



T.C.  
**İSTANBUL UNIVERSITY**  
**INSTITUTE OF GRADUATE STUDIES**  
**IN SCIENCE AND ENGINEERING**



**M.Sc. THESIS**

**PREPARATION AND CHARACTERIZATION OF POLYMER  
NANOCOMPOSITE MEMBRANES FOR WATER TREATMENT  
APPLICATION**

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**Department of Bio and Nanotechnology Engineering**

**Bio and Nanotechnology Engineering Programme**

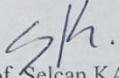
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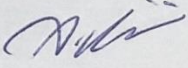
  
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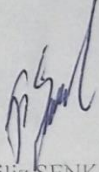
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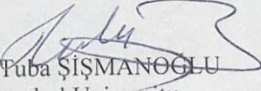
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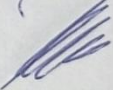
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## **FOREWORD**

(And there is the one whose knowledge is far greater than the knowledge of all others)  
Holy Quran.

I would like to dedicate this thesis to my parents and my family, whose understanding, support, and encouragement made the completion of this studying possible. I would like to thank my supervisor Assit Prof Selcan KARAKUS and co-supervisor Prof Dr. Ayben KİLİSLİOĞLU they guided, advised, and helped me to approach my aim. I would like to thank my brothers, sisters, friends, and everyone who supported me.

June 2017

Attallah Khalaf Taha TAHA

## TABLE OF CONTENTS

<b>FOREWORD</b> .....	<b>i</b>
<b>TABLE OF CONTENTS</b> .....	<b>ii</b>
<b>LIST OF TABLES</b> .....	<b>v</b>
<b>LIST OF FIGURES</b> .....	<b>vi</b>
<b>LIST OF SYMBOLS AND ABBREVIATION</b> .....	<b>ix</b>
<b>ÖZET</b> .....	<b>xii</b>
<b>SUMMARY</b> .....	<b>xiii</b>
<b>1. INTRODUCTION</b> .....	<b>1</b>
1.1. WHAT SO SPECIAL ABOUT NANO .....	1
1.2. WHAT NANO REALLY MEANS .....	2
1.3. WHAT IS NANOTECHNOLOGY .....	2
1.4. NANOSCIENCE .....	3
1.5. APPLICATIONS OF NANOTECHNOLOGY AND NANOPARTICLES .....	3
1.5.1. Definitions .....	3
1.5.2. Dental Nanomaterials .....	3
1.5.3. In Food Science .....	4
1.5.4. In Natural Gas And Oil Science .....	4
1.5.5. In Medical Applications .....	4
1.5.6. In Water And Wastewater Treatment .....	4
1.5.7. Nanotechnology For Biosensor Applications .....	5
1.6. NANOPARTICLES .....	5
1.6.1. Zinc Oxide Nanoparticles .....	5
1.6.2. Gold Nps .....	6
1.6.3. Carbon Nanotubes .....	6
1.6.4. Classification of Carbon Nanotubes .....	7
1.7. LITERATURE REVIEW .....	8
1.7.1. Introduction .....	8

<b>2. MATERIALS AND METHODS.....</b>	<b>27</b>
2.1. MATERIALS.....	27
2.1.1. POLYSULFONE (PSF).....	27
2.1.2. POLYVINYLPIRROLIDONE (PVP) .....	27
2.1.3. POLY(VINYLDENE FLUORIDE) (PVDF) .....	28
2.1.5. 1-METHYL-2-PYRROLIDINONE (NMP).....	29
2.1.6. Zinc Oxide Nanoparticles .....	29
2.2. METHODE.....	30
2.2.1. FTIR.....	30
2.2.2. Sonification.....	30
2.2.3. X-Ray Diffraction .....	31
2.2.4. Scanning Electron Microscopy.....	31
2.2.5. Thermogravimetric Analysis .....	31
2.2.6. Total Organic Carbon Analyzer.....	32
2.2.7. Micrometer Adjustable Film Applicator (Film Casting Knife).....	33
2.3. SYNTHESIS MEMBRANE.....	34
2.3.1. Polysulfone Membrane .....	34
2.3.2. PVDF/PSF/PVP/ZnO and PVDF/PSF/PVP Membranes .....	35
2.4. MATERIAL COSTS .....	36
2.5. THE MECHANISM OF THE MEMBRANE .....	37
<b>3. RESULTS.....</b>	<b>38</b>
3.1. FTIR.....	38
3.1.1. FTIR of Polysulfone .....	38
3.1.2. FTIR of Polyvinylvirolidon .....	39
3.1.3. FTIR of the Membrane Sample Composed of Two Polymers .....	39
3.1.4. FTIR of ZnO Nanoparticles.....	40
3.1.5. FTIR of Membrane Sample Based ZnO.....	41
3.1.6. FTIR of PVDF .....	41
3.1.7. FTIR of PVDF/PSF/PVP/ZnO .....	42
3.2. XRD ANALYSIS .....	43
3.2.1. XRD Analysis of PSF and PVP.....	43
3.2.2. XRD Analysis of PSF/PVP/ZnO .....	43
3.2.3. XRD Analysis of PSF/PVP/PVDF/ZnO.....	44

3.2.4. XRD Analysis of PSF/PVP/PVDF .....	44
3.3. THERMAL GRAVIMETRIC ANALYSIS TGA .....	45
3.3.1. TGA of PSF/PVP/ZnO .....	45
3.3.2. TGA of PSF/PVP.....	45
3.3.3. TGA of PSF/PVP/PVDF .....	46
3.3.4. TGA of PSF/PVP/PVDF/ZnO .....	46
3.4. SEM ANALYSIS .....	47
3.4.1. SEM Analysis For Membrane 18.5 % PSF .....	48
3.4.2. SEM analysis for Membrane consist of PSF and PVP .....	48
3.4.3. SEM Analysis of Surface.....	50
3.5. THE CUTOFF MW REJECTION TEST. ....	56
3.6. STABILITY RESISTOR OF MEMBRANE IN AN AQUEOUS SYSTEM.....	57
<b>4. DISCUSSION.....</b>	<b>58</b>
<b>5. CONCLUSION AND RECOMMENDATIONS .....</b>	<b>60</b>
<b>REFERENCES .....</b>	<b>62</b>
<b>CURRICULUM VITAE .....</b>	<b>67</b>

## LIST OF TABLES

<b>Table 1.1:</b> Inhibition zone of ZnO with bc mono and multi-layer film under US.....	12
<b>Table 1.2:</b> The antibacterial activity and inhibitions zones in mm (mile meter .....	13
<b>Table 1.3:</b> Degradable performance life exhibited on NPs based polymers .....	14
<b>Table 1.4:</b> Zone of inhibitions of cellulose, ZnO and ZnO/CNC against S. aureus .....	15
<b>Table 1.5:</b> Antibacterial of Streptomyces sp. and ZnONPs against E. coli , B.S .....	17
<b>Table 1.6:</b> Zones of inhibition for various concentrations of PIND/AgZnO NPs .....	19
<b>Table 1.7:</b> Shown ratio of PSF/COOH to get antifouling and high flux .....	21
<b>Table 1.8:</b> Shown the ratio of PSF based CNS and DMAc to prepare membrane .....	23
<b>Table 1.9:</b> Shown the concentration of PSF / C60 .....	26
<b>Table 1.10:</b> Concentration of NaCl and rejection.....	27
<b>Table 1.11:</b> Compositions of PSF membrane casting PEG, DMAc, Pluronic F 127 .....	25
<b>Table 2.1:</b> Explain the sample ratio of all membranes .....	35
<b>Table 2.2:</b> Explain costs of material .....	36
<b>Table 3.1:</b> Explain the rejection value in % for many membrane sample.....	56



## LIST OF FIGURES

<b>Figure 1.1:</b> From macro:-materials to atoms: nanomaterials and nano devices that interestin nanotechnologies are at the lower end of the scale (1–100 nm) .....	2
<b>Figure 1.2:</b> TEM microphage showing swnts .....	7
<b>Figure 1.3:</b> TEM image of Ag/ZnO/RGo Nano composite (a) (b) edx spectrum (c) forthe nanoparticle pointed by a red circle .....	9
<b>Figure 1.4:</b> A) XRD of Go,Ag–ZnO bmnps,Ag–ZnO bmnps@Go nanocomposite .FeSEM tem images of Go(band) and Ag–ZnO bmnps@Go nanocomposite(c and e),respectively .High magnification Fe-SEM images of(f)adduct (g)MIP-modified glass surfaces.(h) cross-reactivity study of MIP-and NIP - modifiedelectrodes for arious interfering compounds (Roy et al. 2017).....	10
<b>Figure 1.5:</b> Antibacterial activity pathogens. a: E. coli; b: S. aureus; c: B. subtilis; d:Styphi.....	11
<b>Figure 1.6:</b> Antibacterial activity, micron size ZnO powder and a/ZnO Nps.....	11
<b>Figure 1.7:</b> SEM image of cross section of pure bc (a), ZnO-bc (b),ZnO-BC-ml (c) and ZnO-BC-us (b) .....	12
<b>Figure 1.8.</b> Antibacterial activities of chitosan as blank, CS / PEG/ calcium silicate nanocomposites against grampositive (staphylococcus aureus),gram negative (Pseudomonas aeruginosa) bacteria, fungi (candidia albicans) and aspergillus niger, theblack dart point to the sample and red point to inhibition zones).....	13
<b>Figure 1.9:</b> Antibacterial zone of inhibition of 5 mg/ml of cellulose, ZnO/CNC tetracycline (t) against S. aureus (a) and E. coli (b).....	15
<b>Figure 1.10:</b> The antibacterial average of escherichia coli and staphylococcus use various films under fluorescent light the blank is the nickel foam. ....	16
<b>Figure 1.11:</b> Antibacterial for (a) isolated streptomyces mtcc-3276 streptomyces (b) biosynthesized ZnONp (50 micro g/ml), (c) biosynthesized ZnO (100 micro g/ml.( b Analysis of the zone of inhibition .....	17
<b>Figure 1.12:</b> (A-f). antibacterial activity of various nanocomposites against two p.strains; (a) E. coli (b) E. faecalis, (c) P. mirabilis, (d) B. subtilis (e) S. ....	18
<b>Figure 1.13:</b> (A) control (s. aureus), (b) sample (f dopping ZnO 1:1, after exposure visible light) .....	20
<b>Figure 1.14:</b> Mechanism of photocatalytic antibacterial of ZnO electron transfers fromthvalence band to conduction band and destroys the cell membrane. ....	20
<b>Figure 2.1:</b> Polysulfone (PSF).....	27
<b>Figure 2.2:</b> Polyvinylpyrrolidone (PVP).....	28

<b>Figure 2.3:</b> Poly (vinylidene fluoride) (PVDF).....	28
<b>Figure 2.4.</b> Polyethylene glycol (PEG).....	29
<b>Figure 2. 5:</b> 1-Methyl-2-pyrrolidinone (NMP). ....	29
<b>Figure 2.6:</b> FTIR alpha bruker device.....	30
<b>Figure 2.7:</b> Sonication 300w ultrasonic processor.....	31
<b>Figure 2.8:</b> TG 50 thermal gravimetric device.....	32
<b>Figure 2.9:</b> Toc total organic carbon device. ....	33
<b>Figure 2.10:</b> Micrometer adjustable film applicator. ....	34
<b>Figure 2.11:</b> A) is polysulfone membrane b) is casting knife tools. ....	35
<b>Figure 3.1:</b> FTIR of pure polysulfone shown $\nu_{\text{C-S}}$ .....	38
<b>Figure 3.2:</b> FTIR of polyvinylpyrrolidone PVP pure polymer. ....	39
<b>Figure 3.3:</b> FTIRs for membrane sample mixed (a) PSF 18.5 % w),(b) PVP 0.5 w ) and(c) is membrane formed by mixed (a+b). ....	40
<b>Figure 3.4:</b> FTIR of zinc oxide nanoparticles shown $\nu_{\text{Zn-O}}$ bound.....	40
<b>Figure 3.5:</b> FTIRs for membrane ZnONps PSF 18.5 % w), (b) PVP 0.5 w %), (c) membrane formed by mixed (a+b), (d) is ZnO 10%, and (e) is. (a+b+c+d) .....	41
<b>Figure 3.6:</b> FTIR for polyvinylidene fluoride PVDF.....	41
<b>Figure 3.7:</b> FTIR for a) PVDF 18.5% PSF18.5%, PVP18.5%, (b) ZnO 10% and (c) FTIR is (a+b). ....	42
<b>Figure 3.8:</b> XRD analysis for membrane PSF 18.5% and PVP 0.5%.....	43
<b>Figure 3.9:</b> XRD analysis for membrane PSF 18.5% and PVP 0.5% andZnO 10%. ....	43
<b>Figures 3.10:</b> Membrane contain PSF 18.5%, PVP 18.5%, PVDF 18.5% . ....	44
<b>Figure 3.11:</b> Membrane contain PSF 18.5%, PVP 18.5%, PVDF18.5% 10% ZnO. ....	44
<b>Figure 3.12:</b> TGA for PSF/PVP/ZnO.....	45
<b>Figure 3.13:</b> TGA for PSF/PVP. ....	45
<b>Figure 3.14:</b> TGA for PSF/PVDF/PVP/.....	46
<b>Figure 3.15:</b> TGA for PSF/PVDF/PVP/ZnO .....	46
<b>Figures 3.16:</b> PSF membrane a1-a3)top surface cross section and bottom surface at magnify1 $\mu\text{m}$ ) b1-b3top surface cross section bottom surface at magnify $\mu\text{m}$ 10(c1-c3) top surface cross section and bottom surface at magnify 100 $\mu\text{m}$ . ....	48
<b>Figures 3.17:</b> PSF and PVP membrane shows a1-a3) top surface cross section and bottom surface at magnify 1 $\mu\text{m}$ ) b1-b3top surface cross section and bottom surface magnify $\mu\text{m}$ 10 c1-c3 top surface cross and bottom surface 100 $\mu\text{m}$ .....	49
<b>Figure 3.18 :</b> Membrane PSF18.5% /PVP 0.5% a) 4 $\mu\text{m}$ b) 10 $\mu\text{m}$ c) 20 $\mu\text{m}$ and d) 100 $\mu\text{m}$ .....	50

<b>Figure 3.19:</b> SEM scanning for PSF / PVP/ ZnO were a1) membrane dispersing ZnON 1µm, a2) shown NPs size 1µm and B ,cross section at 10µm , c,d) cross section 0 at 20 µm, e) bottom f) cross section at 100 µm.....	51
<b>Figure 3.20:</b> SEM of membrane PSF/PVDF/PVP 18.5% fo. a-a3 cross section at 4, 10, 20, an 100 µm) b, c) top surface at 10 , 20 µm D) membrane section. ....	52
<b>Figure 3.21:</b> SEM for PSF/PVP/PVDF 18.5% for each one ZnO nps10%. a1)Nps dispersing on the top surface a2) the size on nps b, c , d , f cross section at different magnifications 4, 10, 20, 100 µm). ....	53
<b>Figure 3.22:</b> Dispersing the elements into all the membrane parts for PSF18.5% / PVP 0.5% ZnO 10%) a) zinc b) carbon c) silicon d) oxygen e) sulfur.....	54
<b>Figure 3.23:</b> Dispersing elements into membrane for PSF18.5% PVP 18.5%, PVDF 18.5, ZnO 10%) a) zinc b) oxygen c) sulfur d) flour e) silicon f) carbon.....	55
<b>Figure 5.6.</b> Illustrative the storage prouder. ....	57
<b>Figure 5.1:</b> Ternary polymer matrix / ZnO nanoparticle.....	61

## LIST OF SYMBOLS AND ABBREVIATION

<b>Symbols</b>	<b>Explanation</b>
<b>AG</b>	: Arabic Gum
<b>Ag</b>	: Silver
<b>Au</b>	: Gold
<b>B.S</b>	: Bacillus Subtilis
<b>BC</b>	: Bacteria Cellulose
<b>BMNPS</b>	: Bimetallic
<b>BNNTS</b>	: Boron Nitrite Nanotubes
<b>BP</b>	: Biphenyl
<b>C<sup>o</sup></b>	: Cellules
<b>Cf</b>	: Concentration Final
<b>CFU</b>	: Colony Forming Unit
<b>Ci</b>	: Concentration Initial
<b>Cm<sup>2</sup></b>	: Centimeter Square
<b>CNS</b>	: Cellulose Nano Silica
<b>CNTS</b>	: Carbon Nanotubes
<b>Cu<sub>2</sub>O</b>	: Copper Oxide
<b>CV</b>	: Crystal Violet
<b>Da</b>	: Dalton
<b>Dmac</b>	: Dimethylacetemide
<b>DNA</b>	: Dexoribo Nucleic Acid
<b>E.Coli</b>	: Escherichia Coli
<b>E102</b>	: Commercial Dye
<b>EDX</b>	: Energy Dispersive X-ray

<b>EOR</b>	: Enhance Oil Recovery
<b>FY</b>	: Fiscal Year
<b>G+VE</b>	: Gram Positive
<b>G-VE</b>	: Gram Negative
<b>HIV</b>	: Human Immunodeficiency Virus
<b>IC</b>	: Inorganic Carbon
<b>IMT</b>	: Institute Microelectronics Technology
<b>Lit</b>	: Liter
<b>m/l</b>	: Milliliter
<b>Mb</b>	: Methyl blue
<b>min</b>	: Minute
<b>ML</b>	: Multi-Layer
<b>mm</b>	: Millimeter
<b>Mpa</b>	: Pascal
<b>MSC</b>	: Mesenchymal System Cell
<b>MWCNTS</b>	: Multi Wall Carbon Nanotubes
<b>MWCO</b>	: Molecule weight Cut-Off
<b>N<sub>2</sub></b>	: Nitrogen
<b>NC</b>	: Nano Cellulose
<b>Nm</b>	: Nano Meter
<b>Nmp</b>	: N-Methylprirlydon
<b>NNI</b>	: National Nanotechnology Initiative
<b>Nps</b>	: Nanoparticles
<b>NT</b>	: Nanotechnology
<b>OC</b>	: Organic Carbon
<b>PEG</b>	: Polyethylene Glycol
<b>PIND</b>	: Polyindole Polymer
<b>PPL</b>	: Phenolphthalein
<b>PSF</b>	: Polysulfone
<b>PVDF</b>	: Polyviylorridine Difluoride
<b>PVP</b>	: Polyvinylpyrrolidone
<b>QD</b>	: Quantum Dot
<b>RAS</b>	: Russian Academy Research

<b>RGO</b>	: Reduced Graphene Oxide
<b>S.AUREUS</b>	: Staphylococcus Aureus
<b>S.TYPI</b>	: Salmonella Typi
<b>SEM</b>	: Scanning Electron Microscopy
<b>SWCNTS</b>	: Single Wall Carbon Nanotubes
<b>TEM</b>	: Tuning Electron Microscopy
<b>TiO<sub>2</sub></b>	: Titanium Dioxide
<b>WHO</b>	: World Human Organize
<b>XRD</b>	: X-ray Diffraction
<b>ZnCL<sub>2</sub></b>	: Zinc Dichloride
<b>ZnO</b>	: Zinc Oxide
<b>ZrO<sub>2</sub></b>	: Zirconium Dioxide

## ÖZET

### YÜKSEK LİSANS TEZİ

#### SU ARITMADA KULLANIM AMAÇLI POLİMER NANOKOMPOZİT MEMBRANLARIN HAZIRLANMASI VE KARAKTERİZASYONU

**Attallah Khalaf Taha TAHA**

**İstanbul Üniversitesi**

**Fen Bilimleri Enstitüsü**

**Biyo ve Nano Teknolojisi Mühendisliği Anabilim Dalı**

**Danışman : Yrd. Doç. Dr. Selcan KARAKUŞ**

Polimer karışım esaslı nanotaniciklerdeki son gelişmeler nanoteknoloji için çok önemlidir. Düşük toksisitesi ve yüksek antimikrobiyal etkileri nedeniyle, ZnO gibi birkaç nanotanicik nanokompozit hazırlama aşamaları boyunca oldukça tercih edilir. Ayrıca endüstride kozmetik, boya, ilaç dağıtım sistemi, biyosensör ve tıp gibi birçok uygulama alanı bulunmaktadır. Bu tezde, üçlü polimer karışımları/ (ağırlıkça % 10) ZnO nanotanicikler ultrasonikasyona dayalı basit ve etkili bir yöntemle hazırlanmıştır. Amacımız PS / PVP / PVDF karışımlarına dayanan iyi bir dispersiyon ve yüksek kararlılıkta ZnO nanotanicik elde etmektir. Saf polimer ve üçlü polimer karışım / ZnO nanotaniciklerin termal kararlılığı, termogravimetrik analiz (TGA) ile analiz edildi. Üçlü karışımdaki ZnO nanotaniciklerin morfolojisi ve dağılımı, X-ışını kırınımı, Taramalı Elektron Mikroskopu ve Kızılötesi Spektroskopi ile değerlendirildi. Deneysel sonuçlar, ZnO nanotaniciklerin üçlü polimer karışım matrisinde nanoölçekte homojen bir şekilde dağılmış olduğunu gösterdi.

Haziran 2017, 83 sayfa.

**Anahtar Kelimeler:** Nanoteknoloji, polisülfon, polivinilpirolidon, poliviniliden fluorür,

## **SUMMARY**

### **M.Sc. THESIS**

#### **PREPARATION AND CHARACTERIZATION OF POLYMER NANOCOMPOSITE MEMBRANES FOR WATER TREATMENT APPLICATION**

**Attallah Khalaf Taha TAHA**

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**Department of Bio and Nanotechnology Engineering**

**Supervisor : Asst. Prof. Selcan KARAKUS**

Recent developments in polymer blend based nanoparticles are vital in the field of nanotechnology. Because of their low toxicity and high antimicrobial effects several nanoparticles such as ZnO are preferred during nanocomposite preparation steps. Polymer blend based nanoparticles have proven to have important industrial uses such as in the production of cosmetic, dye, drug delivery systems, biosensor technology and the field of medicine. In this thesis, ternary polymer blends/ (10 wt %) ZnO nanoparticles were prepared by a simple and effective method based on ultrasonication. Our aim was to obtain a good dispersion and high stability of ZnO nanoparticles based on PS/PVP/PVDF blends. The thermal stability of the pure polymer blends and ternary polymer blends/ ZnO nanoparticles was analyzed by thermogravimetric analysis (TGA). The morphology and the dispersion of the ZnO nanoparticles in ternary blends were then evaluated by X-ray diffraction, Scanning Electron Microscope and Infrared Spectroscopy. The experimental results showed that ZnO nanoparticles were dispersed homogeneously in the ternary polymer blend matrix in nanoscale.

Haziran 2017, 83 sayfa.

**Keywords:** Nanotechnology, polysulfone, polyvinylpyrrolidone, polyvinylidone fluoride, sonication, membrane.



## 1. INTRODUCTION

Today, nanotechnology (NT) is operating in diverse fields of science via its operation for materials and devices using different techniques at the nanometer scale Nanotechnology (science at 1-100 nanoscale).(Vaseem et al. 2010)

The history of Nanotechnology goes

back to the lecture given by Richard Feynman in 1959 at Caltech, in his famous talk titled "There's plenty of rooms at the bottom" discussed the idea of molecular machines or nanotechnology.

Norio Taniguchi (1974) uses the term "nanotechnology" in Tokyo to describe the lower limit for this process.

The concepts of Molecular Nanotechnology was put by Drexler in 1979. In 1981, Binnig and Rohrer invented the scanning tunnelling microscope (STM) which allowed Kroto, Smalley, Curl (1985) characterizes fullerene in the form of hollow sphere, ellipsoid or tubby. (1989), scientists at the IBM Research Center. The term nano for fluids was coined by Choi in 1995. Applications of nanotechnology in commercial products began in 2000 and many important discoveries are achieved up to present.(Umer et al. 2012)

### 1.1. WHAT SO SPECIAL ABOUT NANO

Nano' means very small; but why it is so special?

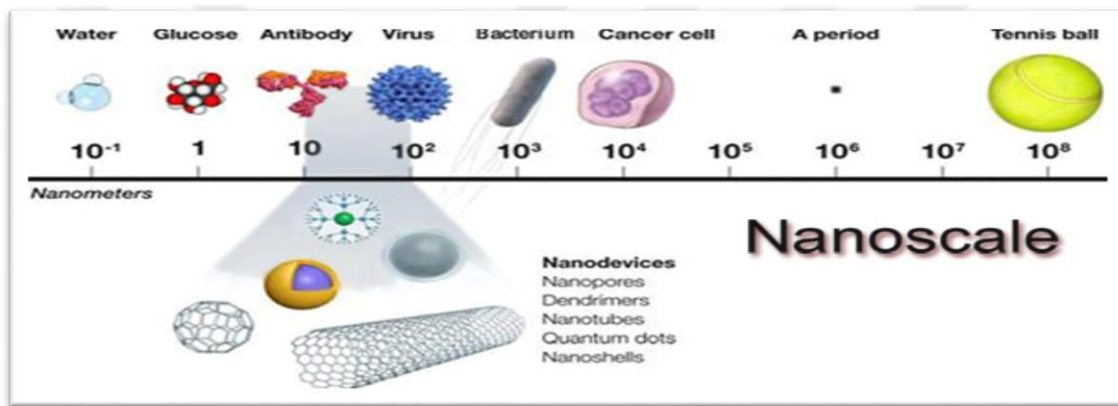
There are many specific reasons why it is nanoscience and nanotechnologies have become so important in the development of materials.

- First, the properties of matter at the nanometre scale change drastically such as electrical conductivity, color, strength, and weight.

- Secondly, extraordinary properties of nanomaterials can be obtained by fabrication of atom by atom via a process called bottom up.
- Finally, nanomaterials have increased surface area-to-volume ratio.(Sutherland 2012).

## 1.2.WHAT NANO REALLY MEANS

A nanometer is one billionth of a meter ( $10^{-9}$  m), about four times the diameter of an atom. Figure 1.1 shows the sizes of some kinds of materials: a human red blood cell is 10,000 nm; a cell of the bacterium *E. coli* is 1000 nm; a viral cell is 100 nm; a polymer coil is 40 nm; a Q-rod is 30 nm with a 10:1 aspect ratio; and a quantum dot (QD) is 7 nm in diameter.(Satalkar et al. 2016)



**Figure 1.1:** From macro:-materials to atoms: nanomaterials and nano devices that are of interest in nanotechnologies are at the lower end of the scale (1–100 nm).(Sutherland 2012).

Some illustrative examples

- Our fingernails grow at the rate of 1 nm per second;
- Head of a pin is about 1 000 000 nm in diameter;
- Human hair is about 80 000 nm in diameter;
- DNA molecule is 1–2 nm wide;
- The transistor of a latest-generation Pentium Core Duo processor is 45 nm(Sutherland 2012)

## 1.3. WHAT IS NANOTECHNOLOGY

The National Nanotechnology leads to Strategic Plan, developed by the Nanoscale Science, Engineering, and Technology Subcommittee defines nanotechnology in the following way: Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers.

A nanometer is one-billionth of a meter; a sheet of paper is about 100,000 nanometers thickness.

Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.

Since its inception in fiscal year (FY) 2001, the National Nanotechnology Initiative (NNI, website: <http://www.nano.gov>) has researched to hasten the responsible development and application of nanotechnology to make new jobs and economic growth, to enhance national security, and to improve the quality of life for all

#### **1.4. NANOSCIENCE**

The most common definition of nanoscience is: Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale. (Sutherland 2012)

#### **1.5. APPLICATIONS OF NANOTECHNOLOGY AND NANOPARTICLES**

##### **1.5.1. Definitions**

The scopes of Nanotechnology overlay a broad domains of application fields related to measurement and manufacturing; electronics; optoelectronics; biotechnology; and Nano materials among patent applications designated to the European Patent Approximately more than 4300 nanotechnology patent applications beside that there were patents in other countries such as USA and Japan and these patents have been using in many kinds of life Nanotechnology and nanoscience have been attracting broad recognition in recent years. (Igami 2008)

##### **1.5.2. Dental Nanomaterials**

Dental nanomaterials promote with the advent of Nano technological research focusing on the production and application of nanoparticles with excellent quality structural features.

- Antimicrobial Dental Nanomaterials.
- Nanomaterials for Curative Dentistry.
- Nanomaterials Conjugated.
- Biomodulation of Dental Tissues. (Padovani et al. 2015)

### **1.5.3. In Food Science**

Nanotechnology has become one of the most important technology in food science for the functionality and applicability:-

- Preservation contra biological harm.
- Preservation contra chemical ingredients.
- Enhancement of physical features.
- Safety concerns.(He & Hwang 2016)

### **1.5.4. In Natural Gas and Oil Science**

Applications of nanotechnology in oil and gas industry are interested in finding out new materials to solve problems and enhance oil recovery (EOR). For example, using organic and inorganic nanoparticles with different applications.,(Bera & Belhaj 2016).

The applications are:

- Petroleum exploration and oil microbe detection.
- In drilling and completion jobs.
- Simulation and modeling process.
- Field services.(Negin et al. 2016)

### **1.5.5. In Medical Applications**

Over the past years, up to now benefits of nanotechnology appeared in the medical field and treatments with some applications are given below;

The surveillance of the mesenchymal stem cells (MSC)(Corradetti & Ferrari 2016)

- Nanotechnology sets up with the hypothermal method for cancer remedy .(Beik et al. 2016)
- Drug delivery monitoring for the remedy and management of neuroAIDS(Nair et al. 2016) and prohibiting and remedying HIV infection.(Liu & Chen 2016)

### **1.5.6. In Water And Wastewater Treatment**

Providing spotless and refresh water to meet human requirements is a major trouble in the 21<sup>st</sup>.

Water is the most fundamental element in life , Worldwide, some 780 million people as yet scarcity access to get better drinking water springs (WHO).(Qu et al. 2013)

- Using the smart Nano filter to enhance and treat water.(Saidi & Zeiss 2016)
- To mitigate floating antimicrobial (metal oxide- NPs based nanocomposites (Al Aani et al. 2016).
- Thin film nanocomposites membrane was used to remove the water vapor from gases.(Baig et al. 2017)
- Elimination of Cyanobacterial cells and Microcystin toxine –LR from drinking water.(Sorlini et al. 2013)
- Elimination of heavy metal ions from water and wastewater.(Zhao et al. 2016)

### **1.5.7. Nanotechnology For Biosensor Applications**

The Nanotechnology is leading in expansion of Nano-Biosensors in nanoscale that have excellent sensing capability for any extreme target by detecting biochemical and biophysical signals(Touhami 2015).

- Detecting oxidized contaminations in water using sulfur oxidized bacteria.(Van Ginkel et al. 2011)
- Online Monitoring of Water Toxicity.(Elad et al. 2011)
- Determination of glucose in Nano molar levels.(Gao et al. 2017)
- To sensitive toxicity of organophosphorus pesticides in environment system in agriculture sectors (Hassani et al. 2016)
- To advance the bio detector system to detect some of the enteric bacteria such as E. Coli in water system using and designing new porotypes as bacteriophages. However, the sensing range was  $10^4$  bacteria per milliliter in 1.5 h.(Franche et al. 2016).
- Liquid crystal biosensor for detecting ischemia modified albumin.(He et al. 2017)

## **1.6. NANOPARTICLES**

### **1.6.1. Zinc Oxide Nanoparticles**

As a significant semiconductor, the ZnO has remarkable properties such as wide band gap, high electron mobility, low toxicity, low cost and easy synthesis.

Zinc oxide has been used in solar cell transistor and optical communications.

In addition, zinc oxide also used as a green material biocompatible and nontoxic in medical applications, food additive, and environmental science. ZnO NPs also gives an excellent antibacterial activity more stable than the organic material.(Wang et al. 2017)

### **1.6.2. Gold Nanoparticles**

Gold (Au) metal in its bulky shape is inert for most chemical activities. When gold prepared in nanoscale between 10 to 100 nm the chemical structure and properties totally change many common methods to synthesize the gold particles in nanoscale are vacuum evaporation method, colloids and deposition-precipitation method. Gold NPs have been using in too many application fields (Yazid et al. 2010)

### **1.6.3. Carbon Nanotubes**

Carbon in the solid phase can exist in three allotropic forms: graphite, diamond, and buckminsterfullerene.

Nanotubes have remarkable particulars which have made the attention of abundant researchers in diverse scopes and can be divided into varied categories, like carbon nanotubes (CNTs), boron nitride nanotubes (BNNTs) and carbon/boron nitride nanotubes.(Fatemi & Foroutan 2017).

The history of carbon nanotube (CNTs) dates back to the modern nanomaterials that have been renowned before more than 25 years, and the CNTs have been described and observed in 1952 by (Radushkevich and Lukyanovich) and in 1976 the single or double wall CNTs observed by (Oberlin et al), and then in 1991 the multiwall carbon nanotube MWCNTs have been defined and described by to Sumio Iijima who the first scientist has been establishing that.(Rakov 2008)

In 2004, a key contribution to the discovery of graphene was made by former and current Russian scientists from the Institute of Microelectronics Technology and High Purity Materials (IMT) of the Russian Academy of Sciences (RAS) CNTs, and graphene as well as revealing the main global players and journals in 2001–2010 (Terekhov 2015).

Carbon nanotube has grown from material of dreams to the real world material that already has applications field. However, the production of carbon nanotubes is growing year by year and this helped to use the carbon nanotubes in various fields such as composites, energy devices, electronics applications and in the medical applications.(Endo et al. 2006)

#### 1.6.4. Classification of Carbon Nanotubes

Single-walled carbon nanotubes (SWCNTs)

- About 1 nm in diameter with micrometer-scale lengths.
- Are unique in molecules, perfect structure, and polymers of pure carbon.

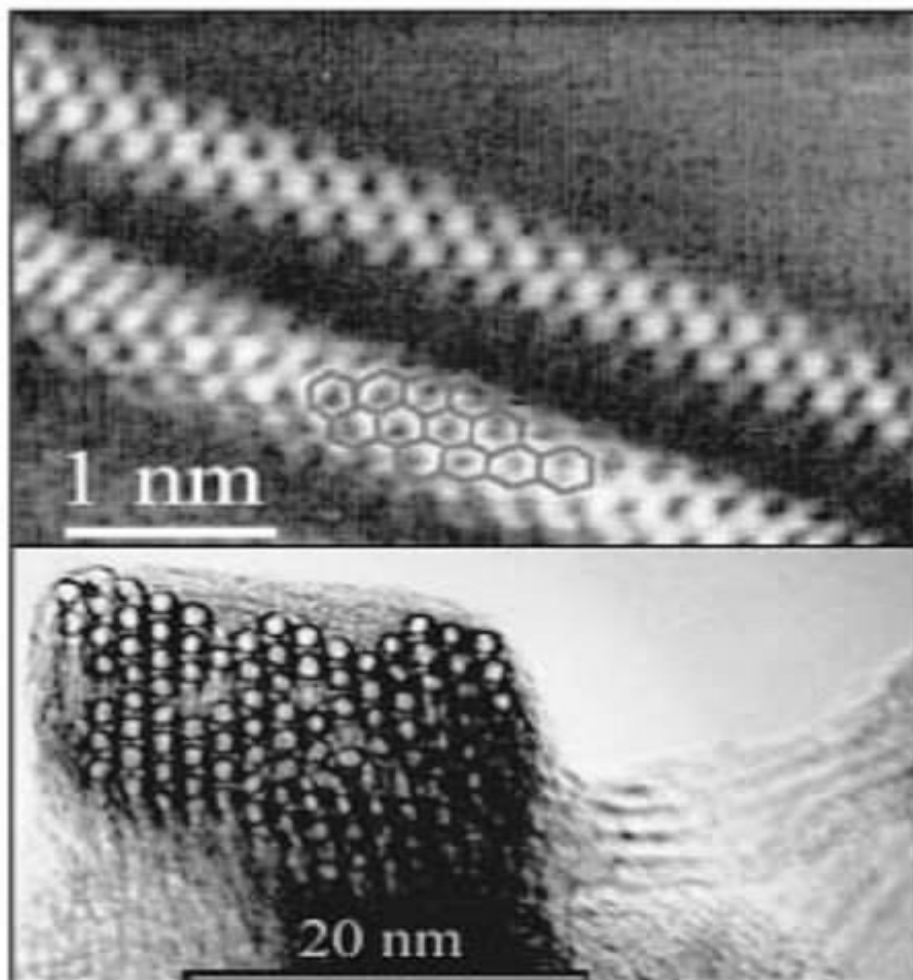
The SWCNTs have remarkable properties such as:-

- Strength  $\sim 100^*$  steel.
- Electrical conductivity ( $\sim$  copper).
- Thermal conductivity ( $3^*$  diamond).

Multi wall carbon nanotubes (MWCNT).

The (MWCNT) have remarkable properties such as:-

- Have internal diameter 2-10 nm.
- External diameter 20-75 nm.
- Low temperate 750c.(Annu et al. 2017)



**Figure 1.2:** TEM micrograph showing swnts (Koo 2006).

## **1.7. LITERATURE REVIEW**

### **1.7.1. Introduction**

In this chapter of my research I will mention and list some of works that applied in field of water treatments and they might use the nanotechnology in their researches.

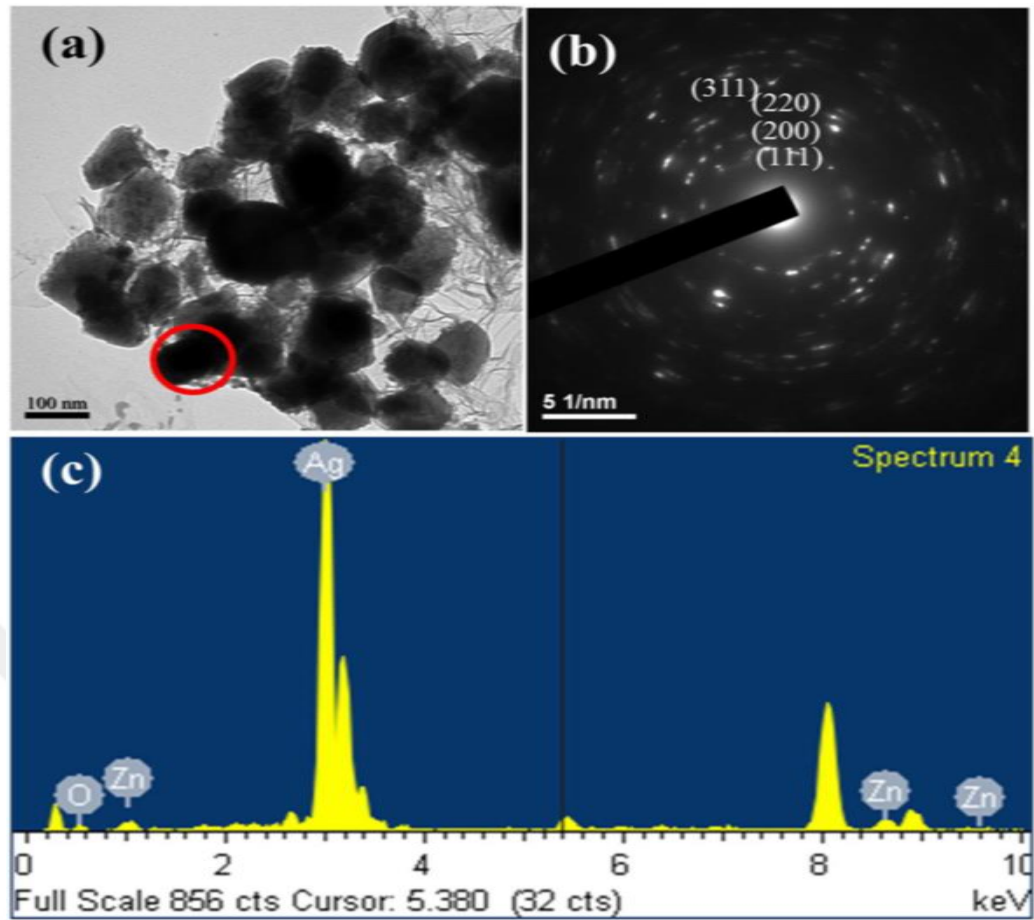
Most of these works have used the ZnO NPs with polymer to treat water and others have used Au or Ag, Tio<sub>2</sub>, Aluminum oxide and more of nanoparticles oxides with different nanocomposites.

Nanoparticles oxides may add to the polymer composites to enhance and support abundant of properties such as mechanical, temperature stability biodegradability and so on.

Ya Chi Ko, et al they serve in bactericidal and other germs and algae and they have promising multi ways to bacteria cidal.

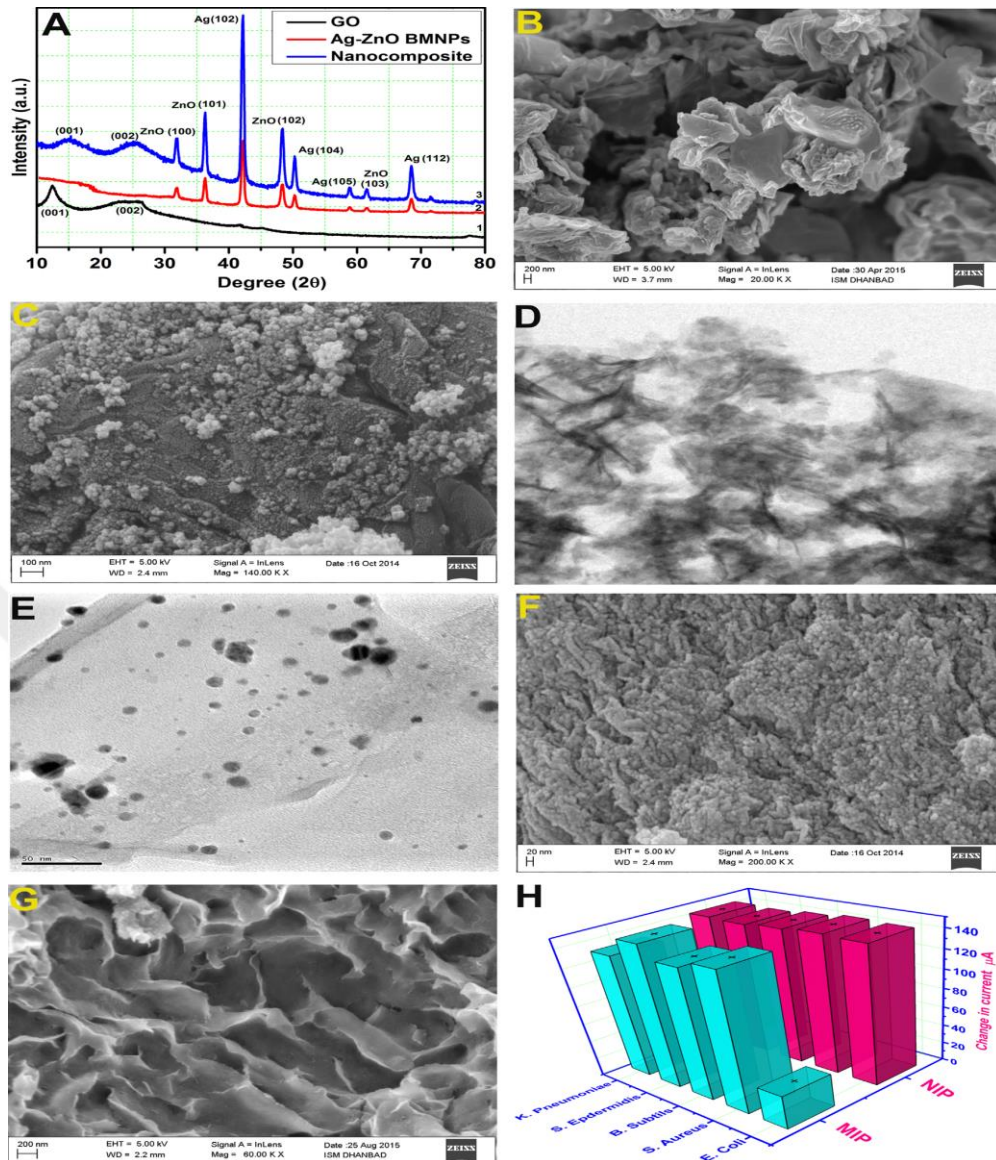
They used ZnO/Ag/rGo.





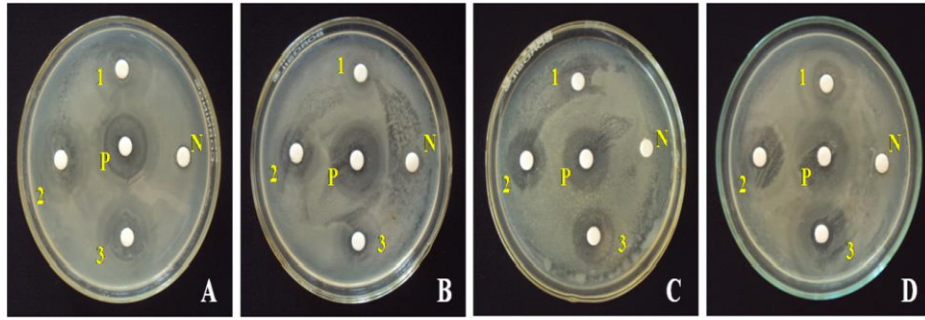
**Figure 1.3:** TEM image of Ag/ZnO/RGo Nano composite (a) (b) edx spectrum (c) for the nanoparticle pointed by a red circle (Ko et al. 2017).

Ekta Roy et al advanced novel method to eliminate and reduce the viability of bacteria and pathogens especially E-coli when they used the ZnO/Ag bimetallic nanoparticles and graphene oxide nanocomposites while a sensor of detection of gram-negative by quick time analysis 5 min can be removed  $10^5$  CFU mL<sup>-1</sup>.(Roy et al. 2017)



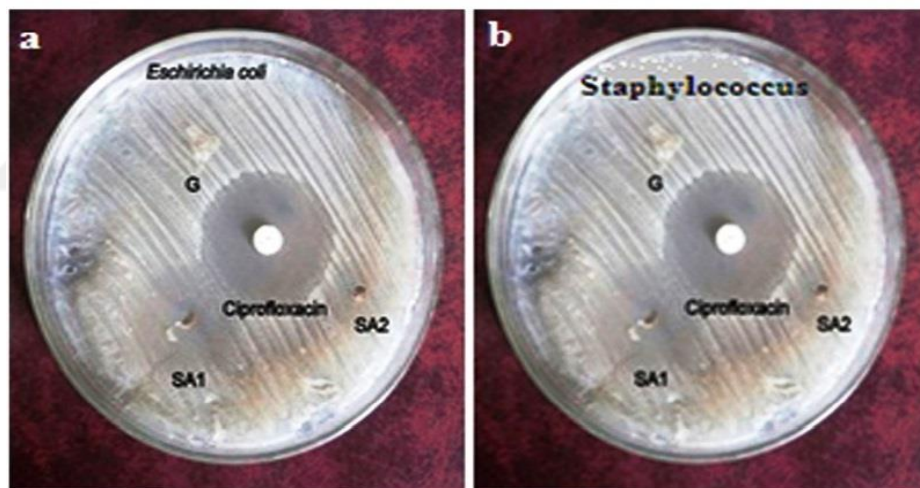
**Figure 1.4:** A) XRD of Go,Ag–ZnO bmnp,Ag–ZnO bmnp@Go nanocomposite .Fe-SEM and tem images of Go(band) and Ag–ZnO bmnp@Go nanocomposite(c and e),respectively .High magnification Fe-SEM images of(f)adduct and(g)MIP-modified glass surfaces.(h) cross-reactivity study of MIP-and NIP-modified electrodes for various interfering compounds (Roy et al. 2017).

M.Murali et al present and synthesize ZnO nanoparticles biologically from leaf extract of *Ceropegia candelabrum* and they applied zinc oxide nanoparticles as antibacterial and antioxidant extended excellent results against many types of bacteria such as *S. aureus*, *B. subtilis*, *E. coli*, and *S. Typhi*. As shown in figure:



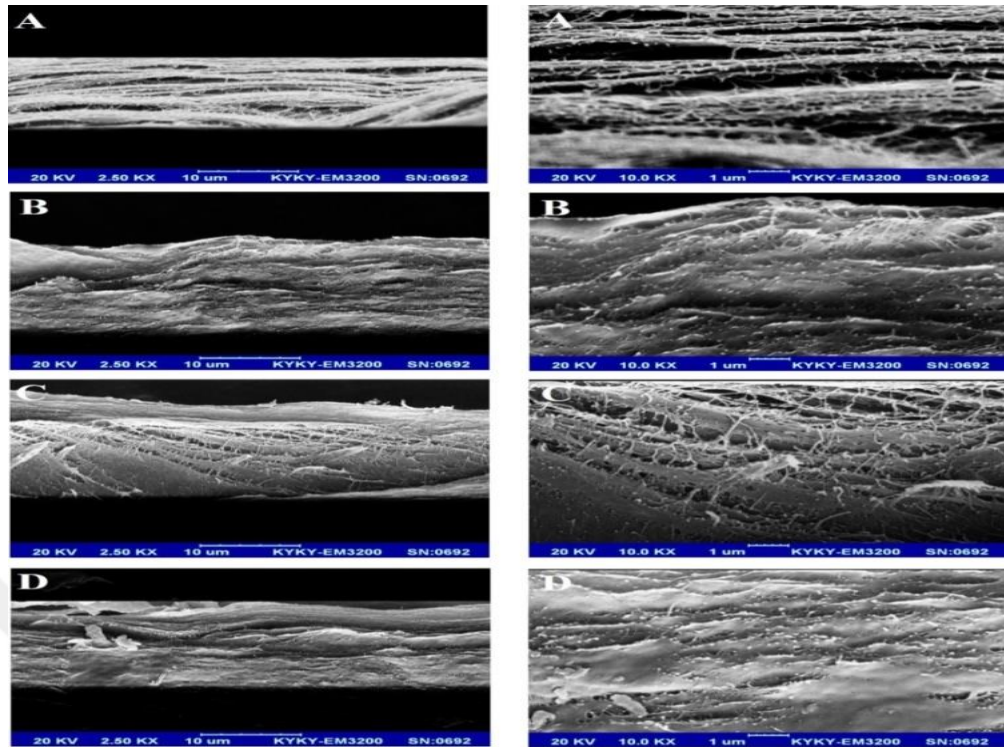
**Figure 1.5:** Antibacterial activity pathogens. a: *E. coli*; b: *S. aureus*; c: *B. subtilis*; d: *S. typhi*.(Murali et al. 2017).

S. Khaleel Basha et al used green ZnO NPs by Alginate biopolymer with Ammonia as antibacterial and exhibit excellent results against two types of bacteria positive gram as a *Staphylococcus aureus* bacteria and *E.coli* bacteria gram negative



**Figure 1.6:** Antibacterial activity, micron size ZnO powder and a/ZnO Nps (Basha et al. 2016).

Fereshteh Shahmohammadi Jebela, et al employ ZnO NPs that 5% of ZnO ratio with BC bacteria cellulose mono and multi-layers bringing the best results against two species of bacteria positive and negative grams *Escherichia coli* and *Staphylococcus aureus* supporting ultrasounds ray as displayed in the table below the inhibition zone was in mm.(Shahmohammadi Jebel & Almasi 2016)

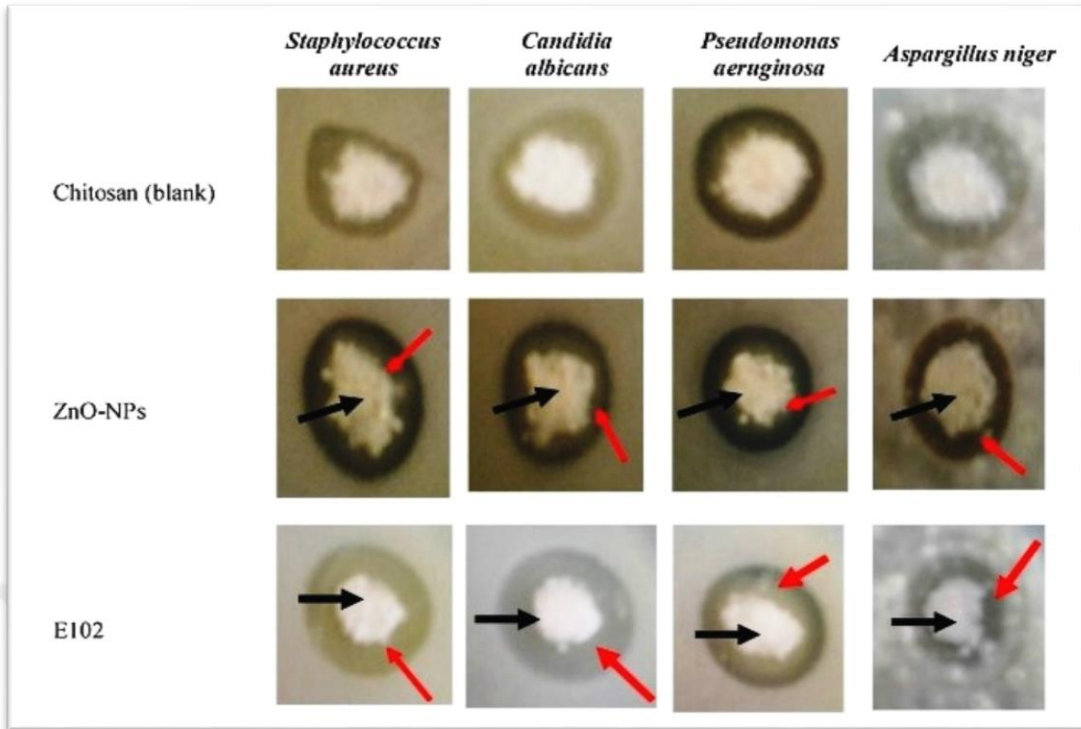


**Figure 1.7:** SEM image of cross section of pure bc (a), ZnO-bc (b), ZnO-BC-ml (c) and ZnO-BC-us (d). (Shahmohammadi Jebel & Almasi 2016).

**Table 1.1:** Inhibition zone when they use ZnO with bc mono and multi-layer film under US against negative and positive gram's bacteria's. (Shahmohammadi Jebel & Almasi 2016).

Film	Inhibition zone in mm	
	S.Aureus	E. coli
BC	0	0
ZnO-BC	11.8	5.6
ZnO-BC	9.8	4.1
ZnO-BC-US	20.4	7.6
ZnO-BC-US-M	19.1	6.1

Ahmed M. Youseef, et al present the hybrid film chitosan/polyethylene glycol and calcium silicate with two types of ZnO NPS and titrazine E102 dye the results obtained excellent activity antibacterial G+ve, G-ve, and fungi as shown in table of the ratio of ZnO NPS 11% and 0.3 gram of (E102) dyes.



**Figure 1.8.** Antibacterial activities of chitosan as blank, CS/PEG/calcium silicate nanocomposites against gram positive (staphylococcus aureus), gram negative (*Pseudomonas aeruginosa*) bacteria, fungi (*candidia albicans*) and *aspargillus niger*, the black dart point to the sample and the red point to the inhibition zones).(Youssef et al. 2017).

**Table 1.2:** The antibacterial activity and inhibitions zones in mm (mile meter) against four types of microbial.

Film	Inhibition zone diameter in mm		
	Chitosan	ZnO-NPS	E102
<i>Staphylococcus aureus</i>	9	10	13
<i>Pseudomonas aeruginosa</i>	11	11	15
<i>Candidia albicans</i>	10	13	15
<i>Aspargillus</i>	12	14	16

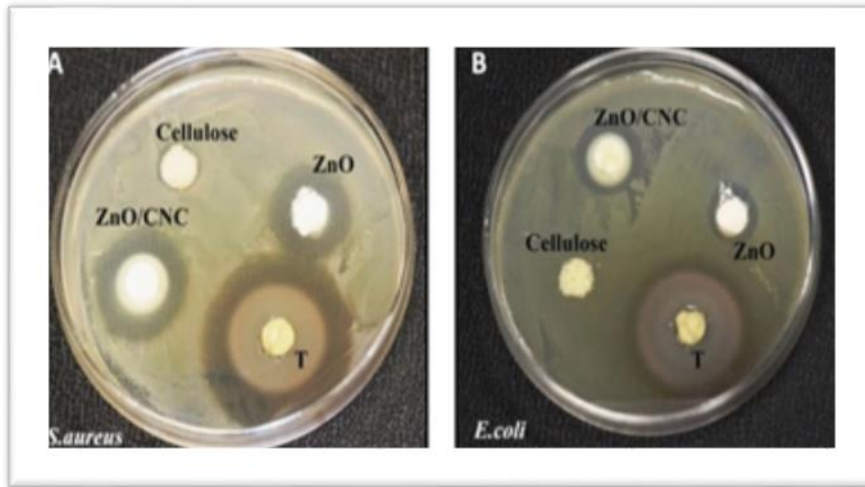
K. Akhil, et al have applied the zinc oxide (ZnO NPs) within four types of polymers as ethylene glycol (EG), gelatin, polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP).because zinc oxide is not stable while dispersing in water so it is far better use modified surface of polymer within ZnO NPs.

The results promised excellent and checked against the *Staphylococcus aureus* and *Pseudomonas aeruginosa* moreover all the particles of ZnO NPs with all four polymers exhibited excellent antibacterial and biofouling action. They also used the methyl blue MB dyes as a standard to measure the degradable rate including ZnO NPs concentration was (0.1, 1, 10 and 100 µg/mL) the degradable performance life exhibited in the table

**Table 1.3:** Degradable performance life exhibited on NPs based polymers.(Akhil et al. 2016).

Samples	Degradation efficiency (%) at	Half time in (min)
	120min	
TiO <sub>2</sub> Degussa P-25	94.3	80.4
ZnO-NPs	87.7	75.9
ZnO-NPs-EG	64.9	37.9
ZnO-NPs-G	56.23	29.8
ZnO-NPs-PVA	47.6	23.4
ZnO-NPs-PVP	71.85	45.8

Kebadiretse Lefatshe, et al have employed study about the Nanocellulose (NC) that synthesized of oil palm empty fruit, the NC collected utilized as a ZnO NPs, the zinc oxide/cellulose nanocomposites display perfect result better than pure ZnO NPs on the degradation of methylene blue (MB) and enhance the antibacterial and biofouling properties ZnO NPs /NC giving good results inhibition of G-ve and G+ve *E.coli* and *S. aureus* as explained ,in the table and the figure, the concentration ratios were (0.5, 1, and 5 mg).(Lefatshe et al. 2017).



**Figure 1.9:** Antibacterial zone of inhibition of 5 mg/ml of cellulose, ZnO/CNC and tetracycline (t) against *S. aureus* (a) and *E. coli* (b).

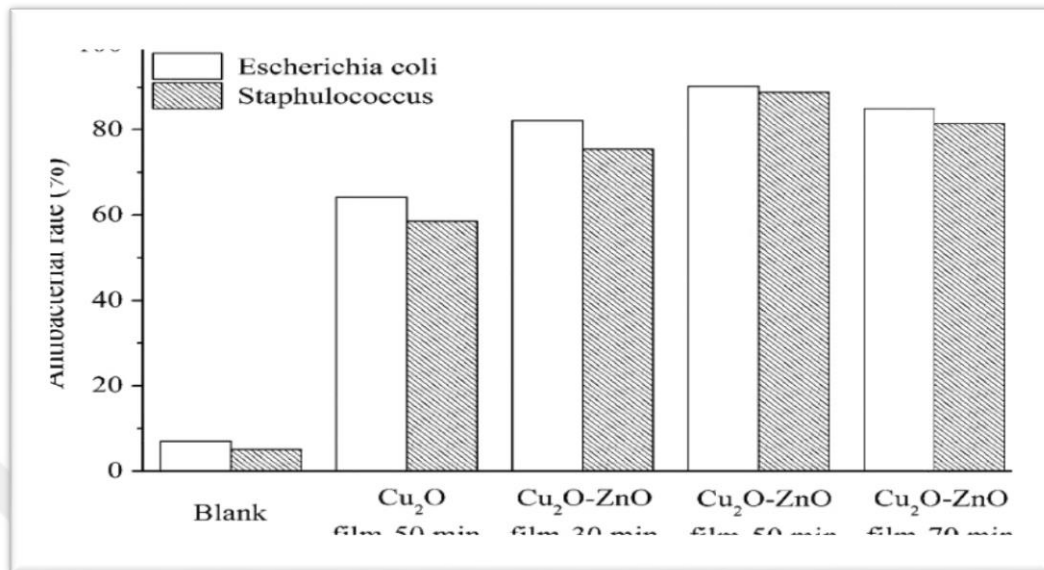
**Table 1.4:** Zone of inhibitions of cellulose, ZnO and ZnO/CNC and Tetracycline (antibiotic v standard) against *S. aureus* and *E. coli*.

Bacterial strains	Concentration of cellulose	Average diameter of inhibition zone in (mm)		
		ZnO	ZnO/CNC	Tetracycline
Gram-positive ( <i>S. aureus</i> )	0.5 mg/ml	14	17	38
	1 mg/ml	14	20	
	5 mg/ml	20	24	
Gram-negative ( <i>E. coli</i> )	0.5 mg/ml	10	11	34
	1 mg/ml	12	15	
	5 mg/ml	14	20	

Wei Hong, et al prepared Cu<sub>2</sub>O/ZnO film to use the electrode position technique the size of Cu<sub>2</sub>O/ZnO was 256-560 nm this film composite showing excellent results as antibacterial groups positive and negative gram in 50 min better than using only Cu<sub>2</sub>O.

The activity process under fluorescence light against the *Escherichia coli* (90.23 %) and *Staphylococcus aureus* (88.78 %) as in the figure.

The blank was the nickel foam without film.



**Figure 1.10:** The antibacterial average of escherichia coli and staphylococcus aureus use various films under fluorescent light the blank is the nickel foam.

Cu<sub>2</sub>O/ZnO composite film-50 min promise a unique and compact structure with a high surface area, stability and degradation property.

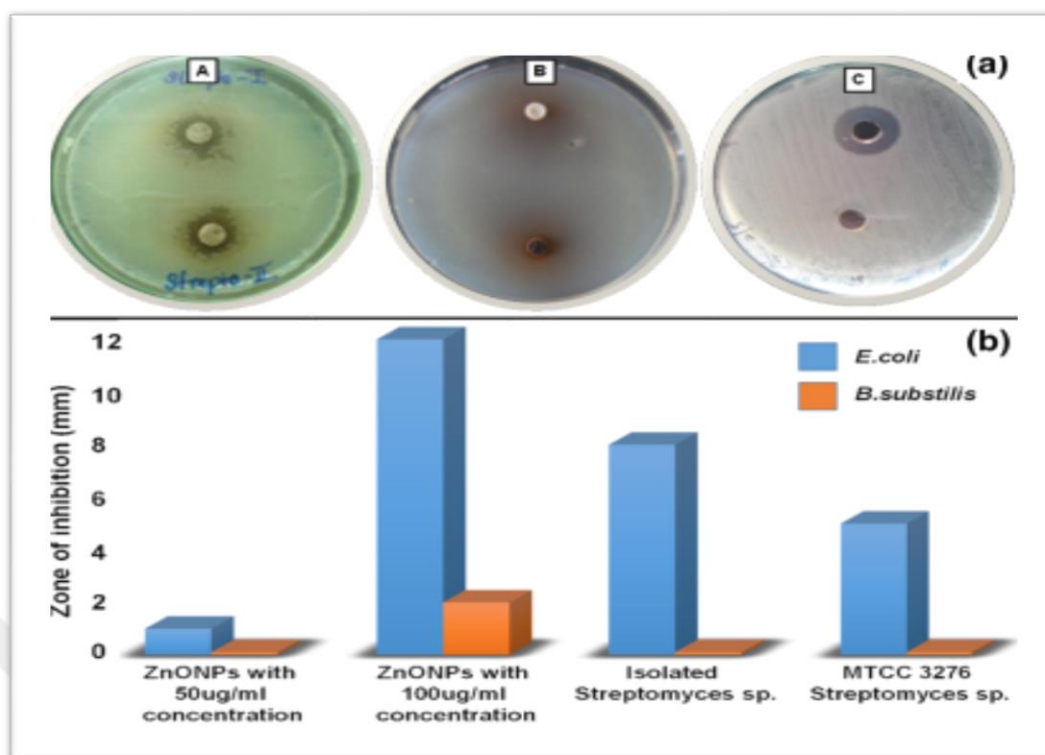
The spectral of all samples film in different time present in FTIR spectra to confirm that the Cu<sub>2</sub>O/ZnO were syntheses.

Cu<sub>2</sub>O/ZnO composite film-50 min promise a unique and compact structure beside a high surface area, stability, and degradation feature.).(Hong et al. 2016)

Junkang Wu, et al use ZnO Nanorod particles as bacterial and affected ammonia oxidize bacteria Nitrosomonas europaea in a chemostat bioreactor when ZnO concentrations were more than 10 mg/L.(Wu et al. 2017)

B. Balraj, et al syntheses ZnONP biologically using Streptomyces SP bacteria the protein in this bacteria was capable of producing ZnCl<sub>2</sub> extract and then forms ZnO NP the size was 20-50 nm and used as an antimicrobial and anticancer agent in vitro the inhibiting zone was large with E.coli 12mm at concentration 100 microgram /ml.as presented in the table below



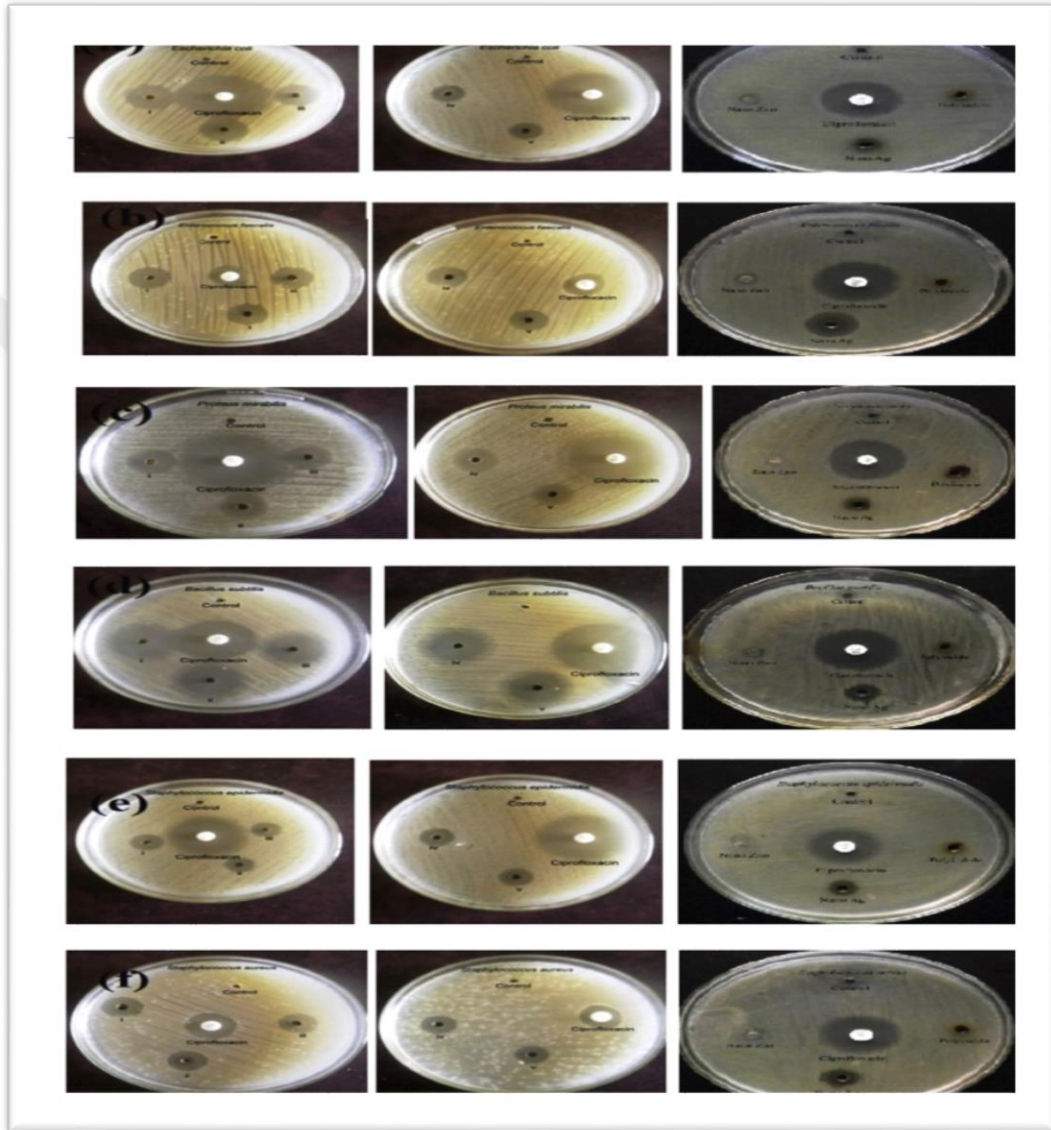


**Figure 1.11:** Antibacterial for (a) isolated streptomyces sp. and mtcc-3276 streptomyces sp (b) biosynthesized ZnO nps (50 micro g/ml), (c) biosynthesized ZnO nanoparticles (100 micro g/ml). (b Analysis of the zone of inhibition. (Balraj et al. 2016).

**Table 1.5.** Antibacterial of Streptomyces sp. and ZnONPs against E. coli, B. subtilis.

Bacterial strains	ZnO NPs Biologically synthesized		Streptomyces species	
	ZnO inhibition zone in (mm) 50 microgram	ZnO inhibition zone in (mm) 100 microgram	Isolated strain %	MTTC 3276 strain
Gram-positive (B. subtilis)	0.1	2	0.1	0.1
Gram-negative (E coli)	1	12	8	5

M. Eolango, et al synthesize ZnO nanoparticles with Ag and polyindole polymer PIND/Ag/ZnO were tested against positive and negative gram five types of bacteria. The results exhibit large inhibition zone of bacteria activity the particle size was 20-25 nm as shown in the following figure

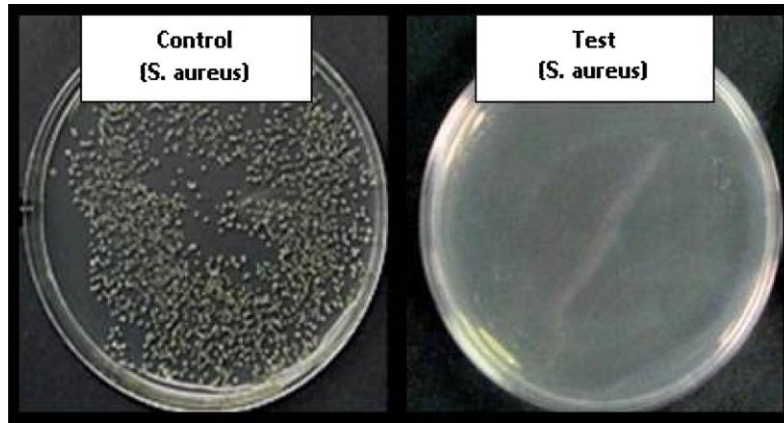


**Figure 1.12:** (A-f). antibacterial activity of various nanocomposites against two pathogenic strains; (a) *E. coli* (b) *E. faecalis*, (c) *P. mirabilis*, (d) *B. subtilis* (e) *S. epidermidis* and (f) *S. aureus*

**Table 1.6:** Zones of inhibition for various concentrations of PIND/AgZnO Nano composites, ZnO, Ag NPs and polyindole (in mm).(Elango et al. 2017).

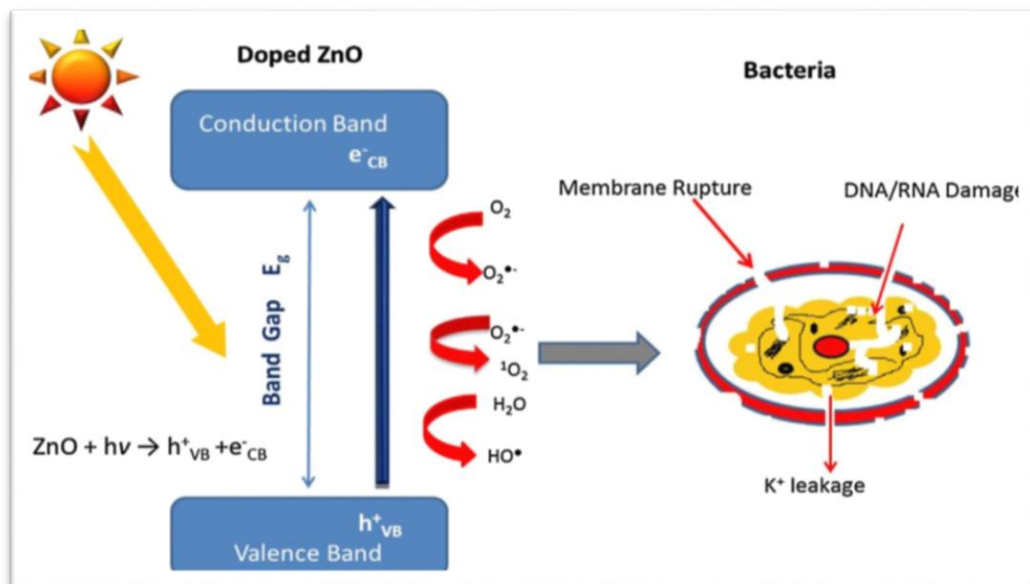
Bacteria	AgZn1	AgZn2	AgZn3	AgZn4	AgZn5	Ag	Zn	Antibiotic 5 µg
S.aureus	15	13	12	12	12	12	3	4
S.epidermidis	12	11	11	13	13	7	4	5
B.subtilis	23	20	20	20	20	11	4	-
P.mirabilis	13	13	13	13	13	8	4	-
E.faecalis	16	14	13	14	13	16	6	4
E.coli	18	17	16	18	17	7	5	5

Joanna Podporska-Carroll, et al have used the sol-gel method to prepare ZnO NPs and then immerse in Flour (F) to provide agent against two types of bacteria gram negative and positive .The composite of F/ZnO is more effective against Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) the result shows that more than 99% of bacteria were killed within 6hrs under the light as shown in the figure and the ratio is 1:1, 1:2 ZnO/F.



**Figure 1.13:**(A) control (*s. aureus*), (b) test sample (f doping ZnO 1:1, after exposure to visible light).(Podporska-Carroll et al. 2015).

The mechanisms of ZnO doped with F to affect bacteria and destroy the cell membrane when the powder exposes to the Sol light might be forming species of oxygens essentially  $\text{H}_2\text{O}_2$  such as  $\cdot\text{OH}$ ,  $^1\text{O}_2$ ,  $\cdot\text{O}_2^-$ ,  $\cdot\text{O}_2\text{H}$ , and zinc ion then transport the electron from valance band to conduction band and next to the bacteria cells to destroy as illustrated in the pattern. 1:14 below.



**Figure 1.14:** Showing the mechanism of photocatalytic antibacterial of ZnO how the electron transfers from the valence band to conduction band and destroys the cell membrane. (Podporska-Carroll et al. 2015).

Renata Dobrucka, et al have reported how to obtain ZnO NPs biologically green method used the type of flower and extract zinc oxide NPs from this solution the flower name is Trifolium pretense this NPs provided great effective when they examined against classes of the bacteria showed extraordinary activity inhibition against S. aureus, E. coli, P. aeruginosa, S. aureus and P. aeruginosa.as an antimicrobial the size of the NPs 60-70 nm.(Dobrucka & D??ugaszewska 2016)

Zhixiao Liu, et al applied study on polysulfone and COOH carboxylated polysulfone (PSF-COOH) to prepare the hydrophilic and antifouling ultra-membrane by introducing the monomer of phenolphthalein-containing the carboxyl to the molecule backbone of polysulfone (PSF).The hydrophilicity, permeation fluxes and antifouling properties of membrane significantly increased where PSF-COOH- is 100% as shown in the table and still showed tensile strength was 4.3 mpa.

**Table 1.7:** Shown ratio of PSF/COOH to get antifouling and high flux.

Polymer	Bisphenol - BPA	Phenolphthalei n PPL	Dichlorodiphenylsulfone DCDPS
PSF	100	0	100
PSF/COOH/20%	80	20	100
PSF/COOH/40%	60	40	100
PSF/COOH/60%	40	60	100
PSF/COOH/80%	20	80	100
PSF/COOH/100%	0	100	100

The materials used in this study are polysulfone PSF, polyvinylpyrrolidone PVP, dichloro diphenyl sulfone (DCDPS) bisphenol (BPA) Phenolphthalein (PPL)

The porosity was calculated regarding the dry and wet weight of the samples by the following Eq.

$$\text{Porosity} = \frac{W_w + W_d}{W_d} * 100\% \quad (1 - 1)$$

The  $W_w$  refers to the weight of wet membrane;  $W_d$  refers to the weight of the dry membrane.  $\rho_w$  refers to the density of water ( $0.998 \text{ g/cm}^3$ ),  $A$  refers to the effective area of the membrane ( $\text{cm}^2$ ), and  $d$  refers to the thickness of membranes (cm). (Liu et al. 2017)

Yehia Manawi, et al they study the Arab gums AG as agent for pore –forming when blending with the polysulfone PS/AG via phase inversion technique with the ratio (0.1-3 w %).

When membrane contains 3% of AG, it gives high rejection of oil, no growth of E.coli on the surface of membrane, the mechanical properties increase 52% compared with PS and enhancement the hydrophilicity the AG promising additive to fabricate the ultrafiltration membrane to use in water treatment. (Manawi et al. 2017)

Xiujuan Guan, et al they study how to micro extraction the floxacine drugs and absorb it from the water and the biological sample by using the polysulfone membrane PS and nickel foam the ratio of polysulfone (1,2,3,4,5 and 7.5% v/v) the material prepared were used to adsorb analytes in water and biological samples and the analyzer coupling with the chromatography analysis the extractions values are 90-104.8% and 97.3-107.1% for each sample water and biological (Guan et al. 2017)

Peyman Pouresmaeel-Selakjani, et al study the cellulose-nanosilica (CNS) nanocomposites with polysulfone membrane PS and Dimethylacetamide DMAC to adsorb and reject the crystal violet dye (CV) from the aqueous solution system was more than 80% the optimize ratio of CNS was 0.25 % w/w PS 20% DMAC 80% as shown in the table:-

**Table 1.8:** Shown the ratio of PSF based CNS and DMAC to prepare membrane.

Sample	PSF (w/w %)	CNS (w/w %)	DMAC (w/w %)
PSF	20	0	80
M 0.05	20	0.05	79.95
M 0.1	20	0.1	79.9
M0.25	20	0.25	79.75
M 0.5	20	0.5	97.5

On the other hand, CNS added as the nanocomposites to enhance many properties as well as tensile, mechanical, thermal stability with glass temperature in order to obtain the cheap matrix fillers into the membrane.

The adsorption efficiency and adsorption capacity calculated depended on formula as below:-

$$\text{Adsorption Efficiency (\%)} = \frac{C_i + C_f}{C_i} \times 100\% \quad (1 - 2)$$

$$\text{Adsorption Capacity (mg/g)} = \frac{C_i + C_f}{W} \times V \quad (1 - 3)$$

While the  $C_i$  is initial concentration of dye,  $C_f$  is final concentration in (mg/L),  $W$  is a mass of adsorbent in g, and  $V$  is the concentration of crystal dye CV (Jahanshahi 2017)

Anastasia V. Penkova, et al were studying the Polysulfone PS membrane based on the fullerene  $C_{60}$  as a matrix mixed with membrane PS/ $C_{60}$ .

A fullerene is a molecule of carbon in the form of a hollow type with multi-shapes

The concentration of  $C_{60}$  0.5% based PS 5% the best value to test for the pervaporation of ethyl acetate- mixture water and improve the chemical, physical and thermal properties.

The pervaporation of ethyl-acetate sorption efficiency explained in the table below:-  
(Penkova et al. 2016)

**Table 1.9:** Shown the concentration of PSF / C60.

Membrane	S Efficiency % 2% Ethyl acetate 98 % water	4% Ethyl acetate 96 % water
PS 0	0.8	8.4
PS/0.3 % C60	1.3	9.7
PS/0.5 % C60	3.2	11.7

Richa Modi, et al study and prepare the thin film composite membrane (TFC) by coating polydomain onto polysulfone asymmetric membrane.

PS ratio was 15% w/w solved in dimethylformamide then immersed in m-phenylene diamine (2% w/v) to form polydopamine layer on PS surface the asymmetric membrane has used to reject NaCl solution.

The separation was 80% in 1000 mg/L. as below in the table.



**Table 1.10:** Concentration of NaCl and rejection.

NaCl conc. (mg/L)	Rejection (%)
500	83.41
800	81.8
1000	80.6

The rejection calculated by using this formula:

$$\text{Rejection Efficiency (100\%)} = 1 - \frac{C_p}{C_f} \times 100 \quad (1 - 4)$$

The  $C_p$  is NaCl concentration before separation,  $C_f$  is NaCl concentration after membrane. (Modi et al. 2016)

Harun Elcik, et al use polysulfone polymer based the Pluronic F127 to limit microbial growths on the surface of membrane the pluronic F127 as a hydrophobic copolymer added to polysulfone membrane to improve the properties of characterization such as morphology, surface roughness, chemical structures and hydrophobicity

**Table 1.11.** Compositions of PSF membrane casting solutions based PEG, DMAc and Pluronic F127

Membrane	PSF (gr)	DMAc (g)	PEG (g)	Pluronic F-127 (g)	F-127/PSF (w/w %)
PSF 0	15	81.25	3.75	0	0
PSF 1	15	80.95	3.75	0.6	4
PSF 2	15	80.65	3.75	1.2	8
PSF 3	15	80.35	3.75	1.8	12
PSF 4	15	80.05	3.75	2.4	16

DMAc is Dimethylacetamide, PEG is polyethylene glycol, Pluronic F 127 is block polymer and PSF is polysulfone.(Elcik et al. 2017)

Pluronic F127 is a difunctional block copolymer surfactant terminating in primary hydroxyl groups. A nonionic surfactant that is 100% active and relatively nontoxic.(Anon 2012)

Ahmad Akbari, et al, applied study to make polysulfone membrane and mix with sulfonated polysulfone PSPSF/PSF the aim of the blending PSPSF/PSF to enhance the mechanical properties and stability of filtration. Then they added the nanocomposite particles TiO<sub>2</sub> to membrane PSPSF/PSF/TiO<sub>2</sub> to increase the selectivity.

The benefits of sulfonate increase the hydrophilicity finally the membranes PSPSF/PSF/TiO<sub>2</sub> showed high separation of dry dyes from textile wastewater and permeability.The ratio of PSPSF/PSF/TiO<sub>2</sub> is 30/70/0.05 wt%.(Akbari & Homayoonfal 2016)

Xi Yang, et al study how to make novel hydrophilicity membrane of PVDF Polyvinylidene fluoride, ZrO<sub>2</sub>, and multiwall carbon nanotubes (MWCNTs) the ZrO<sub>2</sub> and MWCNTs loaded to the PVDF polymer to enhance the membrane properties.

The total membrane consists of PVDF/ZrO<sub>2</sub>/MWCNTs used to separate the oil/water system high flux.

The ratio to synthesize membrane is 19% PVDF wt%, 7% PVP, and 74% DMAc then loaded 1-3% of ZrO<sub>2</sub>-MWCNTs.(Yang et al. 2016)

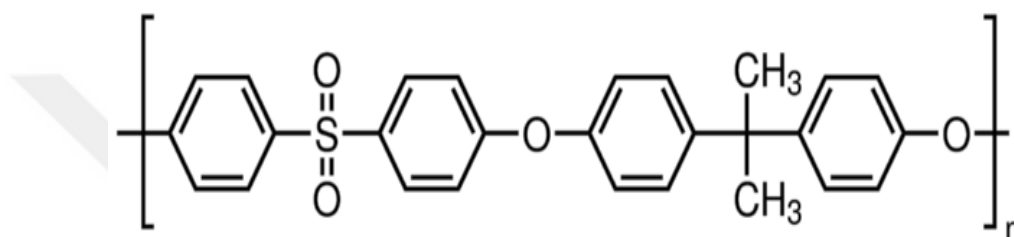
## 2. MATERIALS AND METHODS

### 2.1. MATERIALS

#### 2.1.1. POLYSULFONE (PSF)

PCode 428302 average Mw 35000 by LS, average in 16000 Mn by MS, pellets transparent, were purchased from SIGMA- ALDRICH Chemistry.

Linear Formula:  $[C_6H_4-4-C(CH_3)_2C_6H_4-4-OC_6H_4-4-SO_2C_6H_4-4-O]_n$



**Figure 2.1:** Polysulfone (PSF).

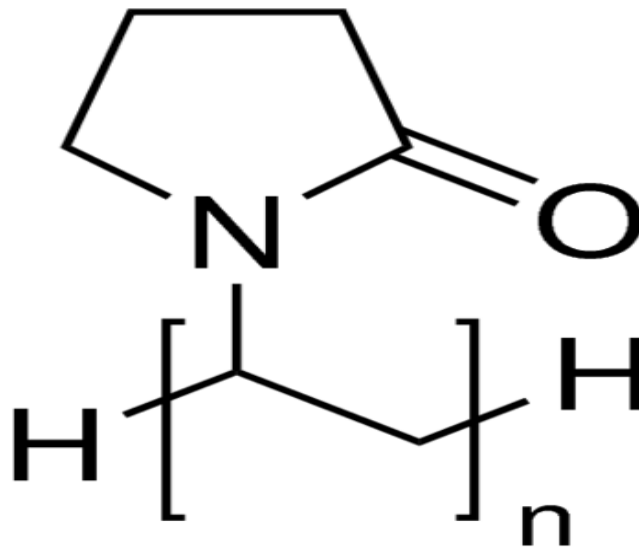
The features of polysulfone are :-

High impact resistance. Temperature range up to 160°C. Excellent steam sterilization stability. Electrical properties are maintained over a wide temperature and frequency range. High resistance to radiation degradation

#### 2.1.2. POLYVINYLPIRROLIDONE (PVP)

PVP CAS-No. : 856568 Mw average 55,000

Linear Formula:  $(C_6H_9NO)_x$

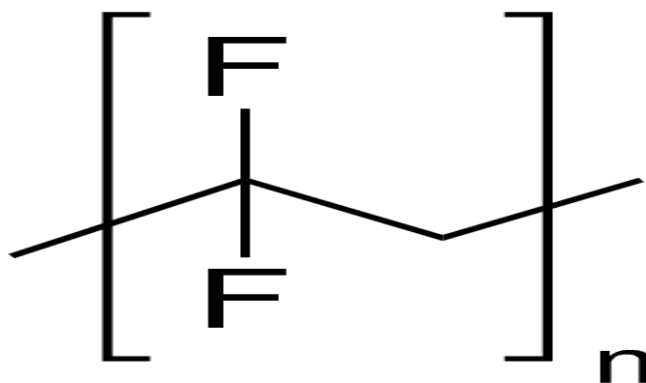


**Figure 2.2:** Polyvinylpyrrolidone (PVP).

### 2.1.3. POLY (VINYLIDENE FLUORIDE) (PVDF)

Mw 534,000 powder CAS number 182702 purchased from SIGMA- ALDRICH Chemistry.

The formula is  $(\text{CH}_2\text{CF}_2)_n$



**Figure 2.3:** Poly (vinylidene fluoride) (PVDF).

#### 2.1.4. POLYETHYLENE GLYCOL (PEG)

PEG CAS number 25322-68-3 Mw 1000 were purchased from SIGMA- ALDRICH Chemistry.

Liner formula is  $(C_2H_4O)_nH_2O$

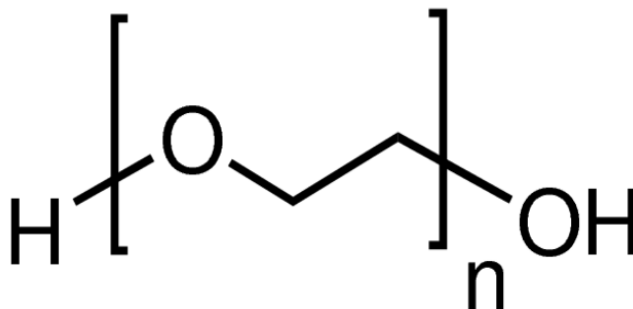


Figure 2.4. Polyethylene glycol (PFG).

#### 2.1.5. 1-METHYL-2-PYRROLIDINONE (NMP)

NMP 99.5 % CAS number 872-50-4 Mw 99.13 were purchased from SIGMA ALDRICH as a solvent.

The formula is:  $C_5H_9NO$



Figure 2. 5: 1-Methyl-2-pyrrolidinone (NMP).

#### 2.1.6. Zinc Oxide Nanoparticles

NPs 99.9+%, 30-50 nm were purchased from Nanografi Company in Ankara.

## 2.2. METHODE

### 2.2.1. FTIR

Were scanned Samples using ALPHA P from Bruker company in ATR system 4000-400  $\text{cm}^{-1}$ . Fourier Transform Infrared Spectroscopy (FTIR) it's a technology device which can recognize the chemical components by using infrared light source at the beginning the sample exposed the sample to several wavelengths of infrared and the device measure the absorbed wavelengths. Then the program takes the raw absorbed data and manage a math process to form readable absorbed spectrum, comparing this spectrum to a library by a program called OPUS you can find a match spectra.



**Figure 2.6:** FTIR alpha bruker device.

### 2.2.2. Sonification

300W Ultrasonic Processor for Dispersing, Homogenizing, and Mixing Liquid Chemicals - MSK-USP-3N- MTI Corporation Company The device 300W ultrasonic processor with a quality sound-proof chamber and stainless steel elevating platform. The device was used for dispersing nano-powder in liquid with a small quantity, homogenize liquid phase and is an ideal tool for preparation new generation of LED phosphor, Li-ion battery slurry and quality thin film by sol-gel method.

Application Processor Head should be dip into sample liquid around 10mm.the Maximum dip in depth is 30mm, over dip may cause power board malfunction.

The specification of device Working Voltage Single Phase 110VAC, 50-60Hz If need using at 220V, Output Power in ultrasonic processor 300 W Max, 20 kHz Max.



**Figure 2.7:** Sonication 300w ultrasonic processor.

### **2.2.3. X-Ray Diffraction**

XRD. X-ray diffraction spectroscopy (XRD) was used to investigate the crystal structure of ZnO and polymers/ZnO. The sample was ground and pressed into the sample holder to get a smooth plane surface, and the diffraction pattern was recorded over at the  $2\theta$  range of  $30^\circ$  -  $120^\circ$ . The  $2\theta$  of ZnO was at  $31.2^\circ$ ,  $34.5^\circ$ ,  $37^\circ$ ,  $48^\circ$ , and  $57^\circ$ .

### **2.2.4. Scanning Electron Microscopy**

Scanning electron microscopy (SEM) was applied for imaging the surface by scanning a focused electron beam over a surface to produce an image and cross-sectional morphologies of membranes.

The electrons in the beam interact with the sample, producing many signals that can be used to get data about the surface topography and structure.

### **2.2.5. Thermo gravimetric Analysis**

Thermo gravimetric Analysis (TGA) measures the amount and rate of change in the loss of weight of a material as a function of temperature or time in the controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to  $1000^\circ\text{C}$  or more. The technique can characterize

materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. TG covers plotted with weight loss % in X axis against the temperature in Y axis

TGA 50 device model SHIMADZU company Japan has used to find the thermal stability of samples and composites. Samples were heated to room temperature until 800 C under N<sub>2</sub> scanning ambient at ramp 10 °C/min.



**Figure 2.8:** TG 50 thermal gravimetric device.

### **2.2.6. Total Organic Carbon Analyzer**

TOC –VCPH CPN Shimadzu corporation company Koyto Japan were used to determine types of carbon in drinking water and other types of water based carrier gas. There are two types of carbon organic and inorganic. Organic carbon (OC) bound with oxygen or hydrogen to form organic components and inorganic carbon (TIC) is the structural basic for inorganic components as gas carbonates and ion carbonate and

The relation between OC and IC is  $TOC=TC-IC$ . The measuring range 0-3000 mg/l.

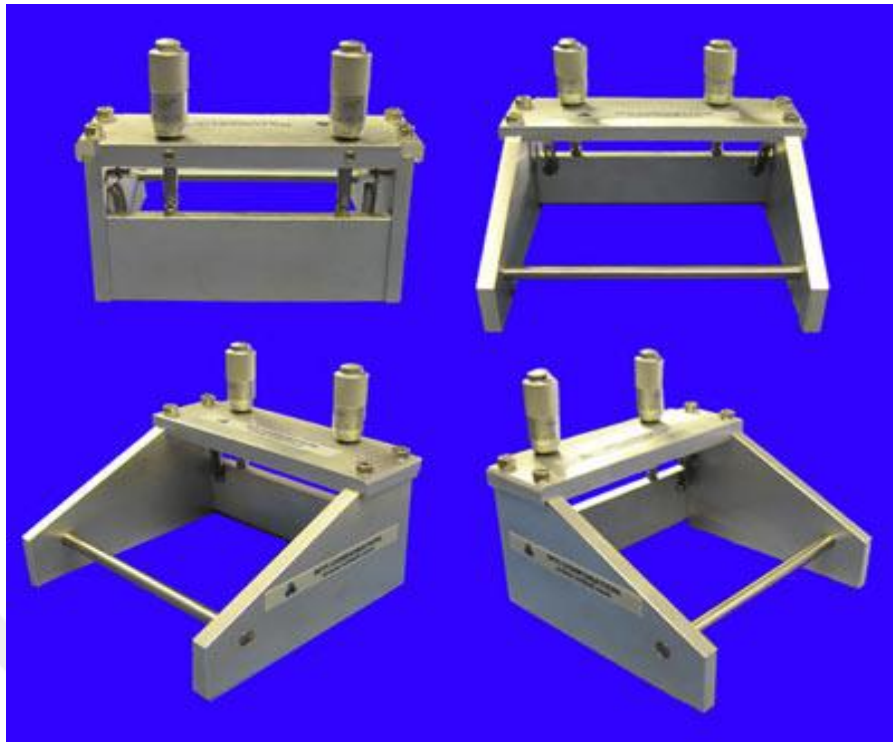




**Figure 2.9:** Toc total organic carbon device.

### **2.2.7. Micrometer Adjustable Film Applicator (Film Casting Knife)**

- Adjustable Film Applicator unique wet film applicator features micrometer heads for knife adjustment.
- The operator clearance by adjusting the micrometers.
- This is excellent tool to make quality film for material research laboratories to make ceramic tape casting, battery electrodes, and various coating at lower cost. Stainless steel knife blade with precision ground edge.
- 100 mm standard width.
- Make wet film thickness between 0 - 9500 microns.
- Micrometer head accuracy is +/- 2 microns.



**Figure 2.10:** Micrometer adjustable film applicator.

## **2.3. SYNTHESIS MEMBRANE**

### **2.3.1. Polysulfone Membrane**

PSF (average Mw 35000 ) and PVP (Mw average 55,000) were dissolved in NMP solvent 99.5% at 60C hotplate with a strong stirrer for 24h and the polymer solution is cast on a glass plate, with casting Knife followed by immersing in distilled water bath to exchange solvent with the nonsolvent.(as shown in figure 2.11(a) and (b) below).

These membranes are generally prepared by the phase inversion process.

Then PFS/PVP/ZnO NPs nanocomposites we prepared with the ratio 18.5% PSF, 0.5 PVP, and 10% ZnO.

To disperse NPs into the polymer we used the sonication method.

For 30 mins at 30 °C intensity power 25%.

In the table below explain the membrane sample ratios for all polymers and NP that have used in the research.

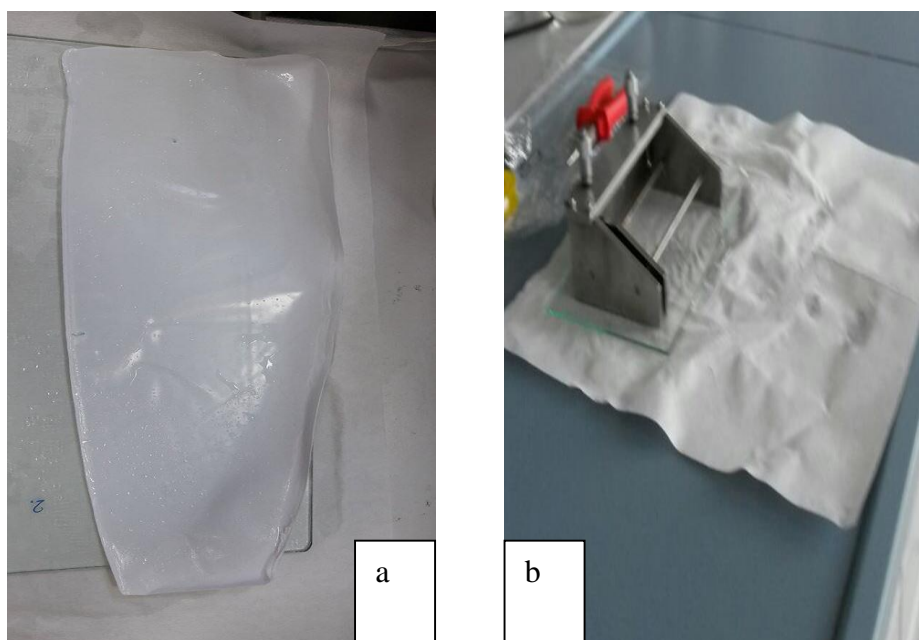
**Table 2.1:** Explain the sample ratio of all membranes.

Sample	PSF %	PVP %	NMP%	PVDF%	ZnO NPs%
1	18	0	82	0	0
2	18	1	81	0	0
3	18.5	0.5	81	0	10
4	18.5	0.5	81	0	0
5	18	2	80	0	0
6	18.5	18.5	81.5	18.5	10
7	18.5	18.5	81.5	18.5	0

### 2.3.2. PVDF/PSF/PVP/ZnO and PVDF/PSF/PVP Membranes

The same procedure was followed to prepare the second membrane samples number 6 and 7 in the table PVDF/PSF/PVP/ZnO and PVDF/PSF/PVP.

The Mw of PVDF are 534,000.



**Figure 2.11:** A) is Polysulfone membrane b) is casting knife tools.

## 2.4. MATERIAL COSTS

The cost of materials listed below in the table.

The prices was taken from sigma website.

**Table 2.2:** Explain costs of material.

Item	Materials	Gr	Price in Euro
1	PSF	500	489
2	PVP	500	189
3	PVDF	500	525
4	NMP	1 Lit	201
5	ZnO NPs	100 gr	37

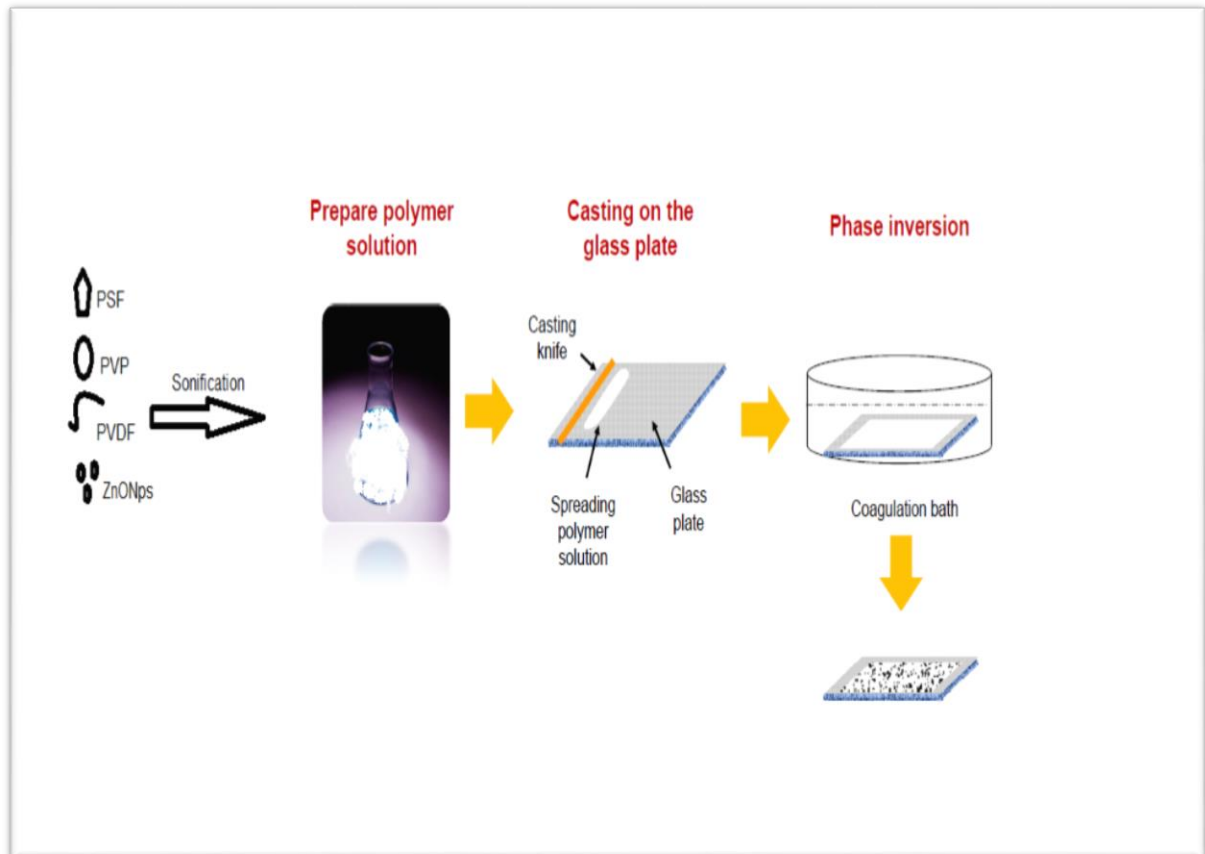
However according to this prices to produce membrane size approximately 50-60 cm<sup>2</sup> thickness is 0.2 mm we used 1.85 gr of PSF, 0.5gr of PVP, 8 gr of NMP and 10% of ZnO.

The cost of this membrane is 3.6 Euro for membrane which has no ZnO nanoparticles.

The price of prepared membrane with 10 % of ZnO NPs becomes 4 Euro

## 2.5. THE MECHANISM OF THE MEMBRANE

The diagram below demonstrate us how is the reaction take place for each polymer to form the membrane. The PVDF and PVP conduction around of PSF surface and after sonication ZnO dispersing on the surface of membrane



**Figure 2.12:** Mechanism of PSF/PVP/PVDF-ZnO nanoparticles.

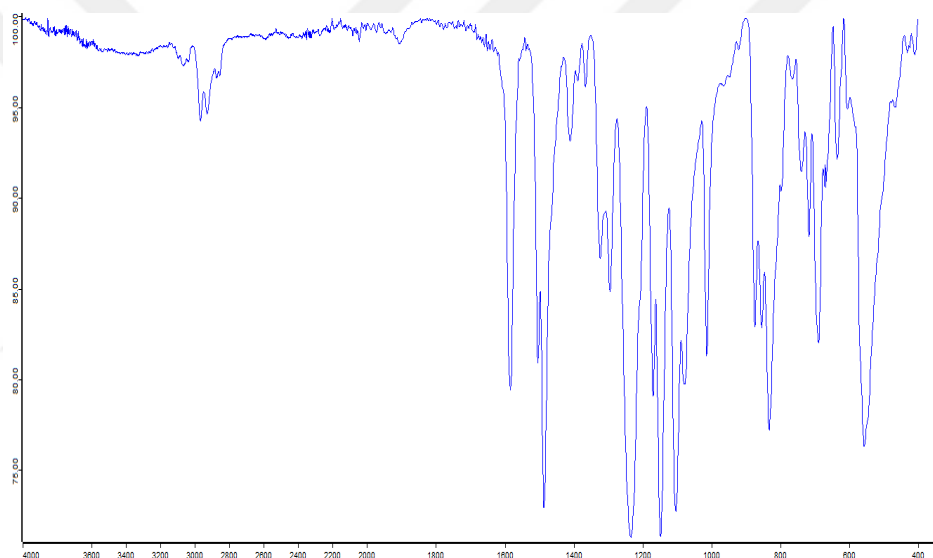
## 3. RESULTS

### 3.1. FTIR

#### 3.1.1. FTIR of Polysulfone

PSF (pure polymer) we can be recognized that absorption bands of the material corresponds to polysulfone groups, being as standard polysulfone  $1150\text{cm}^{-1}$  (O=S=O),  $1500\text{cm}^{-1}$  (O-H),  $1620\text{cm}^{-1}$  (C-C), and  $2966\text{cm}^{-1}$ , the figure 5.1.1 below shown all bounds location.

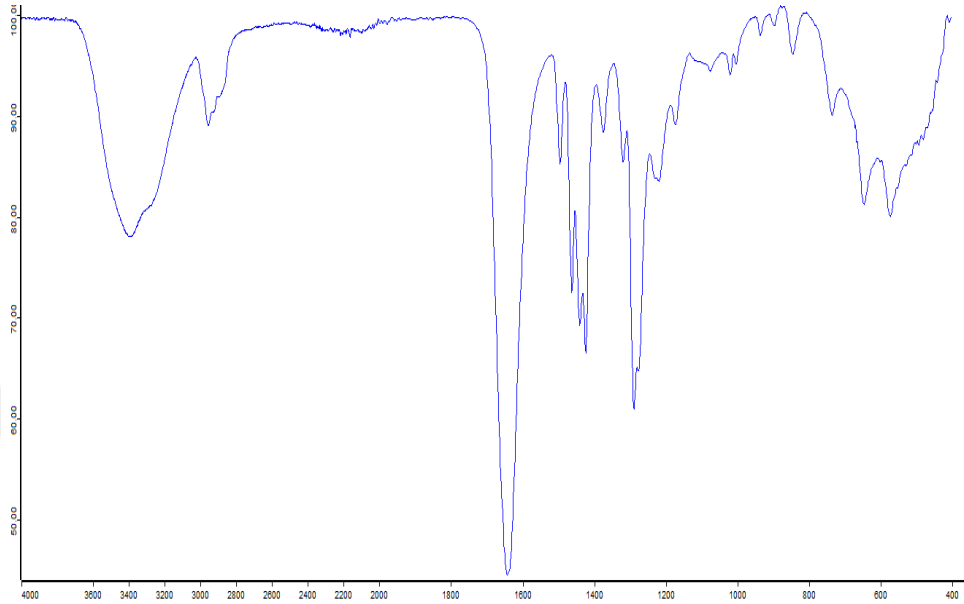
Note: the (x) axis is wavenumber in  $\text{cm}^{-1}$  and (y) axis is transmittion in %



**Figure 3.1:** FTIR of pure polysulfone shown o=s=o.

### 3.1.2. FTIR of Polyvinylvirolidon

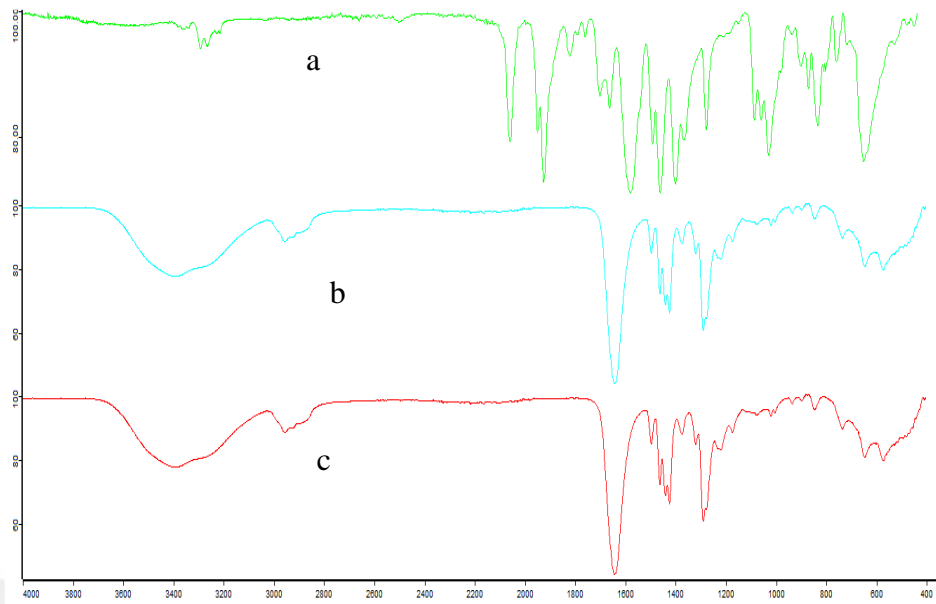
The C=O groups of pure PVP show a good peak at  $1660\text{ cm}^{-1}$ , C-H bound appear at  $2800\text{-}2950\text{ cm}^{-1}$ , and O-H appear range is  $3200\text{-}3400\text{ cm}^{-1}$  in FTIR spectrum .



**Figure 3.2:** FTIR of polyviylvirolidon PVP pure polymer.

### 3.1.3. FTIR of the Membrane Sample Composed of Two Polymers

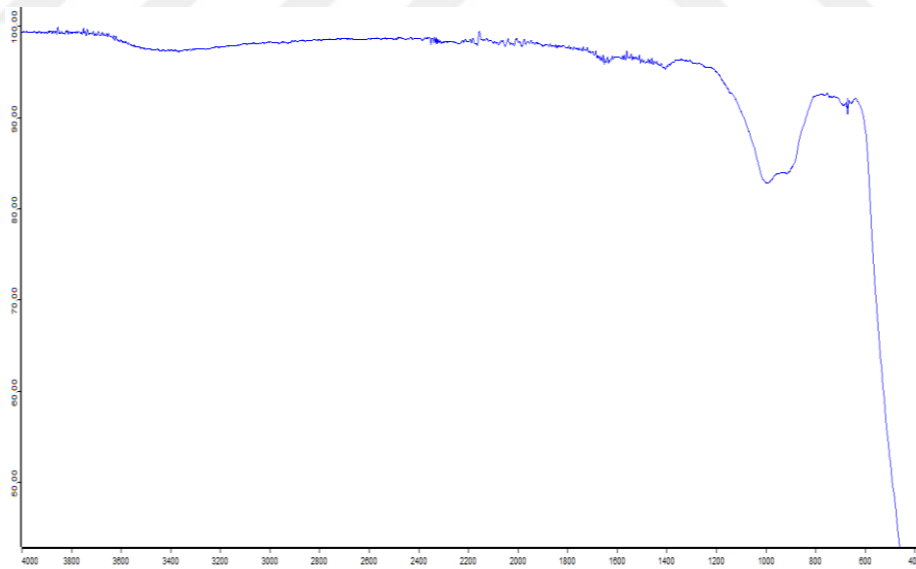
PSF 18.5 % w based PVP 0.5 w and 81% Vol of NMP, the two polymers after mixed formed new IR spectrum component of membrane figure 3.3 present all, in spectrum (c) we can notice the bounds of polysulfone groups,  $1150\text{ cm}^{-1}$  (O=S=O),  $1500\text{ cm}^{-1}$  (O-H),  $1620\text{ cm}^{-1}$  (C-C), and  $2966\text{ cm}^{-1}$  and also PVP bounds group C=O at  $1663\text{ cm}^{-1}$ , C-H bound appear at  $2800\text{-}2950\text{ cm}^{-1}$ , and O-H appear range is  $3200\text{-}3400\text{ cm}^{-1}$  .



**Figure 3.3:** FTIRs for membrane sample mixed (a) PSF 18.5 % w),(b) PVP 0.5 w) and (c) is membrane formed by mixed (a+b).

### 3.1.4. FTIR of ZnO Nanoparticles

Zn-O vibration band ( $420\text{--}540\text{ cm}^{-1}$ ) as below in figure

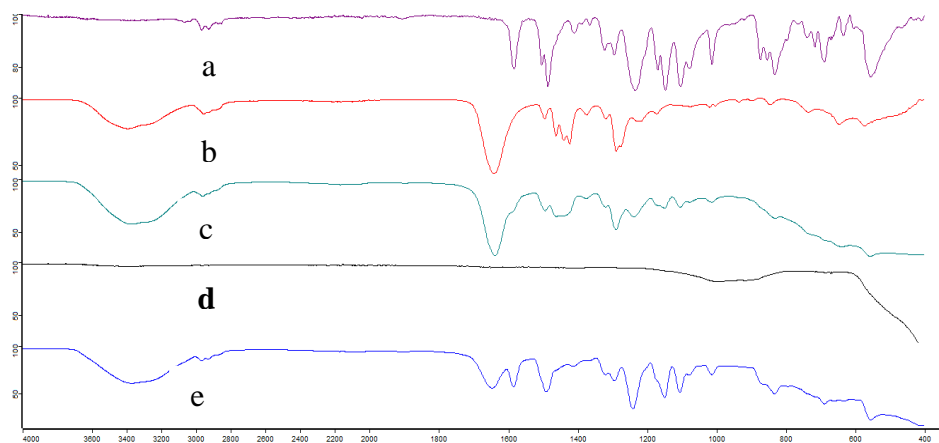


**Figure 3.4:** FTIR of zinc oxide nanoparticles shown zn-o bound.



### 3.1.5. FTIR of Membrane Sample Based ZnO

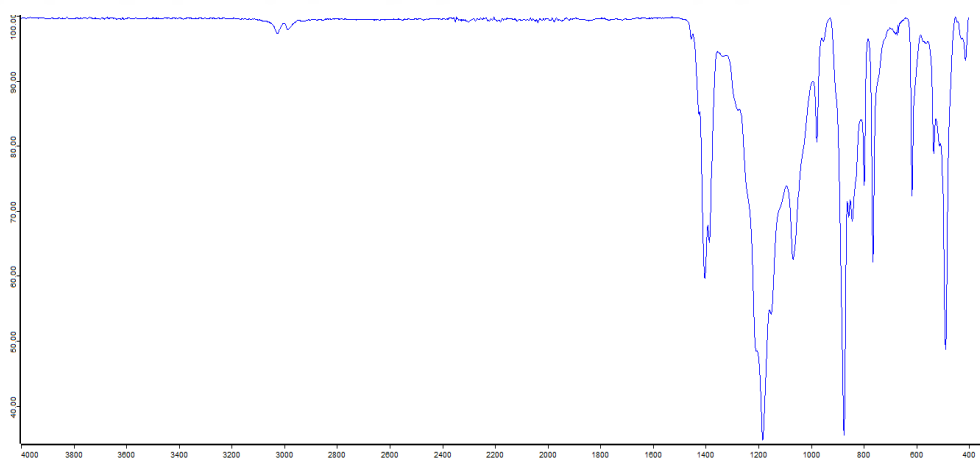
Nano composite the ratio was 18.5 % PSF, 0.5 % PVP, 81% NMP, and the ZnO NPs 10%.



**Figure 3.5:** FTIRs for membrane sample based zinc oxide nanocomposite PSF 18.5 % w), (b) PVP 0.5 w %), (c) is membrane formed by mixed (a+b), (d) is ZnO 10%, and (e) is mixed (a+b+c+d).

### 3.1.6. FTIR of PVDF

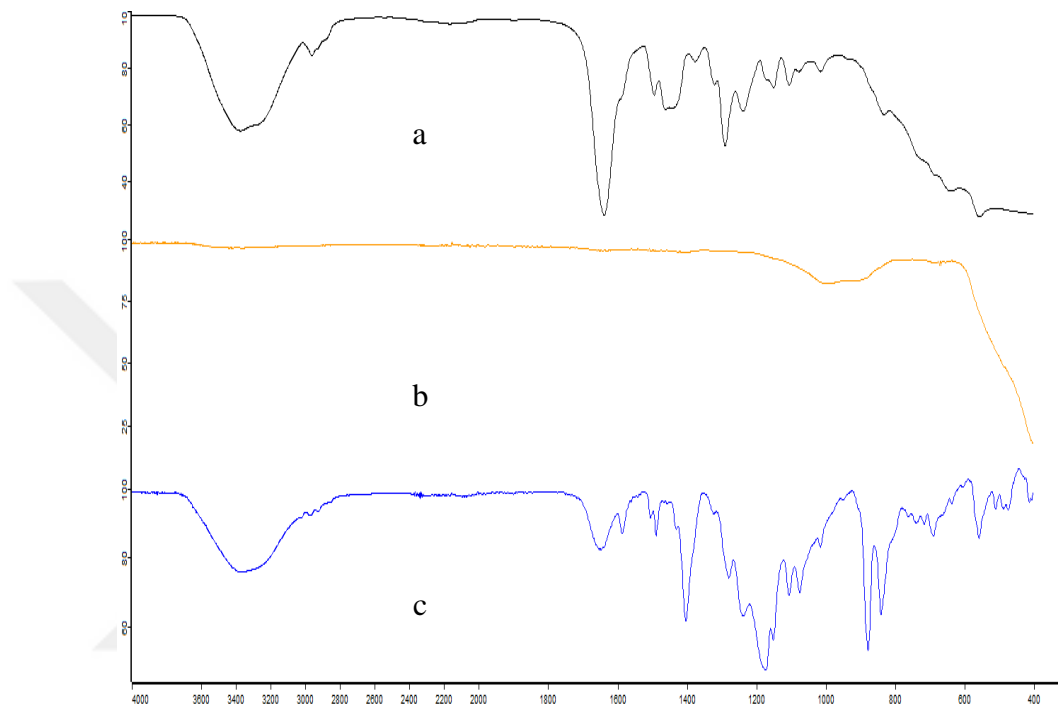
The CH<sub>2</sub> bound in PVDF sample is observed at 3025 cm<sup>-1</sup> and 2985 cm<sup>-1</sup>, C-F bound absorbed at 1000 cm<sup>-1</sup> to 1400 cm<sup>-1</sup> and vibrionic bands (411.6, 487.9, 613,757 and 975 cm<sup>-1</sup>).



**Figure 3.6:** FTIR for Polyvinylidene fluoride PVDF.

### 3.1.7. FTIR of PVDF/PSF/PVP/ZnO

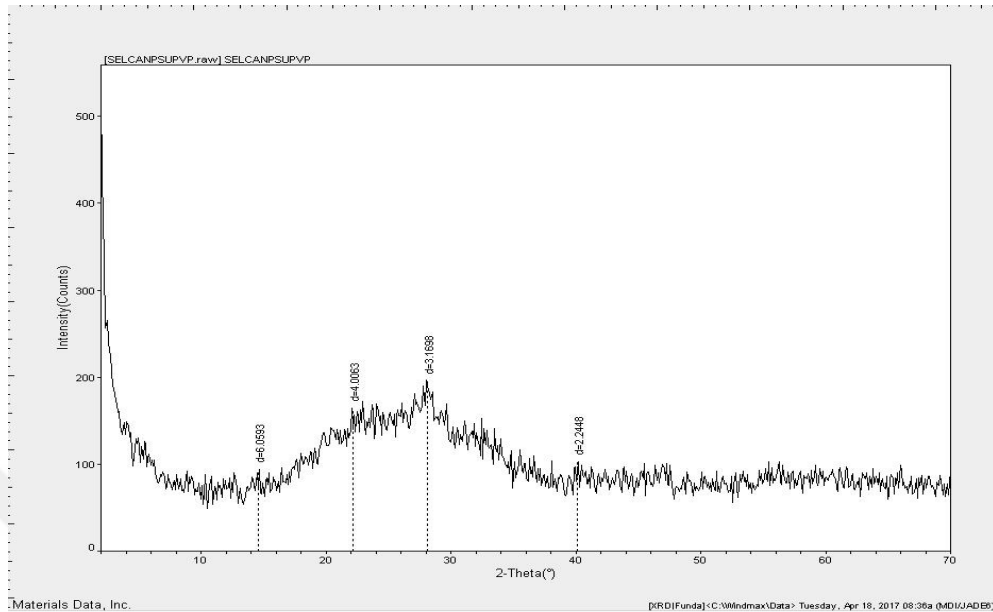
In this figure 3.7 we can noticed fictional groups of each material in component as mentioned in paragraph (3.1.3)



**Figure 3.7:** FTIR for a) PVDF 18.5% PSF18.5%, PVP18.5%, (b) ZnO 10% and (c) FTIR is (a+b).

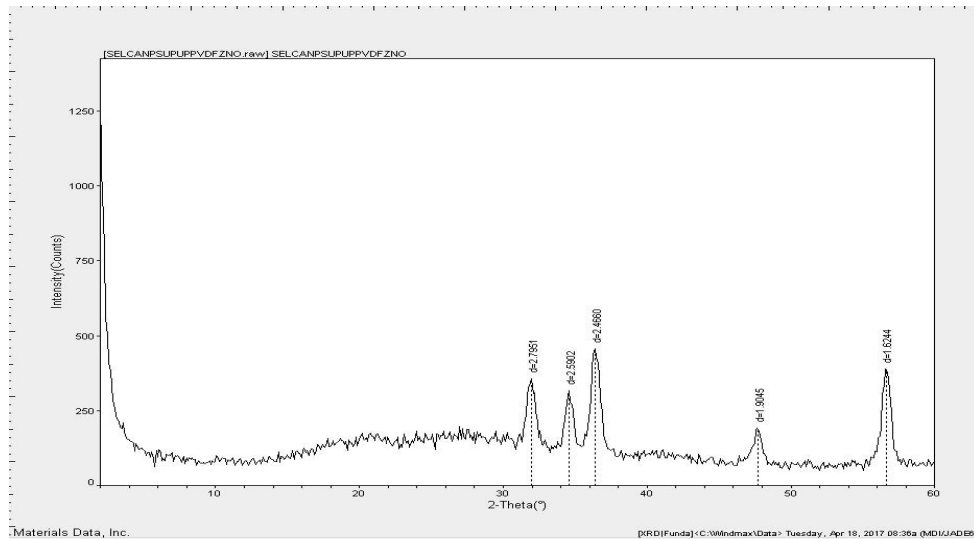
## 3.2. XRD ANALYSIS

### 3.2.1. XRD Analysis of PSF and PVP



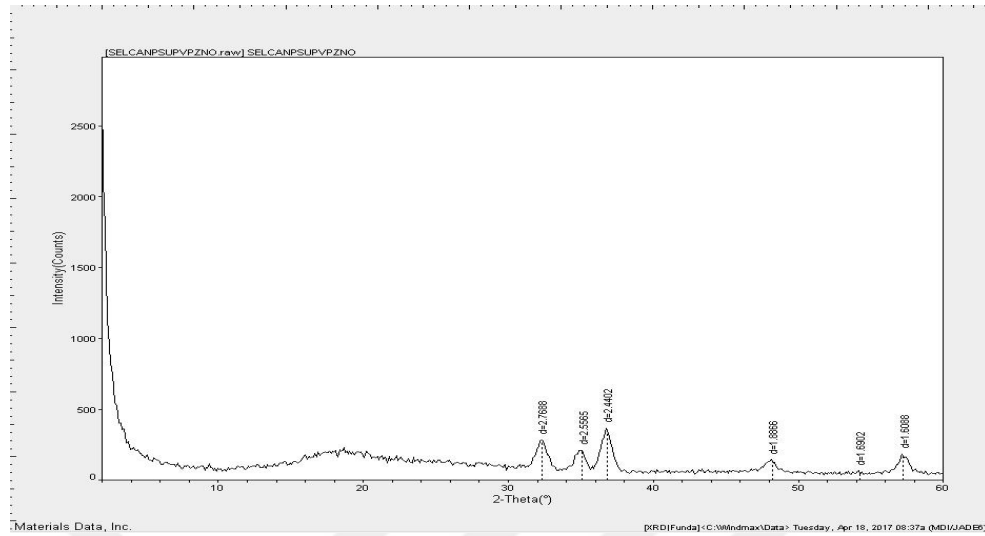
**Figure 3.8:** XRD analysis for membrane PSF 18.5% and PVP 0.5%.

### 3.2.2. XRD Analysis of PSF/PVP/ZnO



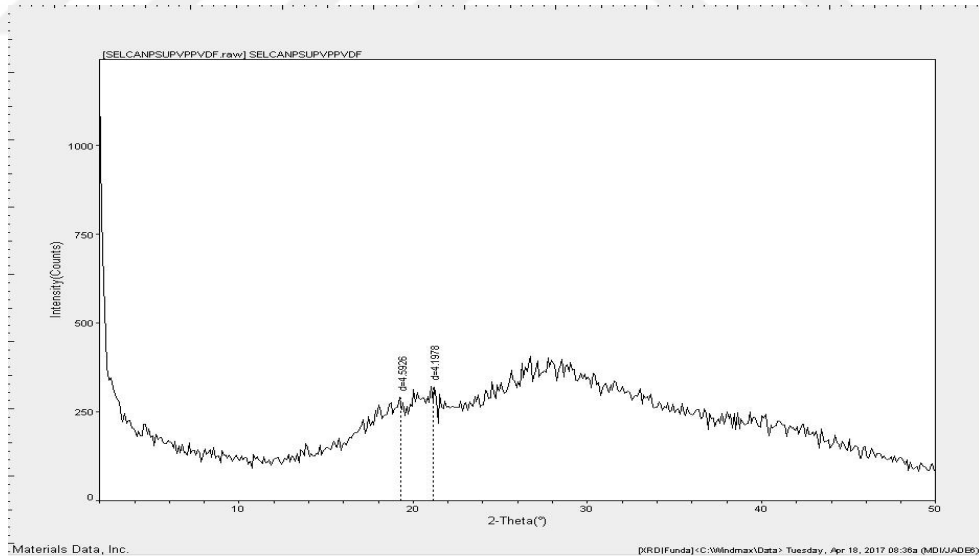
**Figure 3.9:** XRD analysis for membrane PSF 18.5% and PVP 0.5% and ZnO 10%.

### 3.2.3. XRD Analysis of PSF/PVP/PVDF/ZnO



**Figures 3.10:** Membrane contain PSF 18.5%, PVP 18.5%, and PVDF 18.5%.

### 3.2.4. XRD Analysis of PSF/PVP/PVDF



**Figure 3.11:** Membrane contain PSF 18.5%, PVP 18.5%, PVDF 18.5% and 10% ZnO.

### 3.3. THERMAL GRAVIMETRIC ANALYSIS TGA

The ratio of samples are 18.5%PSF 0.5%PVP and 10% ZnO

#### 3.3.1. TGA of PSF/PVP/ZnO

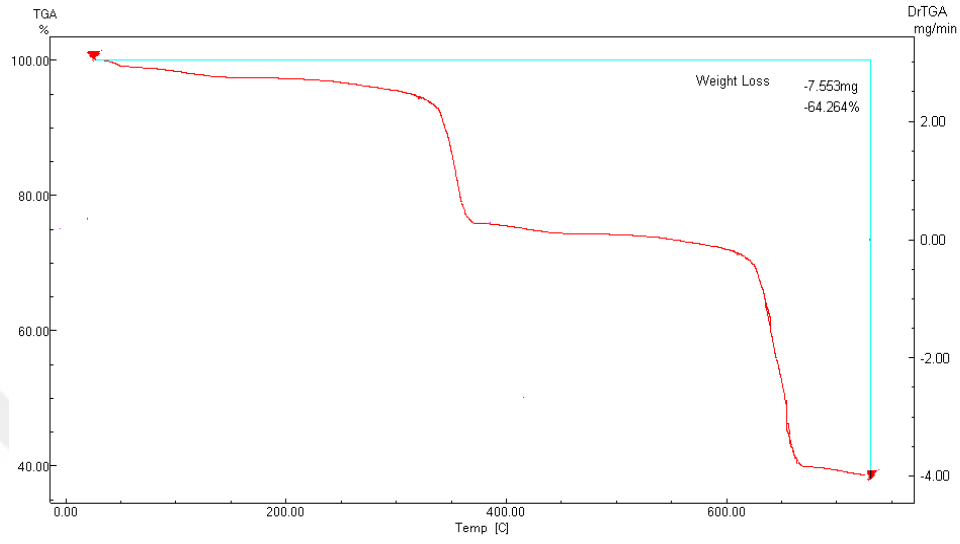


Figure 3.12: TGA for PSF/PVP/ZnO.

#### 3.3.2. TGA of PSF/PVP

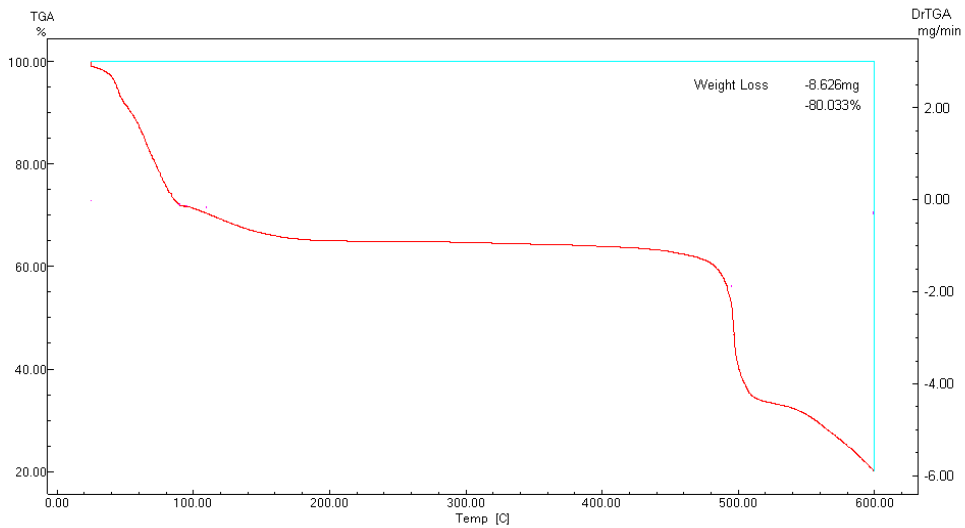


Figure 3.13: TGA for PSF/PVP.

### 3.3.3. TGA of PSF/PVP/PVDF

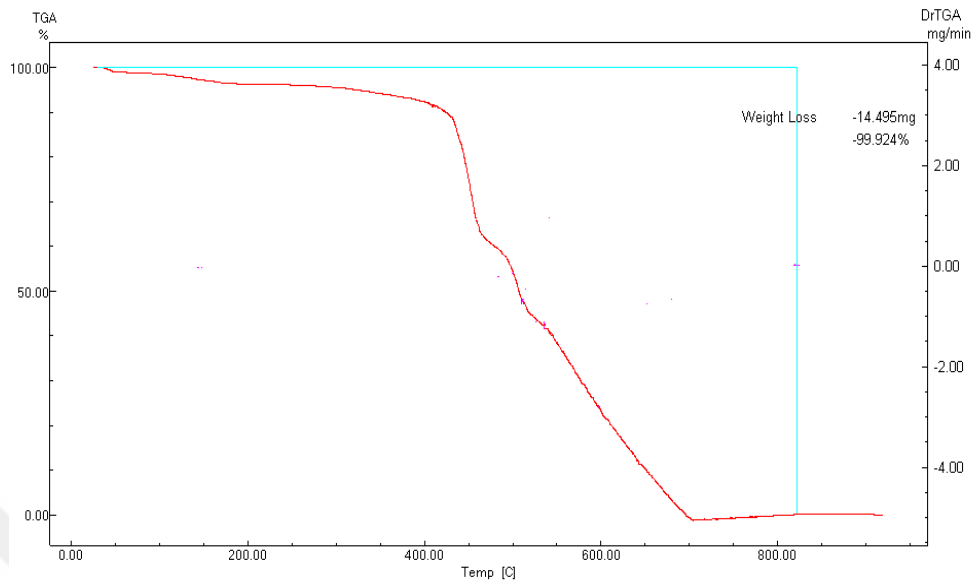


Figure 3.14: TGA for PSF/PVDF/PVP/.

### 3.3.4. TGA of PSF/PVP/PVDF/ZnO

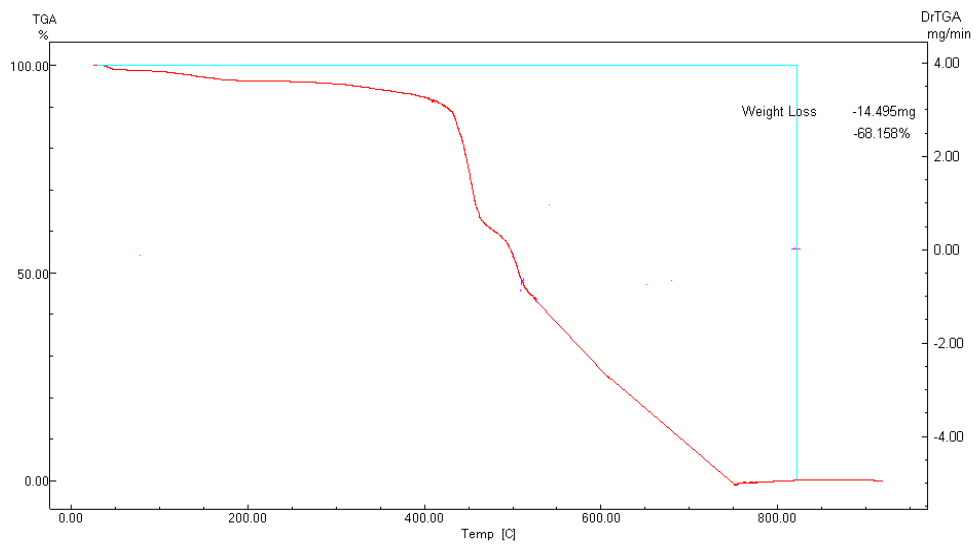


Figure 3.15: TGA for PSF/PVDF/PVP/ZnO

### 3.4. SEM ANALYSIS

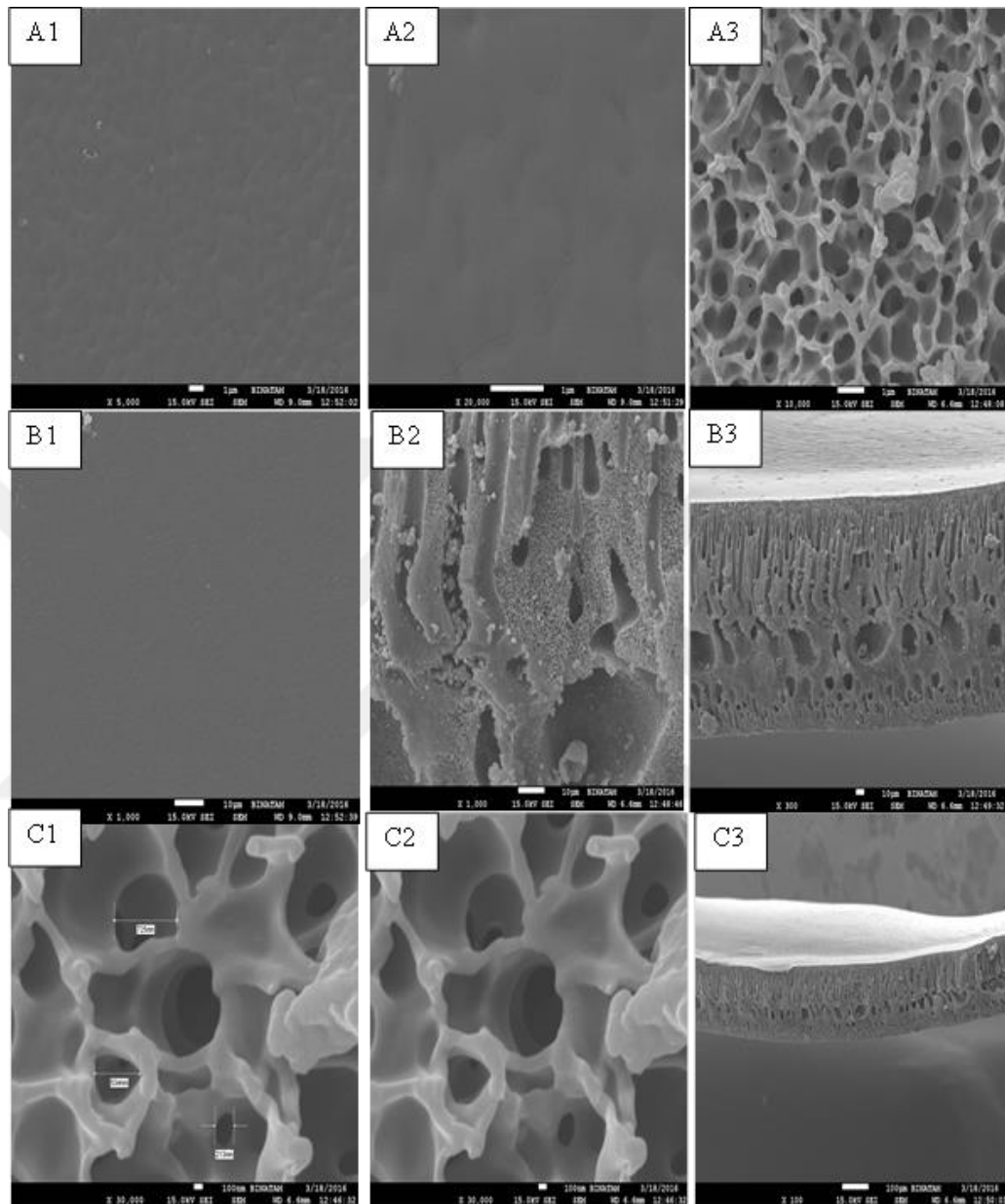
The SEM analysis was applied on all membrane samples to ensure what has happened for the morphological of membrane cross, surface, top and bottom and take a view what changes on. In my research, we have many SEM samples have checked out to evaluate the changes before and after adding one or more one material.

The next figures illustrative the morphology of membrane to study and understand the changes.



### 3.4.1. SEM Analysis for Membrane 18.5 % PSF

The scanning carry out by different magnifications

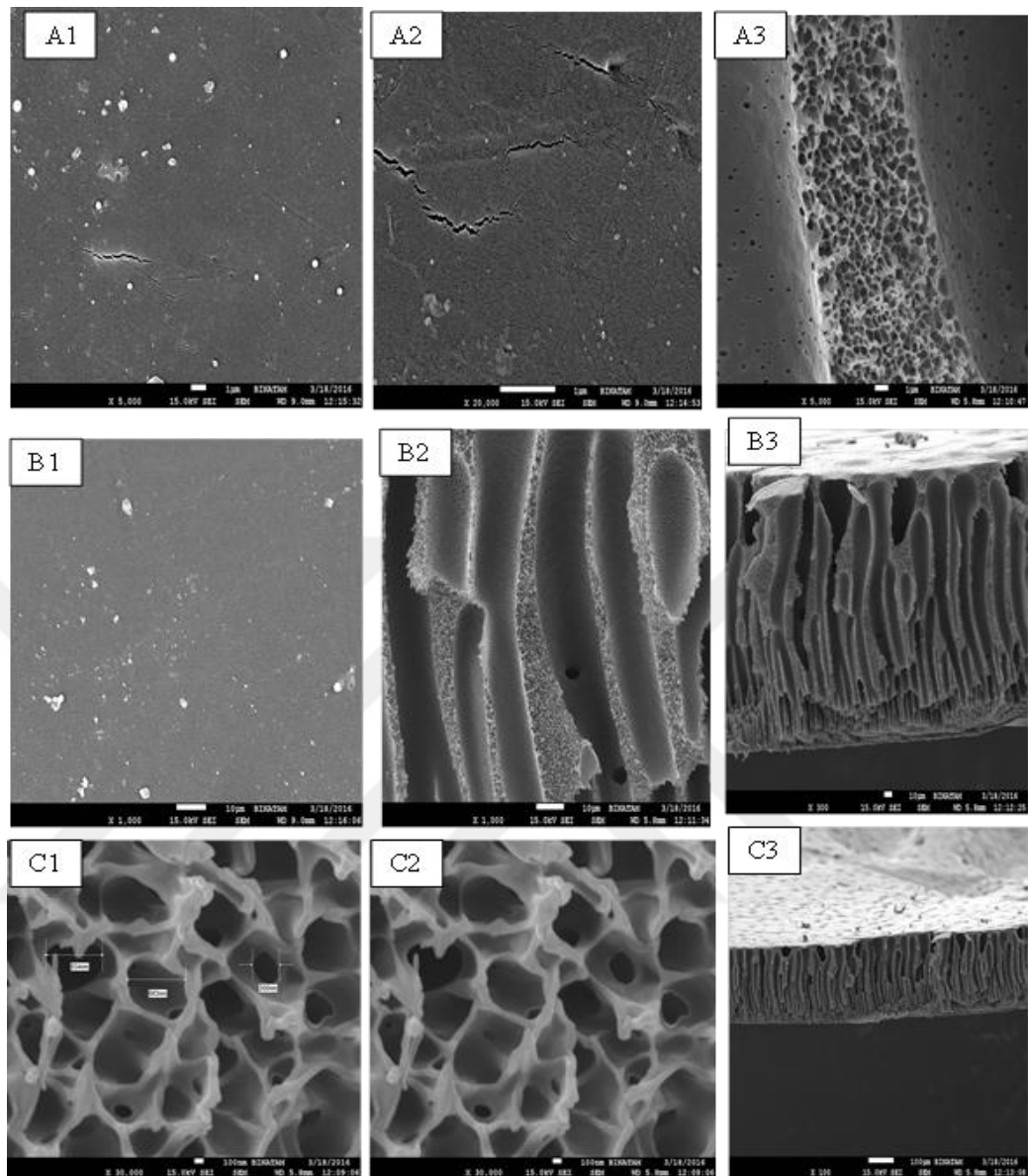


**Figures 3.16:** PSF membrane shows a1-a3)top surface cross section and bottom surface at magnify 1  $\mu$ m) b1-b3)top surface cross section and bottom surface at magnify  $\mu$ m 10 c1-c3) top surface cross section and bottom surface at magnify 100  $\mu$ m.

### 3.4.2. SEM analysis for Membrane consist of PSF and PVP

We can see the changing when added 2% of PVP to PSF the scanning carry out by different magnifications

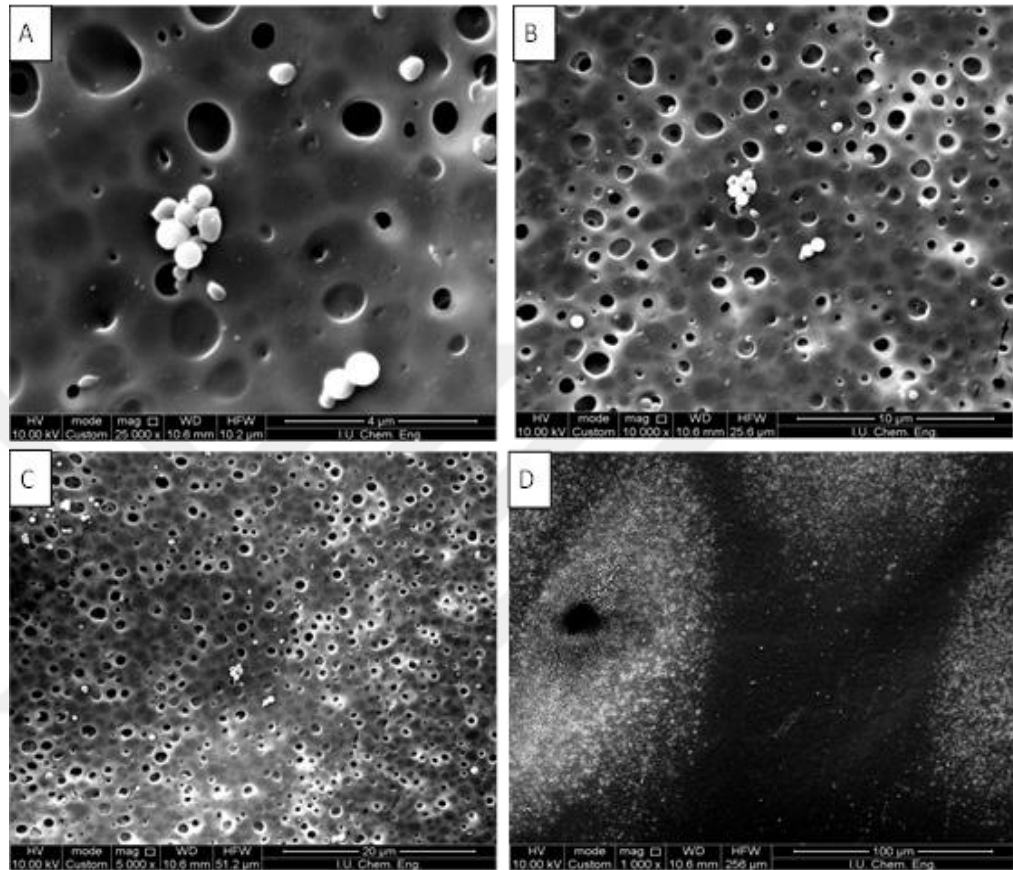




**Figures 3.17:** PSF and PVP membrane shows a1-a3) top surface cross section and bottom surface at magnify 1  $\mu\text{m}$ ) b1-b3top surface cross section and bottom surface at magnify  $\mu\text{m}$  10 c1-c3 top surface cross section and bottom surface at magnify 100  $\mu\text{m}$ .

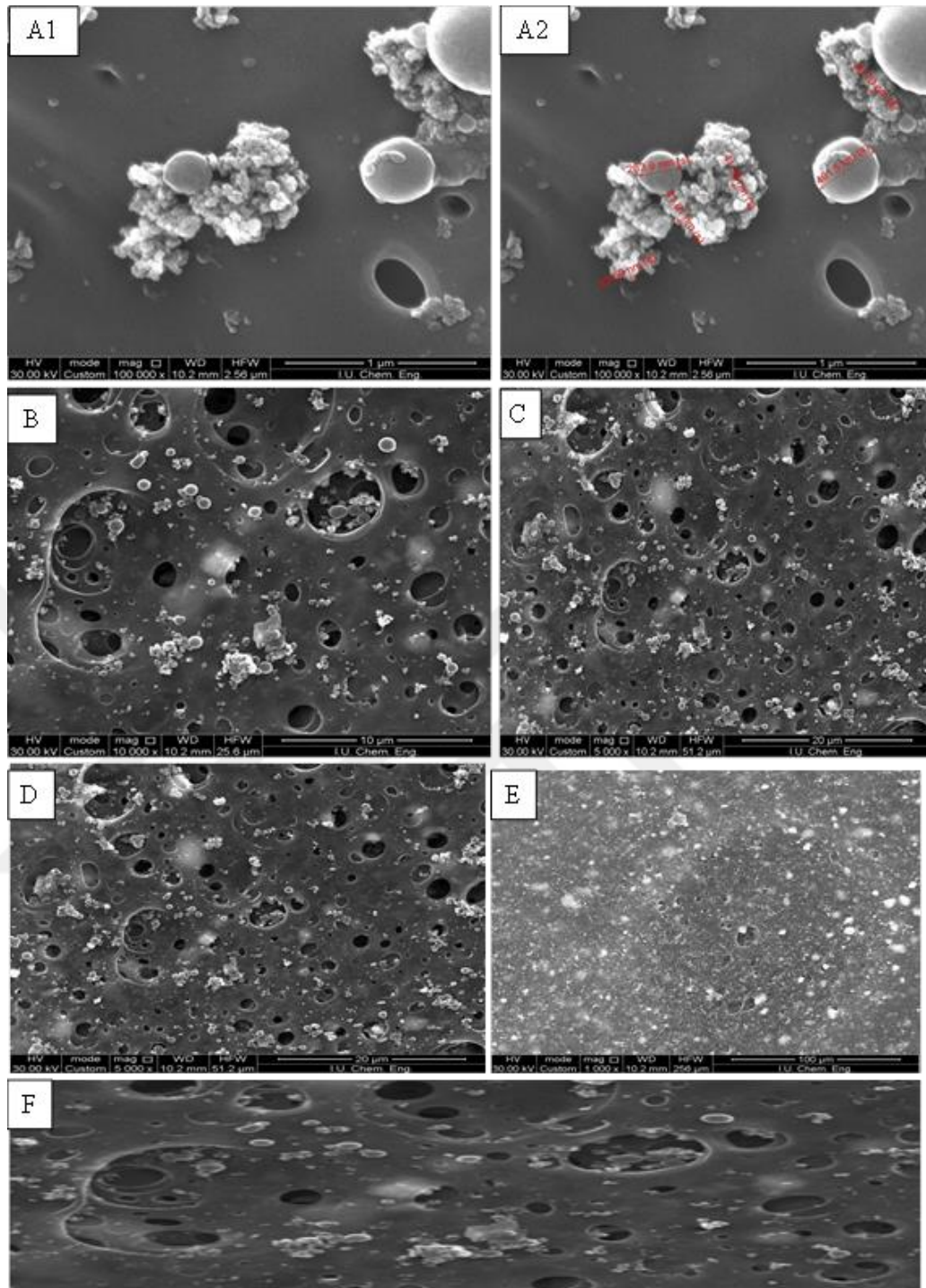
### 3.4.3. SEM Analysis of Surface

By different magnification for sample membrane PSF18.5% /PVP 0.5% we can see no changing happened on the membrane. The scanning magnifications as shown in figure 3.18

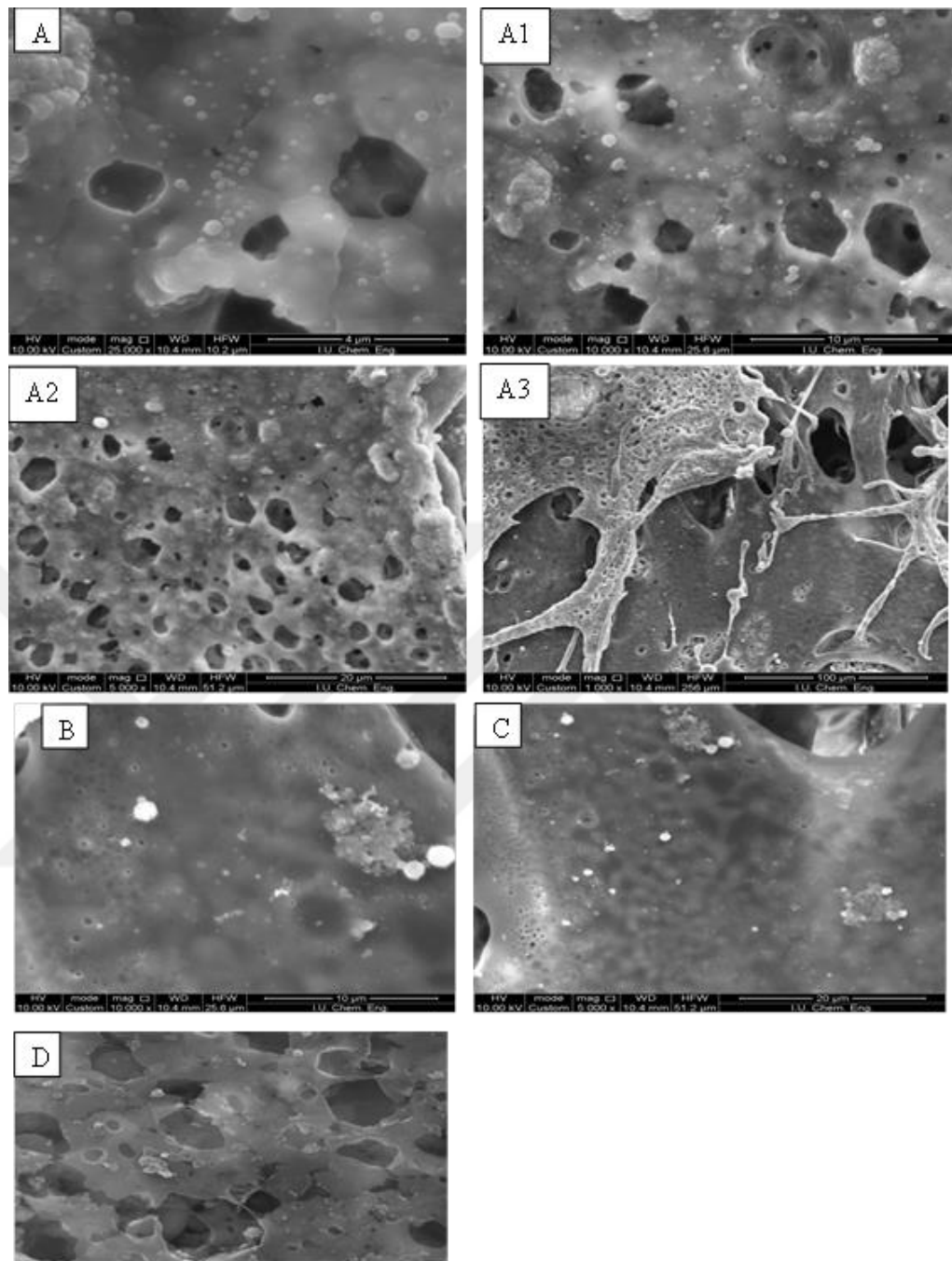


**Figure 3.18:** Membrane PSF 18.5% /PVP 0.5% a) 4  $\mu\text{m}$  b) 10  $\mu\text{m}$  c) 20  $\mu\text{m}$  and d) 100  $\mu\text{m}$ .

For sample membrane PSF18.5% /PVP 0.5% based ZnO NPs 10% we can see the changing happened on the membrane. Dispersing the ZnO NPs into membrane parts and no agglomeration the scanning magnifications as shown in figure 3.18.



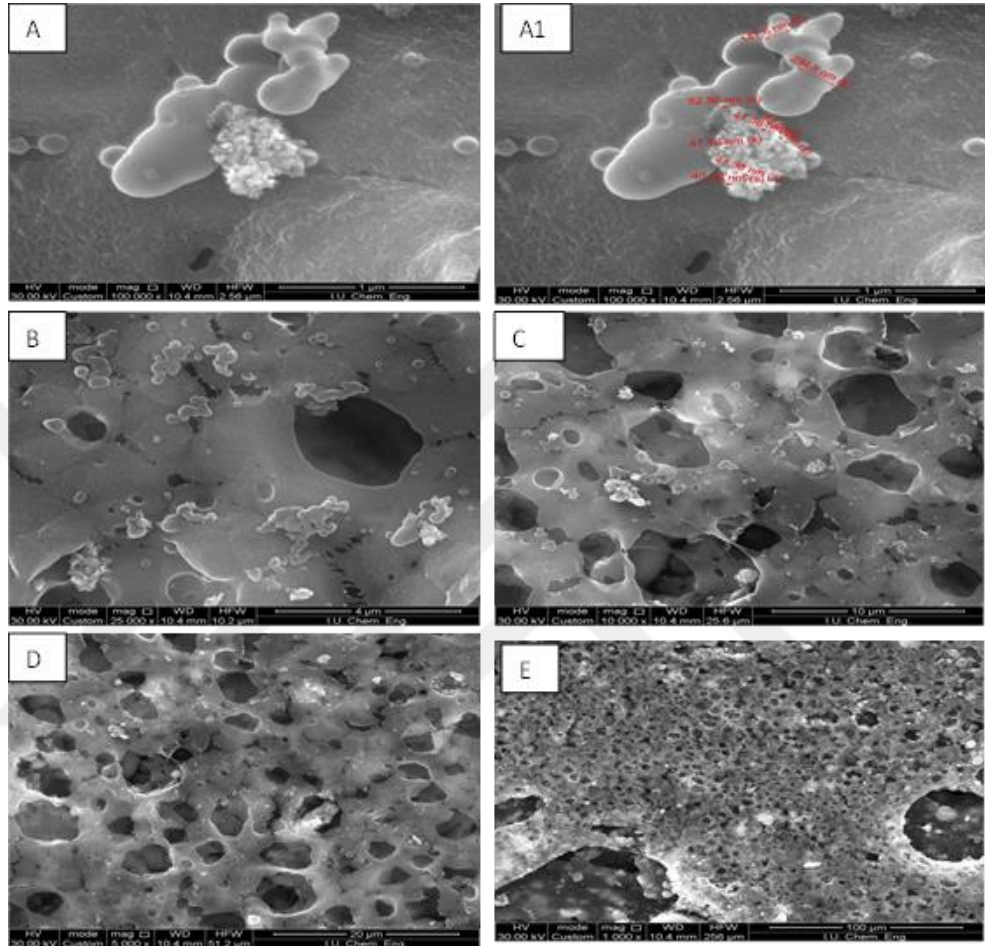
**Figure 3.19:** SEM scanning for PSF/PVP/ZnO were a1) top of membrane dispersing ZnO Nps 1 $\mu$ m, a2) shown NPs size 1 $\mu$ m and B ,cross section at 10 $\mu$ m , c,d) cross section at 20  $\mu$ m, e) bottom f) cross section at 100  $\mu$ m.



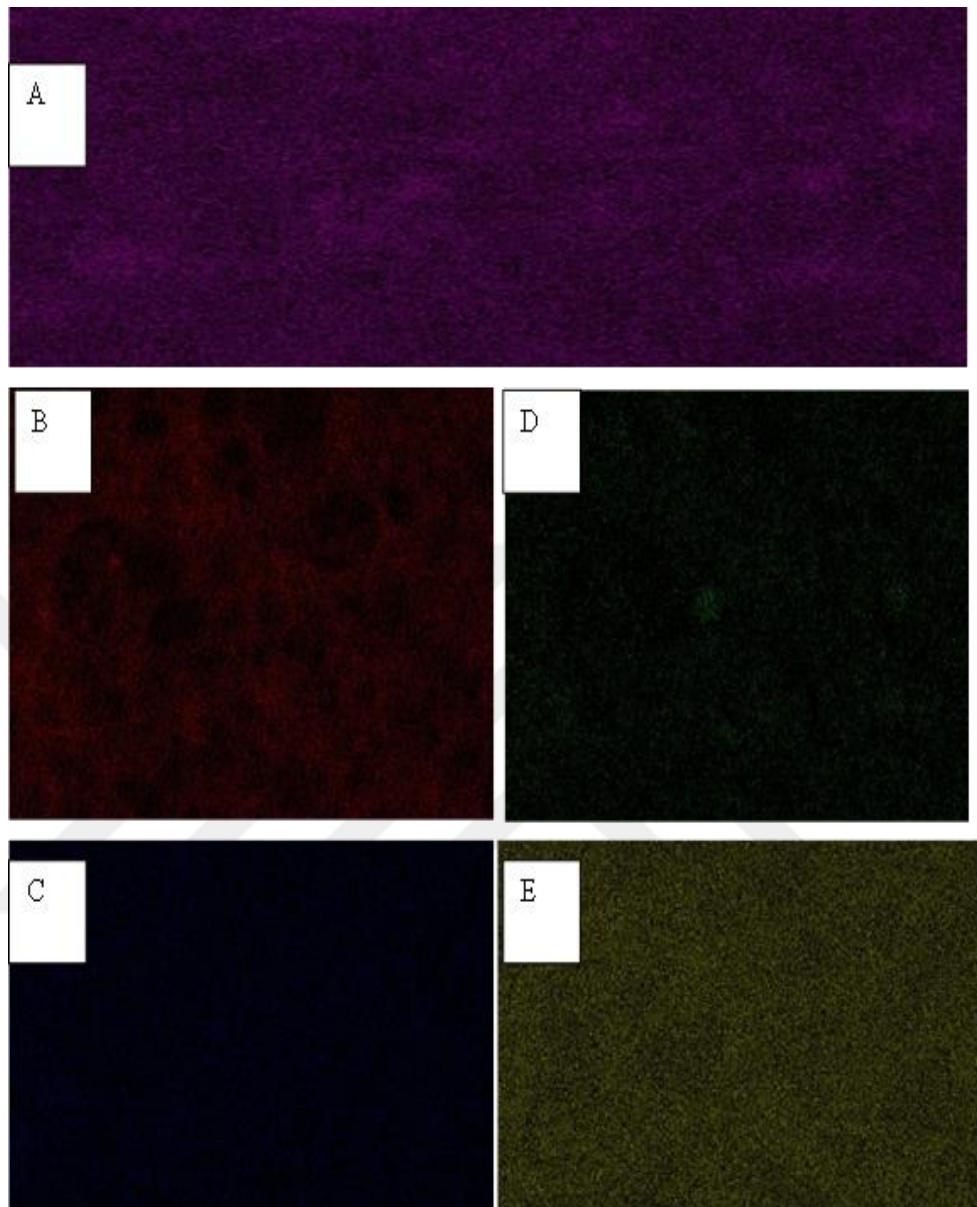
**Figure 3.20:** SEM of membrane PSF/PVDF/PVP 18.5% for each one. a-a3 cross section at 4, 10, 20, and 100 μm) b, c) top surface at 10, 20 μm D) membrane section.

PSF/PVP/PVDF 18.5% for each one ZnO NPs10%.

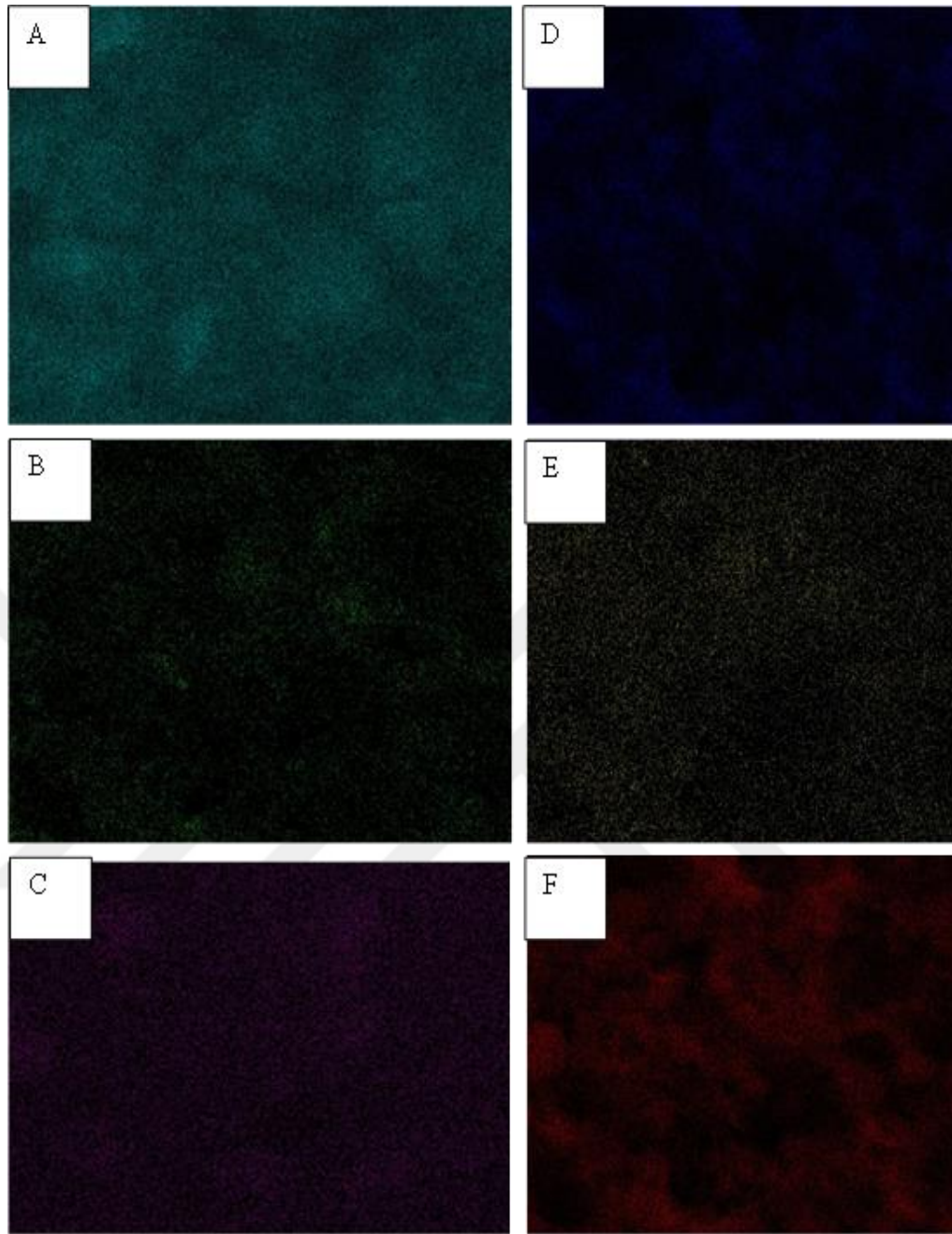
The image shown the dispersing the NPs into membrane and the size NPs. No agglomeration appeared as shown in figure



**Figure 3.21:** SEM for PSF/PVP/PVDF 18.5% for each one ZnO nps10%. a1)Nps dispersing on the top surface a2) the size on nps b, c , d , f cross section at different magnifications 4, 10, 20, 100  $\mu\text{m}$ ).



**Figure 3.22:** Dispersing the elements into all the membrane parts for PSF18.5% / PVP 0.5% ZnO 10%) a) zinc b) carbon c) silicon d) oxygen e) sulfur.



**Figure 3.23:** Dispersing the elements into all the membrane parts for PSF18.5% PVP 18.5%, PVDF 18.5, ZnO 10%) a) zinc b) oxygen c) sulfur d) fluorine e) silicon and f) carbon.

### 3.5. THE CUTOFF MW REJECTION TEST.

Polyethylene glycol (PEG) a molecular weight of 1000 Da, 10kDa, 20kDa was diffused in deionized water to prepare 1 g /L aqueous solutions to define the MWCO and rejection of the membranes. Rejection measurements were performed at the concentration of each solution was estimated via a total organic carbon analyzer (TOC-LCSH, Shimadzu, Japan).

The PEG rejection was calculated of the measured feed ( $C_f$ ) and permeate ( $C_p$ ) concentrations by the MWCO of the membrane calculated by the following equation

$$\text{Rejection Efficiency (100\%)} = 1 - \frac{C_p}{C_f} \times 100 \quad (3 - 1)$$

Where  $C_f$  is total carbon value of PEG feed before membrane.

And  $C_p$  is total carbon value of PEG permeate after membrane.

The table below shows the amount of rejection for many membrane sample compare with commercial membrane to MWCO of 1000 Da.

**Table 3.1:** Explain the rejection value in % for many membrane sample.

Sample	PSF %	PVP %	NMP%	Commercial .membrane	Rejection Peg 1000 Da MWCO %
1	18	2	80		4
2	18	1	81		9
3	18.5	0.5	81		25
				5kd	30

In our research we focusing on how to make membrane able to reject and cut-off Mw 1000Da because the Mw of many microorganisms and their toxics in all types of water might be 1000 Da or less.



### 3.6. STABILITY RESISTOR OF MEMBRANE IN AN AQUEOUS SYSTEM

We are tested the stability of membrane when keep it in an aqueous solution such as water to ensure what's the changes will happen to membrane at this condition below:

- At the room temperature.
- Distill water.
- PH 7.
- Dark place.
- Time more than 45 days.
- Plastic container size 100 ml

The membranes given strong resistor stability and no degradation shown. Here are many picture illustrative the storage.



**Figure 5.6.** Illustrative the storage prouder.

## 4. DISCUSSION

Nano composite the ratio was 18.5 % PSF, 0.5 % PVP, 81% NMP, and the ZnO NPs 10%.

In the final spectrum (e) as shown in figure 3.5 we can recognize all groups of polymers and Zn-O bound.  $1150\text{ cm}^{-1}$  (O=S=O),  $1500\text{ cm}^{-1}$  (O-H),  $1620\text{ cm}^{-1}$  (C-C), and  $2966\text{ cm}^{-1}$  and also PVP bounds group C=O at  $1663\text{ cm}^{-1}$ , C-H bound appear at  $2800\text{-}2950\text{ cm}^{-1}$ , and O-H appear range is  $3200\text{-}3400\text{ cm}^{-1}$  and Zn-O at  $420\text{-}550\text{ cm}^{-1}$ .

The crystallinity and homogeneity of the particle were investigated by XRD regarding the sample contain only PSF and PVP. As it's seen in figure 3.8 below shown there's no peaks appear at theta that's meant there's no crystalline phase in the sample.

While for another sample contain of PSF, PVP, ZnO as shown in figure 3.9 The facets ( $2\theta$  value) observed at 31, 34, 36, 44, and 56.

And it's same for the other two samples in figures 3.10 and 3.11 the samples contain PSF 18.5%, PVP 18.5% and PVDF 18.5% and 10% ZnO.

The thermal gravimetric analysis were done scanned to check the stability of the membrane. The figures below shows the curve of weight loss by use heating.

The first curve for PSF/PVP/ZnO shows that the degradation of sample happened at  $710\text{ C}$  when adding NPs of ZnO that refers some reaction take place in the membrane and the sample loss weight 64%. While the other curve for sample membrane has only PSF/PVP the degradation was in three steps and at  $670\text{ C}$  the sample loss weight 80%.

The TGA of membrane has three materials PSF/PVDF/PVP with ratio 1:1:1) for each one 18.5% the figure down illustrative the thermal stability of this sample. The weight loss started at  $700\text{ C}$  and at  $700\text{ C}$  the sample loss all weight 100%.

Moreover; another sample PSF/PVDF/PVP/ZnO (18.5% for each polymer and 10% of ZnO NPs) mixed with zinc oxide nan particles 10% size 30-50nm the thermal stability increased more than sample without NPs and at 750C the sample loss 68% of weight and keep 35% stable that leads us to understand the behavior of stability it becomes more strong and stable after adding ZnO 10% into polymer sample it explain in TG figure below.

For sample membrane PSF18.5% /PVP 0.5% based ZnO NPs 10% we can see the changing happened on the membrane. Dispersing the ZnO NPs into membrane parts and no agglomeration the scanning magnifications as shown in figure 3.18.

In the SEM figures 3.22 and 3.23 shows the dispersing the NPs into all the membrane parts without any reflection of agglomeration for PSF18.5% /PVP 0.5% ZnO 10% and PSF18.5% /PVP 18.5%, PVDF 18.5% ZnO.

Moreover, we can see in 3.22 pattern for PSF18.5% /PVP 0.5% ZnO 10% anther elements based Zn such as carbon C, oxygen O, silicon Si, and sulfur S.

And in figure 3.23 for another member consist of three polymers PSF18.5% /PVP 18.5%, PVDF 18.5, ZnO 10%)based ZnO NPs we can see six elements in whole membrane. As illustrated in figure 3.23.

## 5. CONCLUSION AND RECOMMENDATIONS

The present study investigated the distribution of zinc oxide (ZnO) in the binary and ternary polymer matrices. Our first aim was the homogeneous dispersion of the inorganic phase (ZnO) through the organic phase. Therefore with different percent (wt/wt) compositions of the organic phase (18/2, 18/1, 18.5/0.5) composed of PSF/PVP were tested and then ZnO nanoparticles were distributed in this system. According to the molecular weight cut-off tests, the best results were achieved in the 18.5/0.5 ratio.

When the durability test was performed, it was observed that the samples were not swollen for one month when kept at pH 7. Similar results were obtained in a study [F. Parvizian et al., 2014] of mixed matrix nanocomposite ion exchange membrane modified by ZnO nanoparticles at different electrolyte conditions. In our study, by comparing the durability time of the binary and ternary polymer matrix/ ZnO nanoparticles, we understood that the ternary polymer matrix gave better results. The interaction between ZnO nanoparticles and polymer in the binary and ternary systems were evaluated by the FTIR spectra of the samples with and without ZnO.

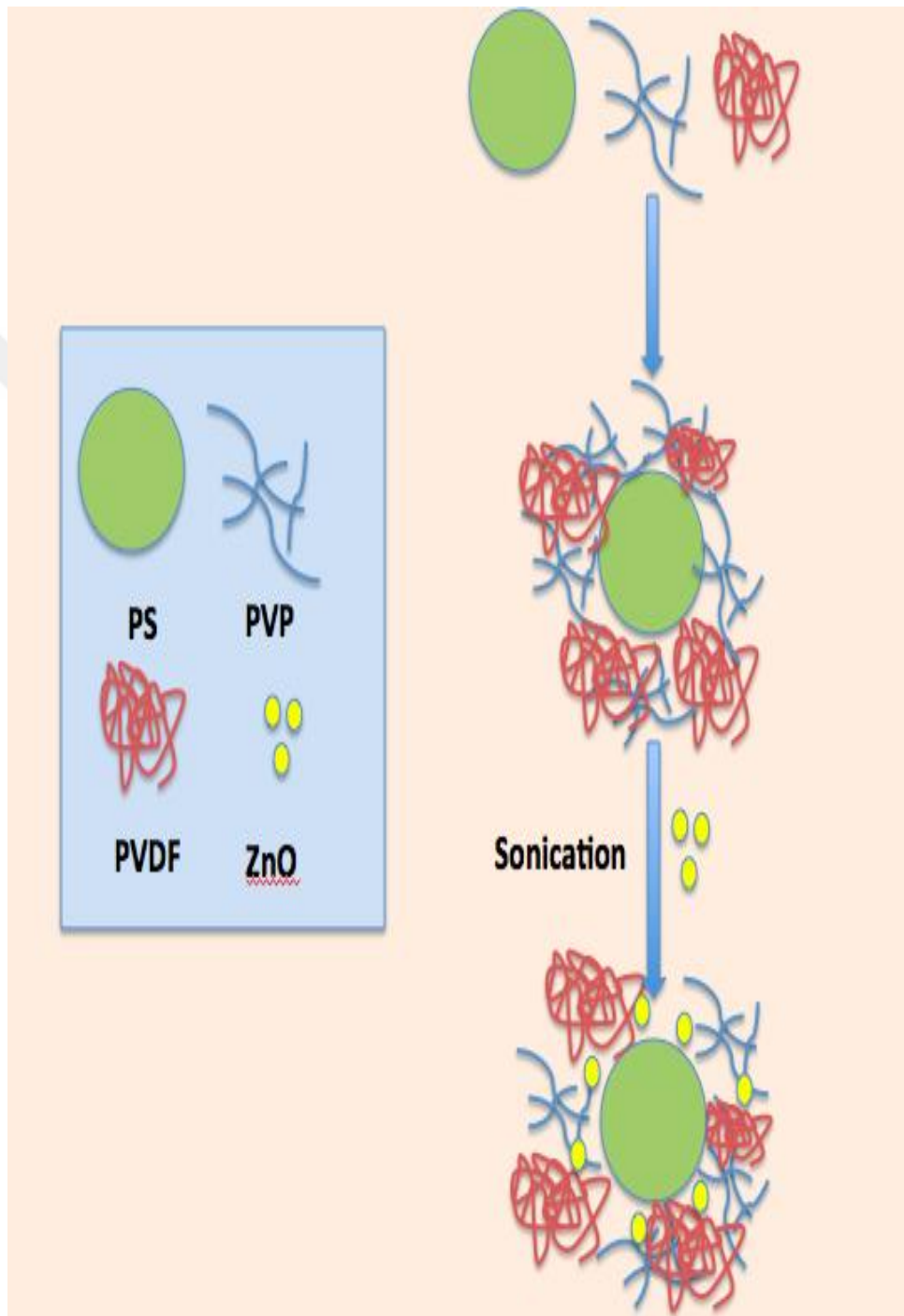
More activated functional groups in the polymer/ ZnO nanoparticle might be the reason for this.

The surface morphology of the structure was nearly smooth and ZnO nanoparticles were distributed homogeneously with a regular and irregular shape. Homogeneity also arose when a cross section was examined on polymer matrix / ZnO nanoparticle. In the literature studies similar to this part of ours with SEM images are encountered.

Some changes in the morphology of the surface due to physical attractions was observed in SEM images. This is consistent with our XRD results.

Finally, SEM images, XRD figures and FTIR peaks of ternary polymer matrix / ZnO nanoparticle showed well particle distribution and also uniform surface. Easy and also rapid process based on ultrasonication (20 kHz) was developed for the synthesis of ZnO nanoparticles in a polymer matrix.

It should be emphasized that the ternary polymer matrix / ZnO nanoparticle is cheap, biocompatible and eco-friendly effective product.



**Figure 5.1:** Ternary polymer matrix / ZnO nanoparticle

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