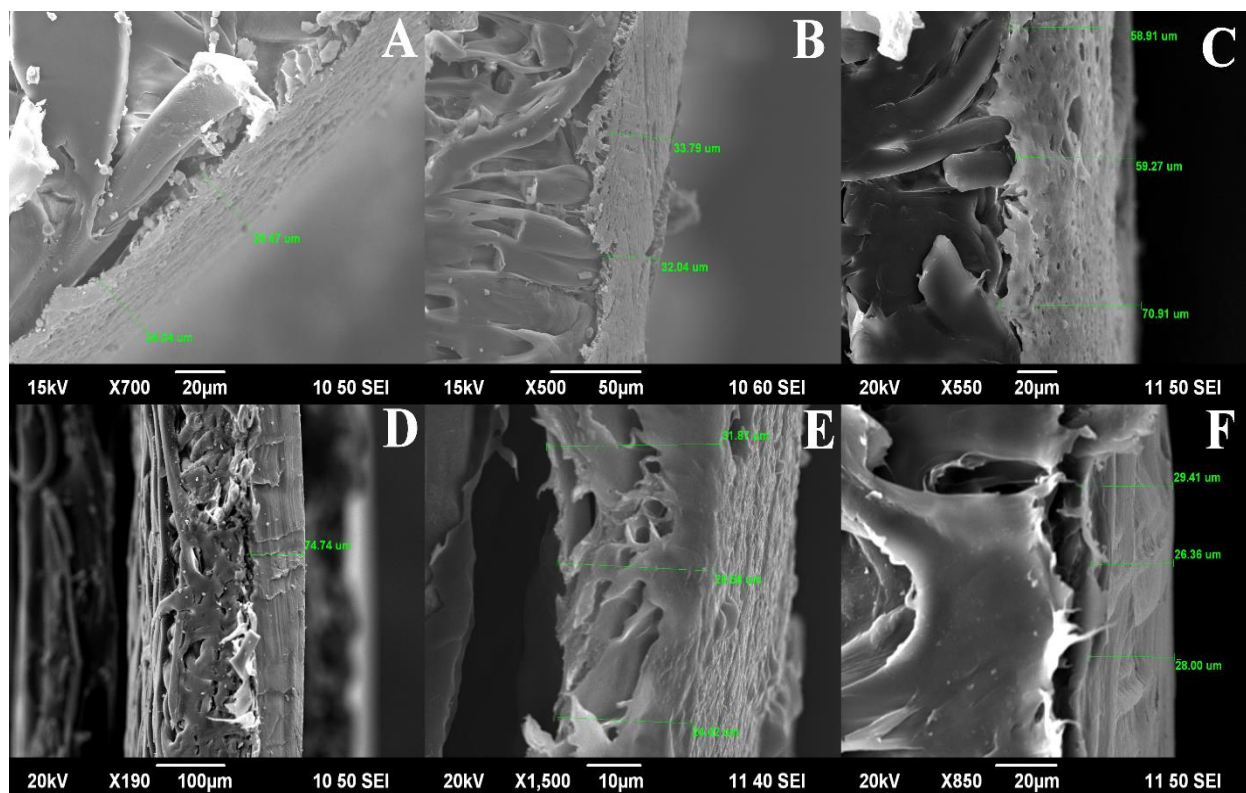


Figure 3.4: The average width of fabricated membranes calculated using SEM. (A) MT-1: 28.99μm, (B) MT-3: 28.49μm (C) MT-4: 63 μm (D) MT-5: 70 μm (E) MT-2: 28.28μm (F) MT-6: 27.92μm

3.3.1.1.4 Energy Dispersive Spectroscopy (EDS)

Elemental analysis showed good results in all membranes only constituent elements were detected in them. The sulfur, oxygen and carbon were main constituents in all membranes because of Polyether sulfone. The titanium element was detected in membranes incorporated with titanium di oxide nanoparticles.

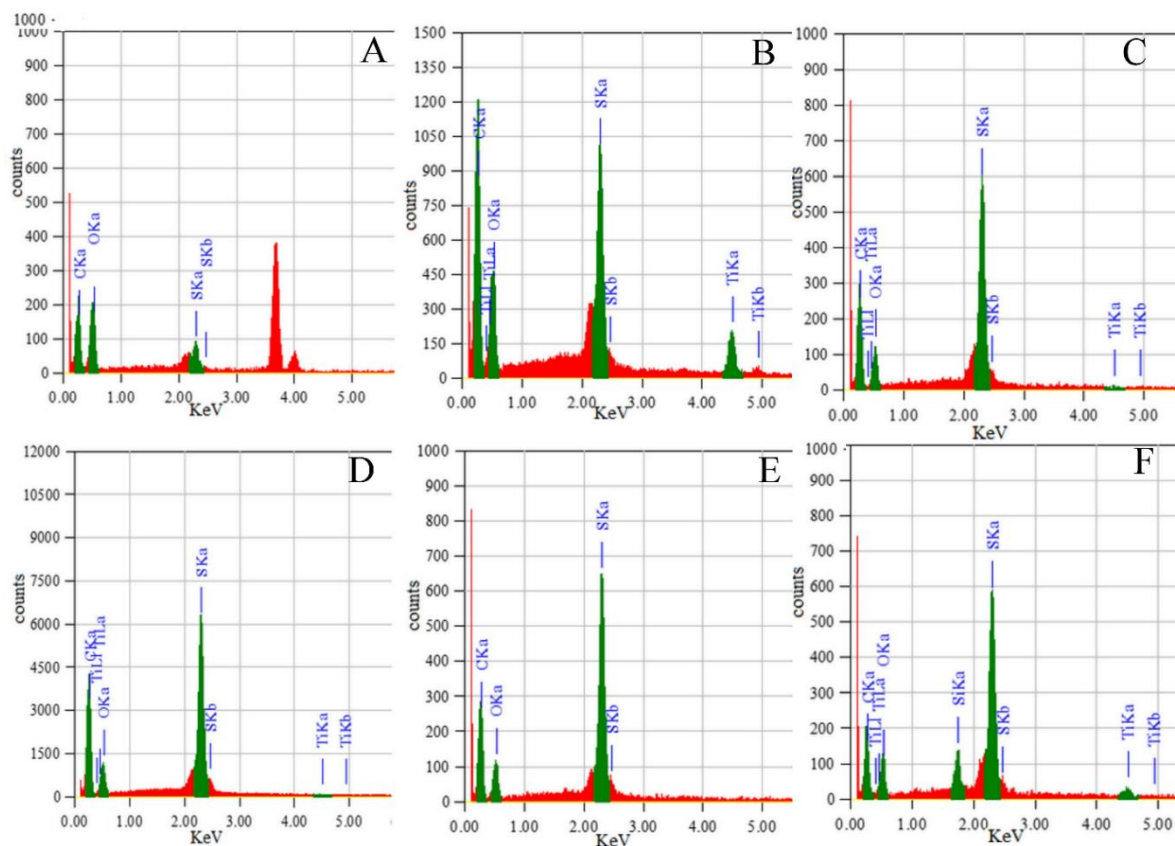


Figure 3.5: EDS of all membranes. (A) MT-1: C (35.45%), O (59.26), S (5.29) (B): MT-3: C (47.67%), O (25.89%), S (16.57%), Ti (9.88%) (C) MT-4: C (54.90%), O (27.68%), S (16.97%), Ti (0.45%) (D) MT-5: C (56.29%), O (26.84%), S (16.79%), Ti (0.08%) (E) MT-2: C (57.47%), O (24.64%), S (17.90%), (F) MT-6: C (41.69%), O (32.48%), Si (3.41%), S (20.50%), Ti (1.92%).

3.3.1.2 Contact Angle Analysis

Contact angle analysis was done for measuring Hydrophilicity. Increase in the hydrophilicity with increasing concentration of titanium dioxide nanoparticles was pragmatic. This may occur because of incorporation of hydrophilic titanium dioxide nanoparticles in the membrane.

Presence of drug also increases the membrane hydrophilicity. So an obvious trend of decrease in contact angle with increasing nanoparticles concentration was observed (Table 1) (Luo et al., 2011) (Rahimpour et al., 2011)

Table 3.2: Contact angle analysis of fabricated membranes

MEMBRANE CODE	MEMBRANE COMPOSITION	CONTACT ANGLE
MT-1	PES	81°
MT-2	PES + Drug	79°
MT-3	PES + 0.4% TiO ₂	78°
MT-4	PES + 0.75% TiO ₂	74°
MT-5	PES + 1.5% TiO ₂	61°
MT-6	PES + 1.5 % Drug + 1.5% TiO ₂	55°

3.3.1.3 Optical Profilometry

Roughness parameter also decreased by increasing particles concentration. This may occur because of hydrophilic nanoparticles on surface. Presence of drug also decreases the membrane roughness in all cases (Rahimpour et al., 2012; Rahimpour et al., 2011).

Table 3.3: Surface roughness of fabricated membranes

MEMBRANE CODE	SURFACE ROUGHNESS (NM)
MT-1	831
MT-2	430
MT-3	802
MT-4	629
MT-5	595
MT-6	375

3.3.1.4 FTIR

FTIR spectrum analysis showed that when all peaks of membranes were compared in the region of 1400 cm^{-1} the control membrane has no peaks. This may occur because of presence of TNPs in other membranes. Higher concentration of TNPs also affects the peaks of membrane with highest concentration.

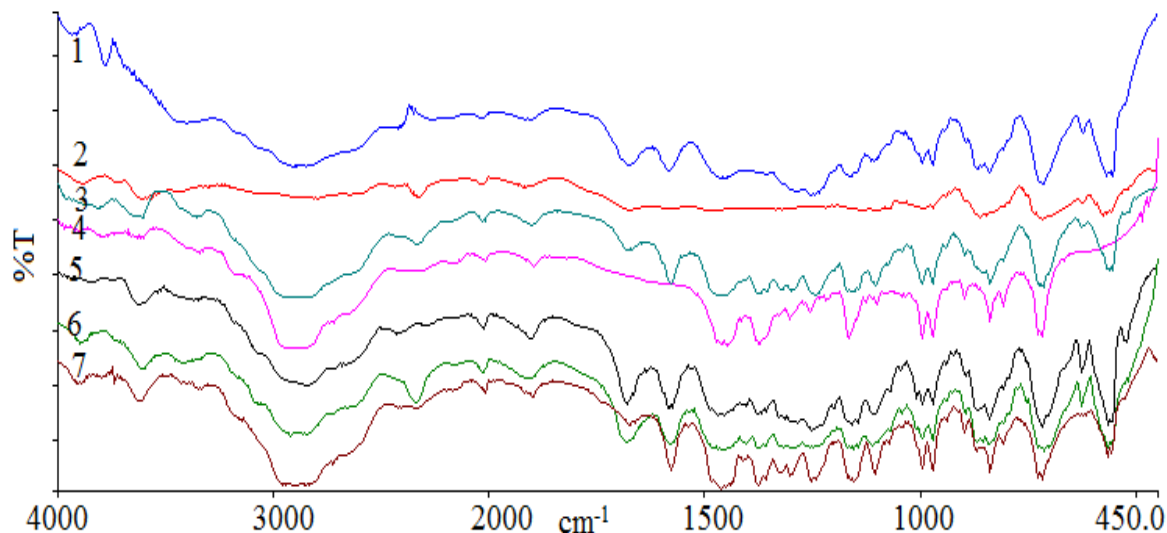


Figure 3.6: FTIR spectrum analysis (1) Polyester support (2): MT-2 (3) MT-3 (4) MT-1 (5) MT-4 (6) MT-5 (7) MT-6

3.3.1.5 Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

TGA analysis showed good stability of membranes as shown in figure (Zhang, Li, & Xia, 2009). Polymer membrane and membrane with 0.4% TiO_2 remain stable till 260°C . However at higher concentration of nanoparticles stability of membranes also increased from 260°C to 275°C and 320°C . TGA of all membranes is listed in table. DTA analysis showed glass transition temperature in all membranes started at 130°C this similarity is may be because of change in phase of polyester fibers. Similarly peak of melting temperature is also similar in all membranes.

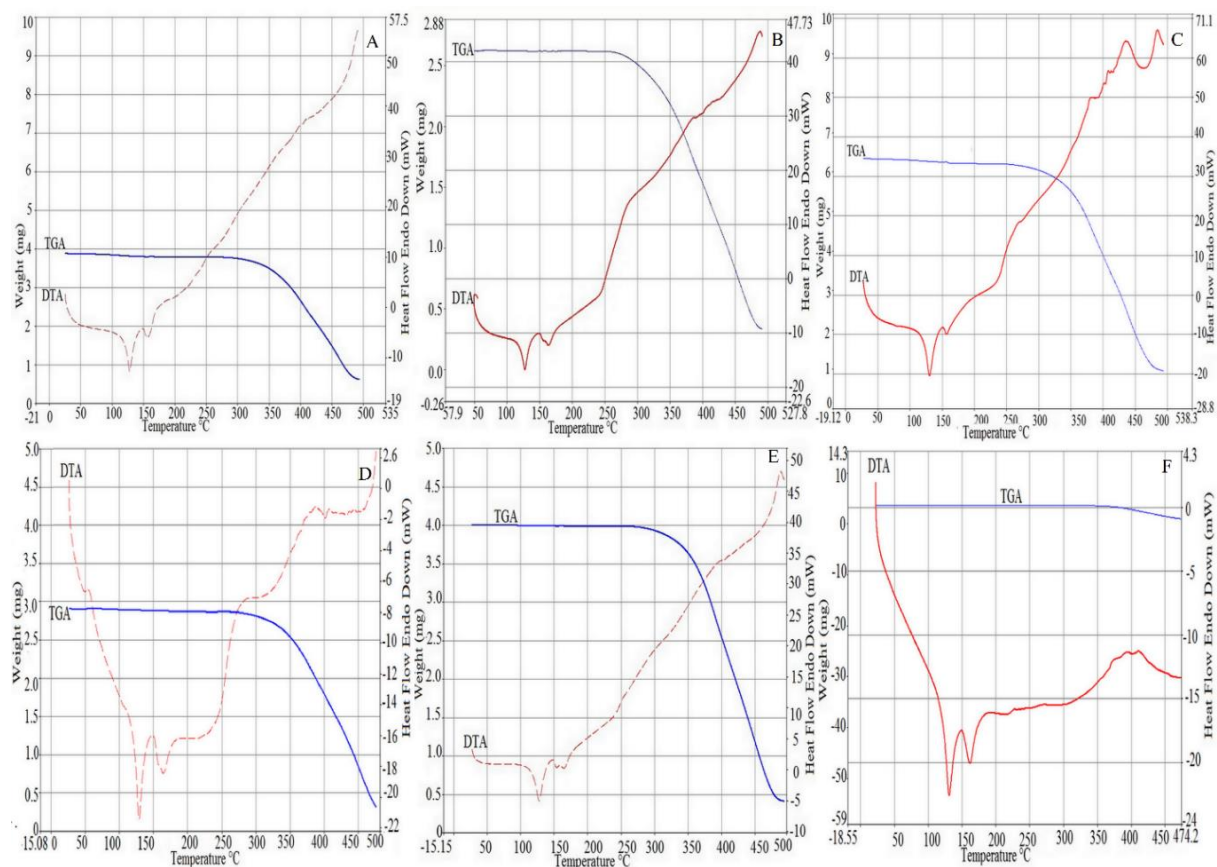


Figure 3.7: Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of all membranes (A) MT-1 (B) MT-2 (C) MT-3 (D) MT-4 (E) MT-5 (F) MT-6

Table 3.4: TGA of all fabricated membranes

MEMBRANE CODE	TGA(°C)
MT-1	260
MT-2	290
MT-3	260
MT-4	275
MT-5	320
MT-6	400

3.3.1.6 Mechanical testing

No specific increase or decrease was observed in this case however in general the membranes showed good mechanical strength which is indication good relation of particles and polymer (Figure 11). The decrease in mechanical strength may occur because of incorporation of higher number inside pores making the interconnected areas weaker than normal.

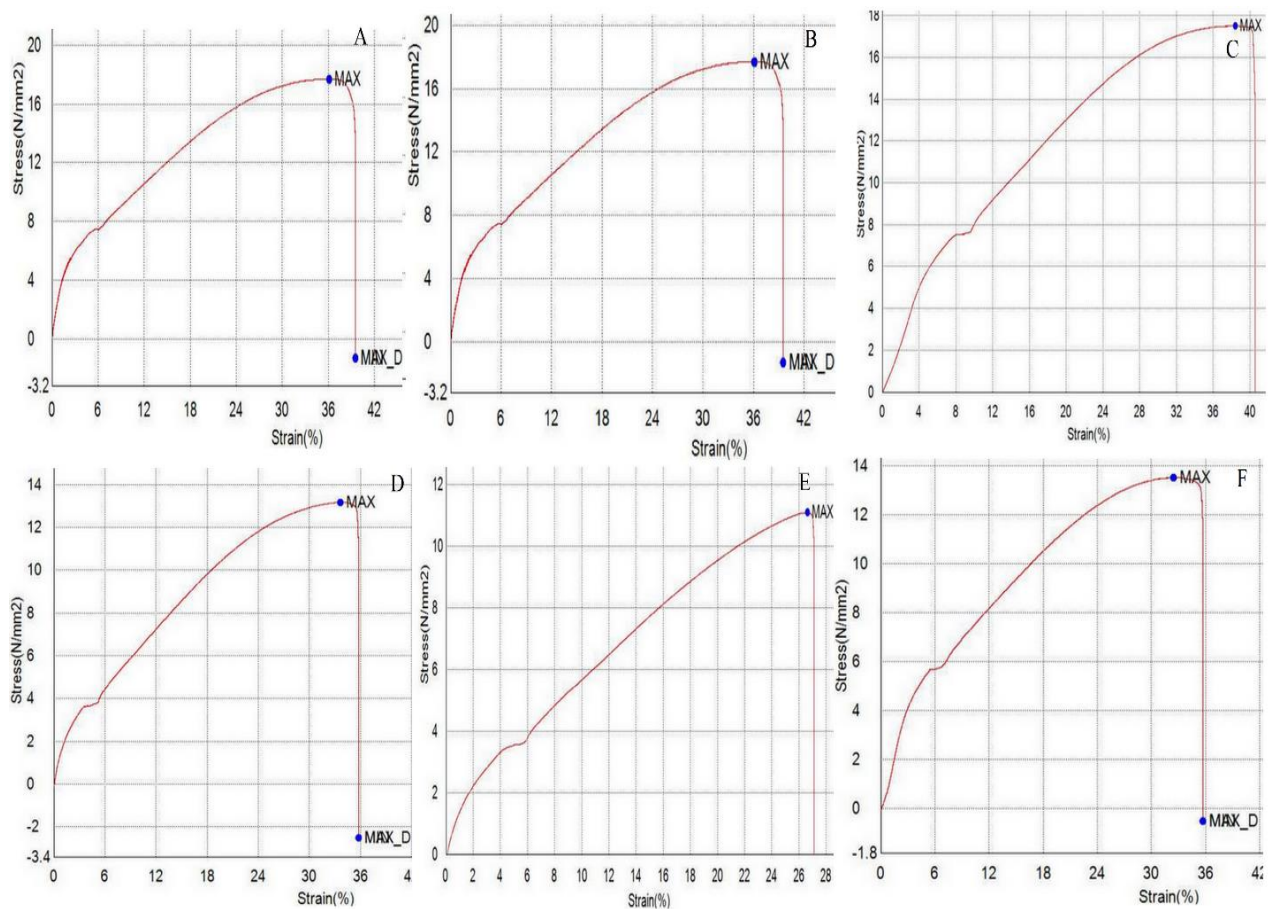


Figure 3.8: Mechanical test of all membranes (A) MT-1 (B): MT-2 (C) MT-3 (D) MT-4 (E) MT-5 (F) MT-6

Table 3.5: Mechanical strength of fabricated membranes

MEMBRANE	YOUNG'S MODULUS (N/MM ²)	MAXIMUM STRESS (N/MM ²)	MAXIMUM STRAIN %
Fiber	0.4986	18.3050	36.7063
MT-1	0.4895	17.6875	36.1274
MT-2	0.5648	18.3116	32.4166
MT-3	0.4556	17.4996	38.4059
MT-4	0.3915	13.1708	33.6414
MT-5	0.4165	11.0891	26.6224
MT-6	0.4164	13.5077	32.4369

3.3.1.7 Water retention test

Maximum water retention was observed in the MT-5 membrane that has maximum percentage of nanoparticles incorporated in it (figure 12). This indicates hydrophilic nature of membrane. As hydroxyl group is present on TiO₂ nanoparticles surface and these particles have high surface area along with high hydrophilicity, the hydroxyl content of the membrane increased significantly therefore the membrane hydrophilicity increased (Luo et al., 2011). The increase in compactness of membrane as depicted by SEM, with increase on nanoparticles concentration can also help to retain more water in the membrane (Luo et al., 2011).

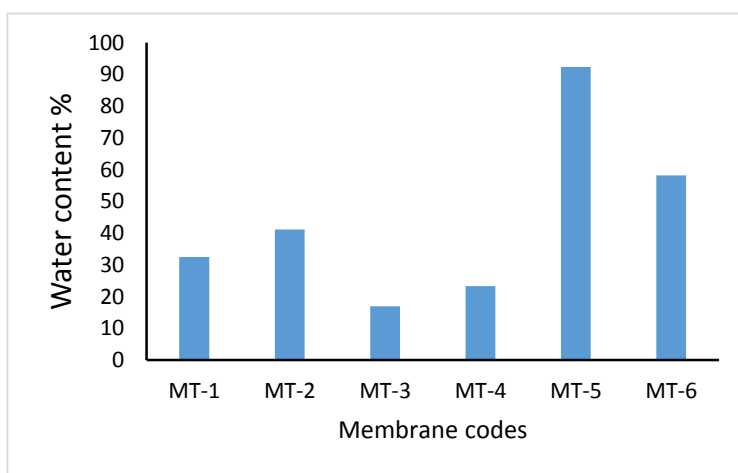
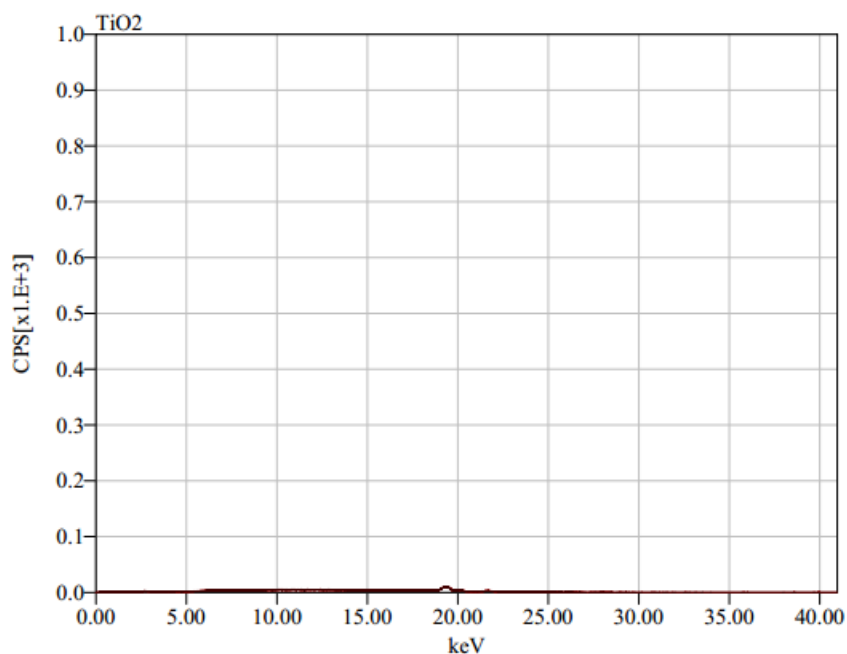
**Figure 3.9:** Water retention shown by all fabricated membranes.

Table 3.6: Water retention test of fabricated membranes

MEMBRANE CODE	WET WEIGHT (GM)	DRY WEIGHT (GM)	WATER CONTENT %
MT-1	0.2426	0.1600	32.5
MT-2	0.1599	0.2720	41.2
MT-3	0.1614	0.1946	17
MT-4	0.1622	0.2177	23.3
MT-5	0.1610	0.2146	92.4
MT-6	0.1400	0.3350	58.2

3.3.1.8 XRF Test

This test was carried out to analyze if there any nanoparticle leaked out from TiO₂ nanoparticles fabricated mixed matrix membrane into the filtered water or not. The results of this test showed that no nanoparticles were present in the filtered water, as the XRF graph was blank and no peak was observed in it. This means that the nanoparticles were efficiently incorporated into the membranes.

**Figure 3.10:** Elemental analysis test of membrane filtrate

3.3.1.9 Membrane flux

It was measured by passing 10ml water at three different known pressures (cmHg). The time taken by each membrane to pass water at each pressure was measured. The TiO₂ nanoparticles make surface hydrophilic. The membrane with better hydrophilicity can attract more water molecules. The addition of TiO₂ increased the membrane hydrophilicity that's why increase in flux was also observed as shown in figure 13. The water molecules can easily permeate through the membrane therefore increases the flux (Luo et al., 2011). The flux improvement was not seen at higher concentration (figure 14) this may occur because of agglomeration of TiO₂. So amount of TiO₂ nanoparticles should be properly controlled (J. B. Li et al., 2007).

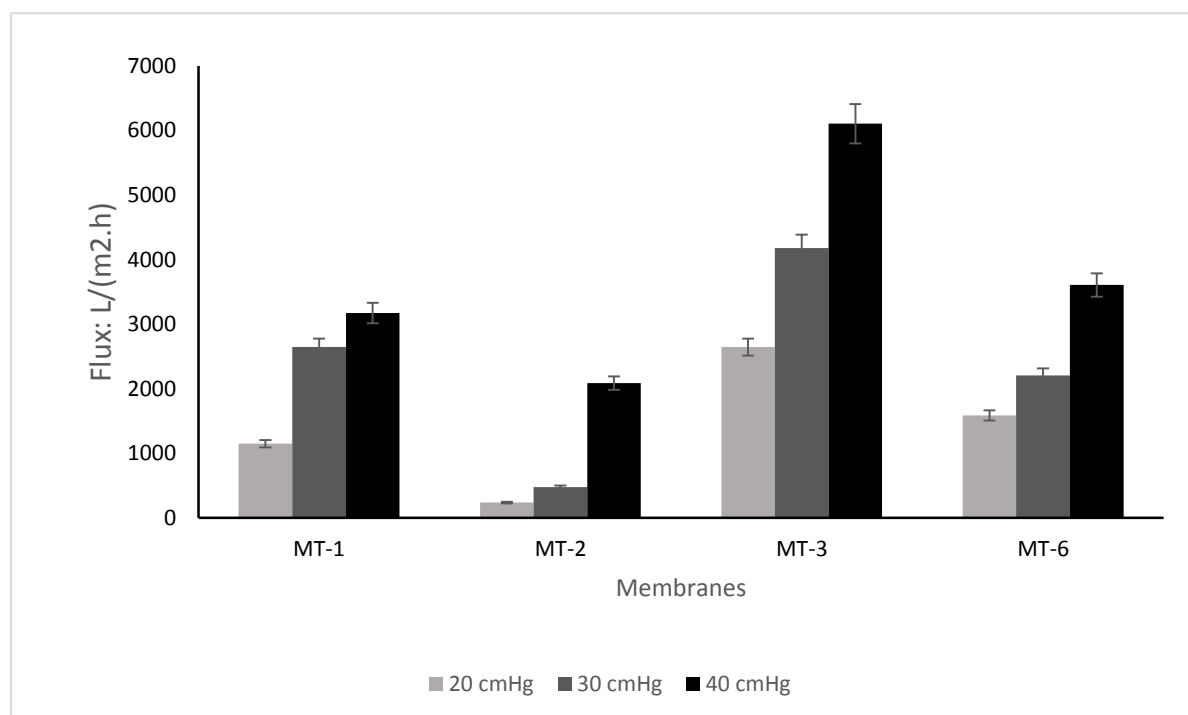


Figure 3.11: Membrane flux increased by adding TiO₂ nanoparticles in the membrane

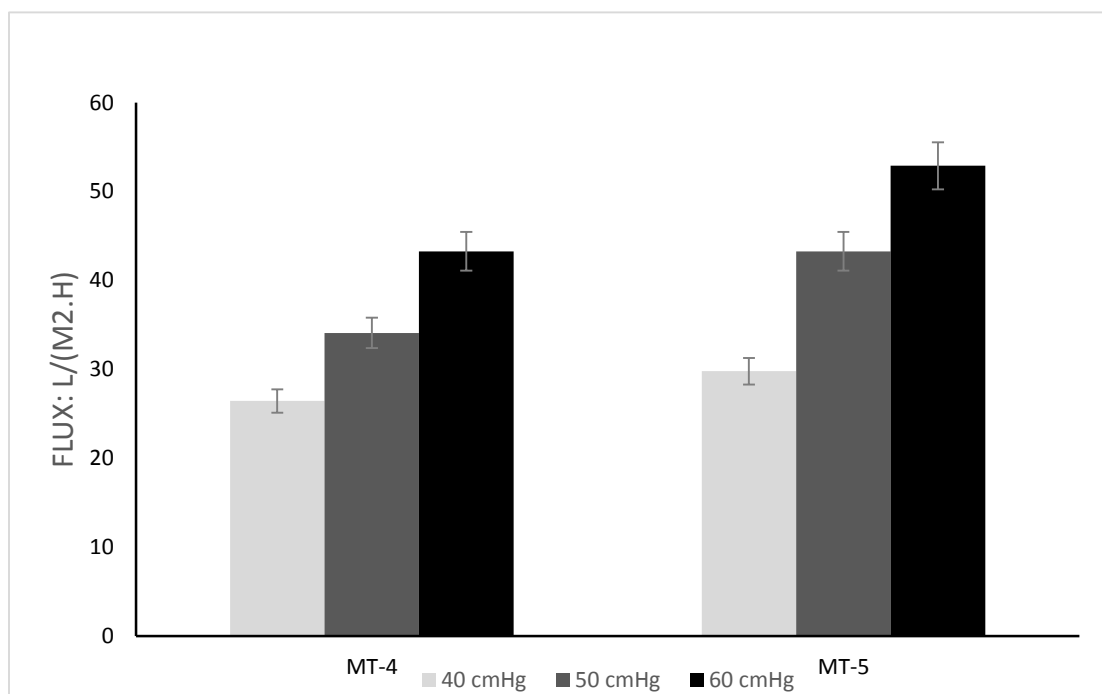


Figure 3.12: Membrane flux not increased in the membranes with higher concentration of TiO₂ nanoparticles

3.4 CONCLUSION

Asymmetric mixed matrix membranes were successfully prepared via phase inversion technique and studied in detail using different characterization techniques. The TiO₂ nanoparticles synthesized in chapter 2 were successfully incorporated into PES membranes. Addition of TiO₂ nanoparticles into the PES membranes affects the morphology, surface properties and other performances of the fabricated membranes. The SEM results exhibited the differences in overall porosity, pore size and width of fabricated membranes. The XRF results also indicated proper attachment of TiO₂ nanoparticles in the membranes as no nanoparticles were detected in the water filtered from the membranes. The contact angles analysis indicated that membranes with incorporated nanoparticles were more hydrophilic as compare to PES alone. The increase in thermal stability, membrane flux and water retention by fabricated membranes showed significant results. These results put forward the promising future of these membranes in the water industry.

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CHAPTER 4
ANTIBACTERIAL ACTIVITY OF NANOPARTICLES AND
MEMBRANES

⁴ A part of this chapter is submitted for publication in Journal of Membrane Science

4.1 LITERATURE REVIEW

4.1.1 Antibacterial activity titanium oxide nanoparticles

Photokilling of bacteria using TiO₂ nanoparticles is also an important property that is under investigation. Lipid membrane of bacteria contain poly unsaturated phospholipid component, its peroxidation is promoted by photocatalysis of TiO₂ nanoparticles, this will cause the respiration loss and ultimately cell death (Maness et al., 1999). This effect is because of generation of reactive oxygen species upon illumination of TiO₂ by UV. The ROS generated are can be HO[•], H₂O₂ and O₂^{•-}. Mostly HO[•] is considered as main cause of antibacterial effect produce by these particles (Gogniat, Thyssen, Denis, Pulgarin, & Dukan, 2006). In an experiment complete killing of bacteria by TiO₂ upon illumination was achieved in 50 minutes. Another important aspect mentioned in this study that smaller size of these particles may also help in killing bacteria by invading in their cell walls. They also test that the coating of orthopedic materials with these particles can prevent infections. So this property can be added to medicinal facilities where the aim is to prevent infections (Tsuang et al., 2008).

4.2 EXPERIMENTAL

4.2.1 Testing antibacterial activity of TiO₂ nanoparticles

Antibacterial activity of TiO₂ nanoparticles was checked against *E. coli* and MRSA.

The protocol followed to find out antibacterial activity of nanoparticles is mentioned below.

4.2.1.1 Antimicrobial effect by mixing nanoparticles in liquid media

To check antibacterial activity three different concentrations of TiO₂ nanoparticles taken were:

1. 0.0075 gm of TiO₂ nanoparticles per 15ml of liquid nutrient agar
2. 0.015 gm of TiO₂ nanoparticles per 15ml of liquid nutrient agar
3. 0.0225 gm of TiO₂ nanoparticles per 15ml of liquid nutrient agar

These particles were exposed to UV (intensity: 30W, wavelength: 320nm) for one hour and then mixed in liquid nutrient agar. Agar was then poured in petri plates and allowed to cool. The 10⁻³ dilutions of *E. coli* and MRSA were spread over the cooled agar plates containing different concentrations of nanoparticles. The plates were incubated at 37 °C for 24 hours. This step was further investigated by exposing each of the above mentioned concentrations of TiO₂

nanoparticles with three different timing of UV exposure and then the effect of time was also compared.

4.2.2 Testing antibacterial activity of fabricated membranes

The antibacterial activity of membranes was checked by preparing 10^{-6} dilutions of *E. coli* and MRSA (Methicillin-resistant *Staphylococcus aureus*). Polyether sulfone membrane and membranes with drug only (no filler in it), were used as control membranes. In first step dilution were prepared. The Inoculum of bacteria was added in nutrient broth and was placed in incubator to allow bacteria to grow properly. 1ml from this broth was added in 9ml of distilled water to form 10^{-1} dilution, from this dilution 1ml was added into another 9ml of distilled water to form 10^{-2} dilution, this process was repeated until 10^{-6} dilutions of each bacteria were obtained for every membrane.

Dilutions of both bacteria were spread over agar plates these were taken as control. The 10^{-6} dilution prepared for each membrane was passed through the membrane fitted in filtration assembly. The resulting filtrate was finally spread over the prepared agar plate. The plates were incubated at 37 °C for 24 hours. This step was further investigated by exposing each of the membrane with three different timings of UV exposure and then the effect of time was also compared. The Statistical analysis (one way ANOVA) was performed for calculating p-value using independent T test.

4.3 RESULTS AND DISCUSSION

4.3.1 Antibacterial activity of nanoparticles by mixing them in liquid agar

The activity of nanoparticles against MRSA and *E. coli* was obtained by taking three different concentrations of nanoparticles. The results showed that the antibacterial activity increased by increasing amount of nanoparticles. It can be seen in the figure 5 that plate with 0.0075gm of TiO₂ nanoparticles showed maximum growth of bacteria, almost whole agar plate is covered with bacterial growth. While this trend of bacterial growth is decreased in other two agar plates as the concentration of nanoparticles is increased. The plate with maximum concentration of nanoparticles showed minimum bacterial growth on it. This trend of growth was similar with both *E. coli* and MRSA.

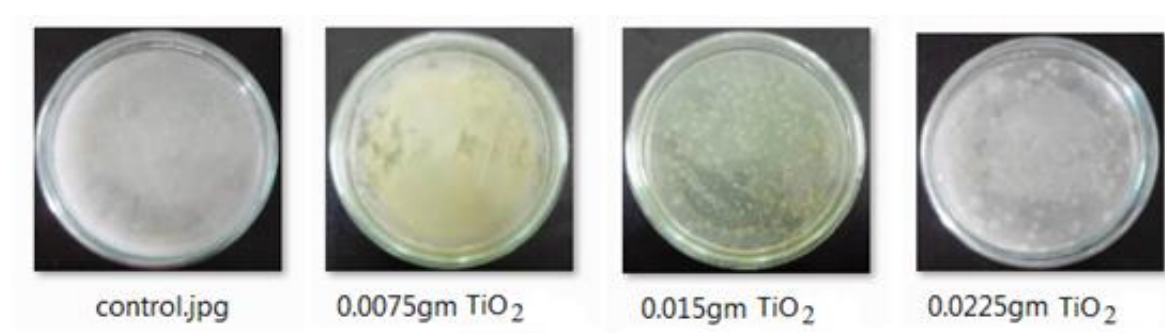


Figure 4.1: Antibacterial activity of TiO₂ nanoparticles against MRSA

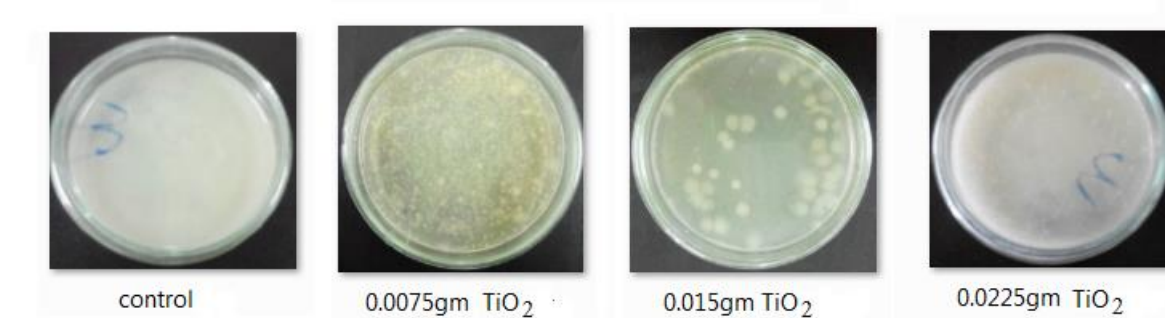


Figure 4.2: Antibacterial activity of TiO₂ nanoparticles against *E. coli*

4.3.2 Antibacterial activity of fabricated membranes

The fabricated membranes with TiO₂ nanoparticles exemplified the superlative properties in characterization techniques. This test was then carried out to find out antibacterial activity of these membranes with and without UV light irradiation. The titanium dioxide nanoparticles incorporated mixed matrix membranes were exposed to UV light (intensity: 30W, wavelength: 320nm). The filtered water of membranes was spread over the agar petri plates. After incubation of petri plates for 24 hours, the results of control membranes plates were compared with plates of membranes incorporated with nanoparticles. The antibacterial activity of fabricated membranes was proved by the decrease in bacterial colonies over the agar plates, due to photocatalytic bactericidal effect of TiO₂ nanoparticles. The activity of all membranes is plotted in the form of graph (figure 16). The maximum killing was observed in membrane with maximum nanoparticles when compared with other membranes. In second experiment effect of time variation of UV exposure was investigated (figure 17) maximum killing was seen when membranes were exposed for 90min. This specified that increasing duration of UV exposure the antibacterial

activity of membrane also changed because of increased exposure of nanoparticles to UV. Mostly studies suggested that this bactericidal effect of TiO₂ nanoparticles/photocatalysis is because of the generation of reactive oxygen species generated by UV exposure. These ROS attack bacterial cell membrane and also initiate lipid peroxidation reactions that ultimately cause cell death (Rahimpour et al., 2012). The evident of similar study suggested that TiO₂ photocatalysis causes rapid cell inactivation at regulatory and other signaling levels. The coenzyme independent respiratory chains are also decreased by it. It also decreases assimilation and of transport of phosphorus and iron ions. The capacity for synthesis and degradation of Fe-S clusters (heme groups) also decreases. These factors collectively contribute in the cell wall modification and high biocidal performance of TiO₂ nanoparticles (Kubacka et al., 2014). The statistical analysis results were significant at various levels, as antibacterial activity of all fabricated membranes showed p value less than 0.05. The PES membrane with 0.15% TiO₂ nanoparticles showed minimum p value that is 0.000004 and 0.000025 against *E. coli* and MRSA respectively.

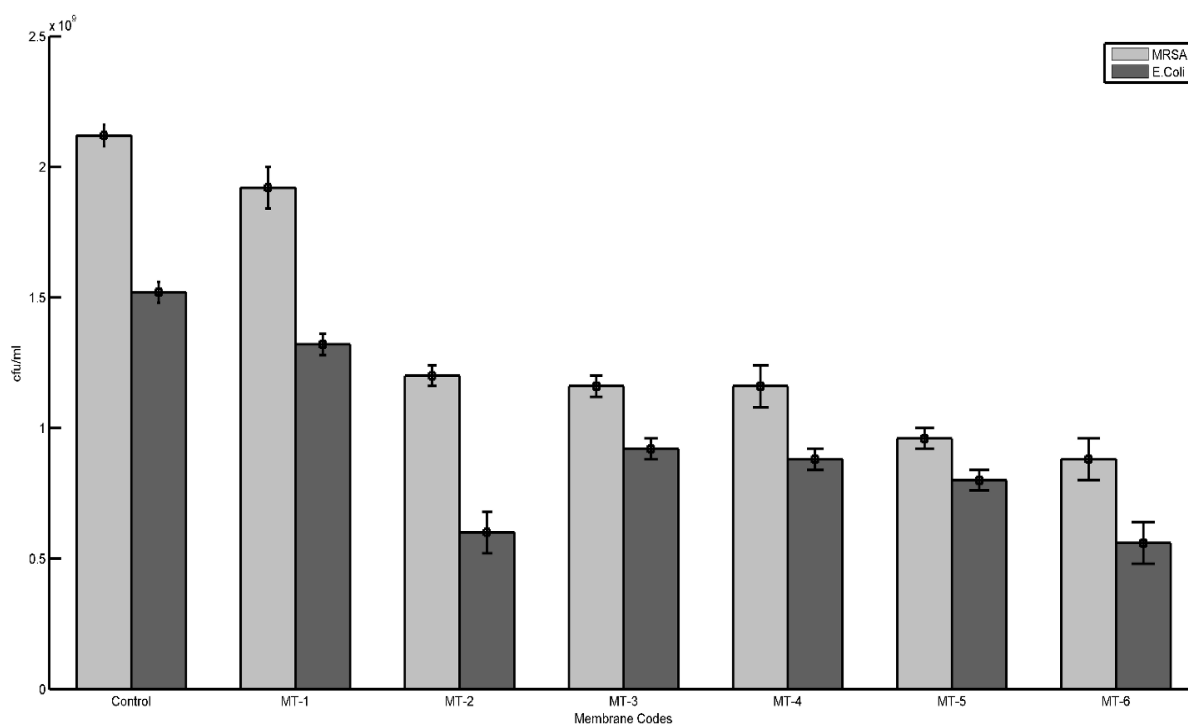


Figure 4.3: Antibacterial activity of fabricated membrane against MRSA and E.coli bacteria

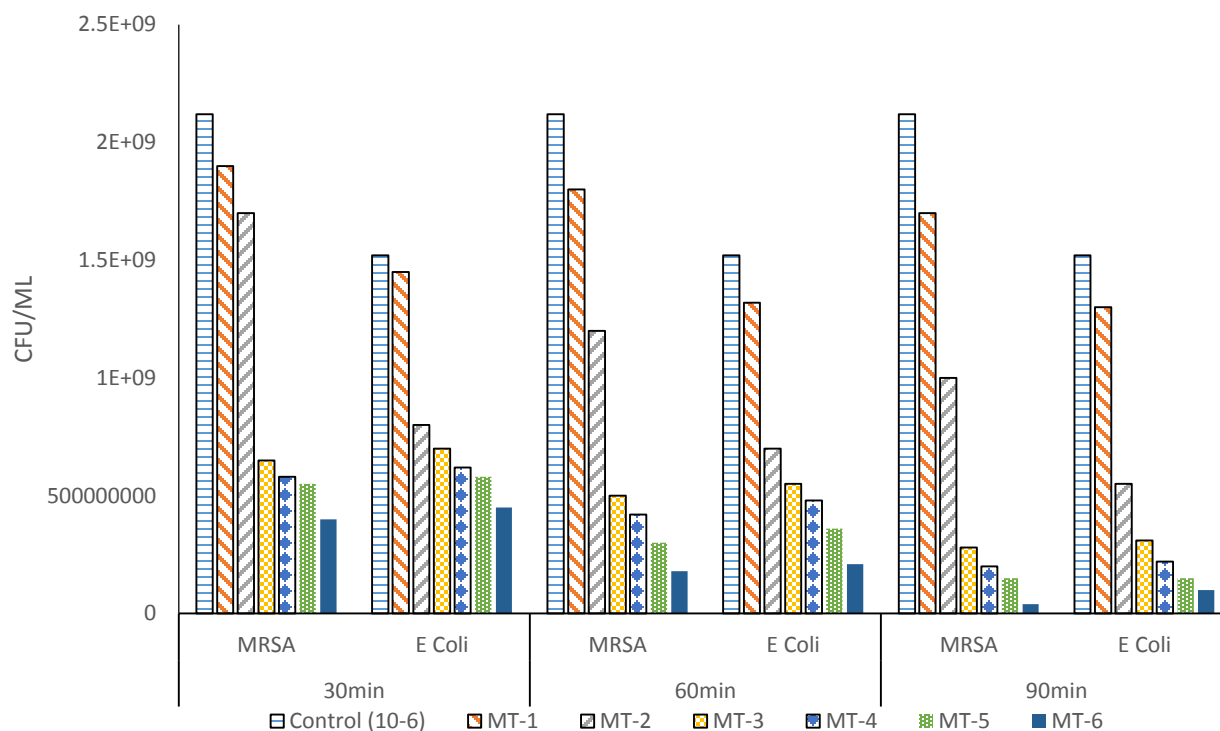


Figure 4.4: Antibacterial activity of membranes by varying UV exposure duration

4.4 CONCLUSIONS

TiO₂ mediated bactericidal and photo catalytic activities were clearly demonstrated in the study. These TiO₂ nanoparticles are effective in killing bacterial colonies of *E. coli* and MRSA grown over the agar plates. The bacterial colonies present in water were also eliminated by the help of these TiO₂ nanoparticles incorporated in the membranes. These results provide main evidence for the use of these nanoparticles for antibacterial activities. As it can be concluded from the above results that increasing concentration of nanoparticles along with increasing UV exposure duration ultimately increases the antibacterial activity of these nanoparticles in agar plates and in membranes too.

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**CHAPTER 5: STUDY CONCLUSIONS AND
FUTURE RECOMMENDATIONS**

5.1 Study conclusions

1. The Functionalized TiO₂ nanoparticles fabricated membranes for water purification/treatment were successfully synthesized as depicted by the results of characterization techniques.
2. The membrane morphology, surface and other properties were overall altered by the addition of TiO₂ nanoparticles. The filtrate XRF showed membrane synthesis with proper attachment of functionalized nanoparticles. The membrane performance such as hydrophilicity, thermal stability and water flow were enhanced while decrease in roughness and mechanical strength of membrane -by increasing nanoparticles was observed.
3. The Killing of *E. coli* and MRSA by TiO₂ nanoparticles was confirmed. The antibacterial activity (under UV irradiation) of membranes showed reduction in bacterial colonies. The activity increased by increasing duration of UV exposure.

5.2 Future recommendations

1. As these nanoparticles have broad spectrum against microorganisms so they can be utilized for antibacterial activities.
2. The photo catalytic effect of these nanoparticles can be employed in other biomedical applications like coating bandages, filters for other uses that can utilize hydrophilic character of these nanoparticles
3. By adjusting proper ratio of polymer and nanoparticles purification can be enhanced
4. Doping with other nanomaterial can also be investigated
5. Addition of different drugs and their effect can also be studied
6. Research should be done at practical level that would help to in proper use of these membrane filters.

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Supervisor: Dr. Nasir M. Ahmad

Signature: _____

Co-Supervisor: Dr. Muhammad Nabeel Anwar

Signature: _____