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FABRICATION AND CHARACTERIZATION OF GRAPHENE OXIDE COATED EGGSHELL MEMBRANE

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MASTER OF SCIENCE THESIS

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GRAFEN OKSİT KAPLI YUMURTA KABUĞU MEMBRANININ İMALAT VE KARAKTERİZASYONU

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Meryem MUSLU

Signature

Dedicated to my family

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LIST OF SYMBOLS

β	Beta
CO_2	Carbon dioxide
Cl	Chlorine
Cu	Copper
CuO	Copper Oxide
°	Degree
C_2H_5OH	Ethanol
>	Greather than
HCl	Hydrochloric acid
H_2	Hydrogen
H_2O_2	Hydrogen peroxide
OH	Hydroxide
MgAl	Magnesium aluminide
Mg^{+2}	Magnesium ion
MgO	Magnesium oxide
CH_4	Methane
μm	Micrometer
mm	Millimeter
M	Molarity
Nm	Nanometer
N_2	Nitrogen
O	Oxygen
%	Percentage
H_3PO_4	Phosphoric acid
$KMnO_4$	Potassium permanganate
pH	Potential of hydrogen
C_3H_8	Propane
rpm	Revolutions per minute
S	Second
Ag	Silver
AgNP	Silver nanoparticle

NaCl	Sodium chloride
H_2SO_4	Sulfuric acid
T	Temperature
°C	The degree celsius
TiO_2	Titanium dioxide
ZIF	Zeolitic imidazolate frameworks
ZnO	Zinc oxide

LIST OF ABBREVIATIONS

CESM	Carbonized eggshell membrane
CNT	Carbon nanotube
CZ-ESM	Copper oxide-zinc oxide-eggshell membrane
EMP	Eggshell membrane powder
EPD	Electrophoretic deposition
ESM	Eggshell membrane
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide
GQDS	Graphene Quantum Dots
LBL	Layer-by-layer
LDH	Lactate dehydrogenase
MB	Methylene blue
MCCG	Magnetic-cyclodextrin-chitosan/graphene oxide materials
MESM	Methyl esterified eggshell membrane
MO	Methylene orange
MRGO	Magnetite /reduced graphene oxide
MV	Methylene purple
OPP	Organophosphorus pesticide
PC	Polycarbonate
PEC	Polyelectrolyte complex
PEI	Polyethylenimine
PSf	Polysulfone
SEM	Scanning Electron Microscopy
SEP	Soluble eggshell membrane protein
SPE	Solid phase extraction
SPT	Spray pyrolysis technique
TFC	Thin film composite
UV	Ultraviolet

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ABSTRACT

Fabrication and Characterization of Graphene Oxide Coated Eggshell Membrane

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Department of Chemical Engineering

Master of Science Thesis

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Removal of dye in water is very important for human and environmental health. Although various studies have been carried out to remove these dyes in recent years, it can be difficult to find a simple, low-cost, efficient and environmentally friendly method. For this purpose, we produced a simple membrane to investigate the dye rejection property of the eggshell membrane, which has good surface interaction and high adsorption ability thanks to the functional groups in its structure, which has been regarded as waste for centuries. We functionalized this membrane surface with GO nanoparticles with high dispersion ability. First, GO solutions were produced by the Modified Hummers' method. Then, eggshell membranes were mechanically separated from the eggshell without using any chemical material, unlike previous studies, and eggshell membrane/graphene oxide membranes were prepared. Another aim of this study is to examine the effect of different graphene oxide ratios on the pure eggshell membrane.

Characterization of the samples was done using Filtration Test, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Contact Angle and UV-Vis Spectrophotometer measurement. Morphological analysis showed that the addition of GO at different rates changed the porosity and surface roughness of the membrane. The contact angle results revealed that the addition of GO nanoparticles to the eggshell membrane made the structure more hydrophilic.

Keywords: Eggshell membrane, graphene oxide, dye rejection, osmosis.

ÖZET

Grafen Oksit Kaplı Yumurta Kabuğu Membranının İmalat ve Karakterizasyonu

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Danışman: Prof. Dr. Hasan SADIKOĞLU

Eş-Danışman: Dr. Öğr. Üyesi Muhammed Enes ORUÇ

Sudaki boyanın giderimi insan ve çevre sağlığı açısından oldukça önemlidir. Son yıllarda bu boyaların uzaklaştırılması için çeşitli çalışmalar yapılmış olsa da, basit, düşük maliyetli, verimli ve çevre dostu bir yöntem bulmak zor olabilmektedir. Bu amaçla, yüzyıllardır atık olarak kabul edilen, yapısındaki fonksiyonel gruplar sayesinde iyi yüzey etkileşimine ve yüksek adsorpsiyon yeteneğine sahip yumurta kabuğu zarının, boya reddetme özelliğini araştırmak için basit bir membran üretimi gerçekleştirdik. Bu membran yüzeyini ise yüksek dispersiyon yeteneğine sahip GO nanopartikülleri ile işlevselleştirdik. İlk olarak, Modifiye Hummers' yöntemi ile GO çözeltileri üretilmiştir. Daha sonra, yumurta kabuğu zarları önceki çalışmalardan farklı olarak herhangi bir kimyasal malzeme kullanılmadan, mekanik yolla yumurta kabuğundan ayrılmış ve yumurta kabuğu zarı/grafen oksit membranları hazırlanmıştır. Bu çalışmanın bir diğer amacı, farklı grafen oksit oranlarının saf yumurta kabuğu zarı üzerindeki etkisinin incelenmesidir. Numunelerin karakterizasyonu Filtrasyon Testi, Taramalı Elektron Mikroskobu (SEM), Fourier Dönüşümlü Kızılötesi Spektroskopi (FTIR), Temas Açısı ve UV-Vis

Spektrofotometre ölçümü kullanılarak yapılmıştır. Morfolojik analiz, farklı oranlarda GO ilavesinin membranın gözenekliliğini ve yüzey pürüzlülüğünü değiştirdiğini göstermiştir. Temas açısı sonuçları, GO nanopartiküllerinin yumurta kabuğu membranına ilavesiyle yapıyı daha hidrofilik hale getirdiğini ortaya koymuştur.

Anahtar Kelimeler: Yumurta kabuğu zarı, grafen oksit, boya reddi, osmoz.

1 INTRODUCTION

1.1 Literature Review

Dyes in water cause serious adverse effects for both humans and the environment [1]. Therefore, it is of great importance to remove it from water even at low concentrations found in water. This problem can be solved by the use of nanoporous membranes with various uses [2]. With these composite materials produced, it becomes possible to remove both paint and pollutants such as salt and heavy metal ions from the water.

To improve salt and dye rejection, polymer nanocomposite can be produced by adding nanometer-sized nanofillers to polymers. This results in a significant reduction in salt and dye rejection. Nanofillers with high aspect ratio can be incorporated into polymer structures with micron-level pore diameters, and thus, this composite structure formed can prevent the passage of even very small molecules such as paint, salt and heavy metals dissolved in water. These membranes, which are produced with nanofillers, exhibit wide pore distribution besides curved pore paths [3].

Graphene oxide (GO) is an ultra-thin two-dimensional material that can be used as a nanofiller, which has opened a new era among carbon nanomaterials and has found a wide application area for itself. Due to its superior physical, mechanical and convection properties, it has attracted a lot of attention among composite materials and has found a wide range of application areas. Much research has been done on high quality flexible graphene sheeting materials and graphene-polymer composite materials [4]–[6]. However, it is recommended to use graphene oxide formed by the oxidation of graphite instead of graphene due to its disadvantages such as low stability, forming and dispersion difficulty [7]. Since GO is a free-standing structure, it is used in composite form, that is, either by mixing it with the polymer structure or by making a surface coating.

The incorporation of GO nanosheets into polymers has also performed remarkably during adsorption for different environmental water pollutants such as paints. However, while the composites included in the polymer structure may not fully show the desired properties, a material with superior properties than those produced with surface coating can be obtained. Various techniques are also used in the surface coating of thin films. Among these methods, EPD (electrophoretic deposition) and drop casting are easy, fast and low cost methods [8], [9]. However, for high density nanoparticle addition, drop casting is a faster, simpler and lower cost method.

The eggshell membrane, on the other hand, is a biomaterial in protein structure that has been seen as waste for years and contains various functional groups. In addition, it is easily shaped, environmentally friendly, non-toxic, easily functionalized, and has good physical and chemical resistance, making it a versatile material [10]. In recent years; Various studies have been carried out with ESM (eggshell membrane) in environmental applications, regarding the removal of various toxic materials, heavy metals and dyes from water [11]–[13]. In addition to all its positive features, it has high adsorption property and there are pores with a size of 5 μm among the fibers in its structure. In this study, it was thought that this fibrous eggshell membrane could be used as a selectively permeable biomaterial in filtration applications.

This study aims to maximize dye rejection by adding graphene oxide (GO) to the structure of an eggshell membrane (ESM), which is seen as waste, using the drop casting method. Thin films were produced from a stable, homogeneous GO suspension by drop casting over eggshell membrane (ESM).

GO filler was included in order to have lower paint permeability against paints, and the coating conditions required for this thin film to have minimum paint permeability were investigated. The filling material used during this process has a high aspect ratio, shows a homogeneous distribution parallel to the surface and does not form aggregates, this is important in terms of reducing the passage of dye molecules and improving their mechanical properties. In this study, ESM/GO nanocomposites were produced by drop casting method and thin films with

superior dye rejection properties were obtained. It was observed that the ESM/GO membrane functionalized with a high percentage of GO nanoparticles showed superior dye rejection performance compared to the membrane with a lower percentage of GO.

1.2 Objective of the Thesis

Polymer / nanoparticle materials used for organic dye removal from water have disadvantages such as low interaction between polymer and nanoparticle, low efficiency and toxicity. Therefore, this thesis focuses on the use of environmentally friendly, easy-to-supply, low-cost, non-toxic eggshell membranes that provide good surface interaction but are considered waste, thanks to the functional groups in their structure. Our first goal is to show the effect of functionalizing the pure eggshell membrane with nanoparticle on the morphological and chemical properties of the membrane. Our second goal is to investigate the effect of the accumulated GO ratio in the membrane structure. In order to reach achieve this goal the outline of the thesis of experimental part and the characterization part. Composition and the filtration overview is in Figure 1.1.

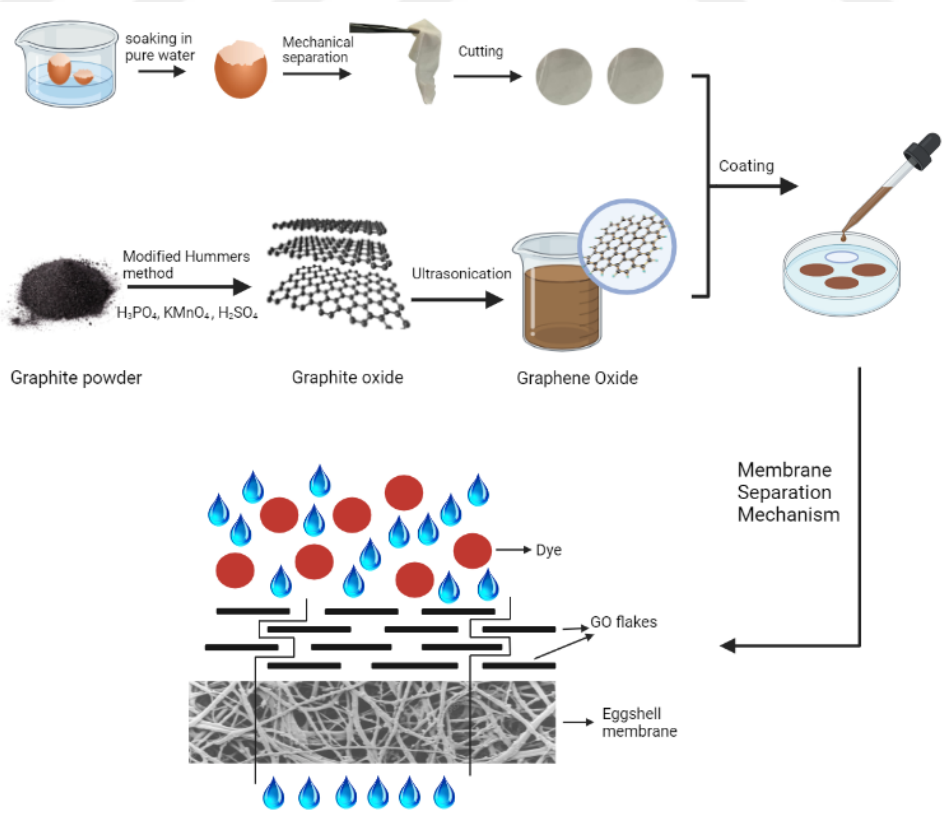


Figure 1.1 Overview

1.3 Hypothesis

The appropriate nanoparticle functionalized membrane will provide pore size that will prevent the passage of water-dissolved dye, and the dye molecules will increase the efficiency in dye rejection by following a winding path created by nanoparticles deposited on the surface. Therefore, we assume that using waste eggshell membrane (ESM) with fibrous protein structure will only allow water passage, but will adsorb dye molecules and act as a barrier, as well as this environmentally friendly nanocomposite material produced will have an important place in environmental applications and water filtration.

2
BACKGROUND

2.1 Graphene Oxide (GO)

One of the materials used to increase the barrier property of polymers against organic dyes and salt is graphene. Graphene is an ultra thin two-dimensional plate [14]. In recent years, composite materials have received tremendous attention in the structural science community due to their superior mechanical and handling properties. These features; excellent sealing, flexibility, impermeability to molecules, outstanding thermal stability [15]. Numerous studies have been conducted on high quality flexible graphene coating materials [16], [17] and graphene-polymer composite materials [18], [19]. However, graphene sheets have a hydrophobic nature and therefore tend to precipitate. This makes it difficult to produce homogeneous graphene layers. However, GO obtained from graphite has a hydrophilic structure thanks to the functional groups it contains and is easily dispersed in water and polymers [20], [21]. Considering its easy processability and superior dispersion ability, making GO-polymer composite materials is relatively easy and effective than graphene [22], [23]. It has been investigated that the electronegativity and hydrophilic structure that GO gains thanks to the functional groups on its surface provides great advantages in water treatment and can significantly increase the rejection of dyes, salts and heavy metals by adding to polymer membranes [24].

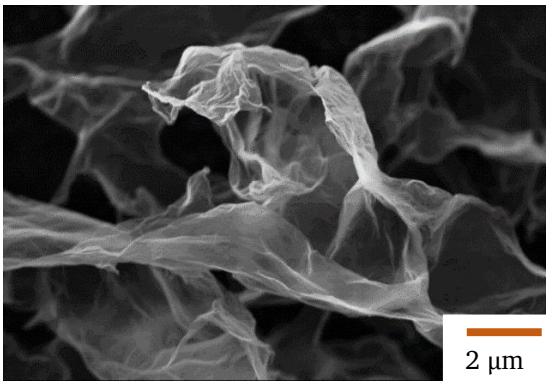


Figure 2.1 Graphene oxide scanning electron microscopy image

Morelos-Gomez et al. [25], using the spray coating method, has produced a membrane that is both easily scalable and provides high salt rejection when exposed to strong cross-flow for extended periods of time. It used an environmentally friendly and simple method for this. The membrane obtained from the aqueous graphene oxide/deoxycholate/low-layer graphene dispersion was found to have 85% and 96% rejection for an anionic dye and NaCl, respectively. In addition, it was concluded that the membrane has high strength. Looking at the desalination performance and chlorine resistance of these graphene-based membranes, it has been found to be a promising material for practical water separation applications. Sun et al. [26], developed a simple one-step solvothermal strategy for dye removal using cost-effective and non-toxic precursors and prepared magnetite/reduced graphene oxide (MRGO) nanocomposites. MRGO nanocomposites, produced thanks to the excellent properties of magnetic nanoparticles and graphene, showed a high rejection efficiency of 94% for malachite green and 91% for rhodamine B. Liu et al. [27], showed that 3D graphene oxide (GO) sponge has high efficiency and speed in organic dye removal. The effects of various parameters such as temperature, pH, contact time, efficiency and speed of dye adsorption, mixing speed, on dye rejection were investigated. This three-dimensional (3D) GO sponge was produced from a graphene oxide (GO) suspension using the centrifugal vacuum evaporation method and used to demonstrate the removal of methylene purple (MV) and methylene blue (MB) dyes. In the adsorption tests, high adsorption efficiency was obtained as 98.8% for MV and 99.1% for MB. It was observed that he reached the equilibrium state within 2 minutes [27].

Fan et al. [28], investigated magnetic-cyclodextrin-chitosan/graphene oxide materials (MCCG) membranes used as an excellent adsorbent for MB dye removal using a simple chemical route. Based on thermodynamic parameters, it has been emphasized that adsorption is endothermic and spontaneous in nature. By examining the thermodynamics, adsorption kinetics and isotherms in detail, it has been shown that the adsorbent can be easily reconstituted for reuse with almost no reduction in its adsorption capacity. The hydrophobicity of β-cyclodextrin and high surface area of GO were effective at fast adsorption and excellent cleaning

capacity. You et al. [29], reported that graphene oxide membranes would provide a practical solution for filtration and provide 100% desalination. Ganesh et al. [30], proposed high performance graphene oxide (GO)/polysulfone (PSf) membranes for pure water flow and salt rejection by wet phase inversion. It was found that salt rejection performance improved with the addition of GO, and salt rejection increased with the increase in the pH value of the feed solution. Kim et al. [31] developed a membrane that provides high water flow and salt rejection through the free radical polymerization process. The effectiveness of pressure and solution loading on the membrane was investigated. It was observed that the produced membrane maintained a very high NaCl rejection of 98.5% at different pressure values and had a water flux of 33.5 $Lm^{-2}hr^{-1}$.

Kim et al. [32] designed a high performance GO/poly (N-isopropylacrylamide-co-N, N'-methylene-bisacrylamide) desalination membrane. It has been observed that this GO composite membrane with a thickness of less than 40 nm has a GO interlayer spacing of 0.48 nm. Excellent chlorine tolerance and mechanical stability achieved 99.9% NaCl rejection and high water flow values of 25.8 L m^{-1} $hour^{-1}$.

2.2 Graphene Oxide Coating Methods

According to the membrane position and structure of nanoparticles, nanocomposite membranes; It can be produced in 4 different ways: conventional nanocomposite, thin-film nanocomposite (TFN), thin-film composite (TFC) with nanocomposite substrate, and finally surface coated nanocomposite. A typical representation of these membranes is available in Figure 2.2. The nanoparticle structures shown in the figure also represent nanofibers, nanosheets and nanotubes.

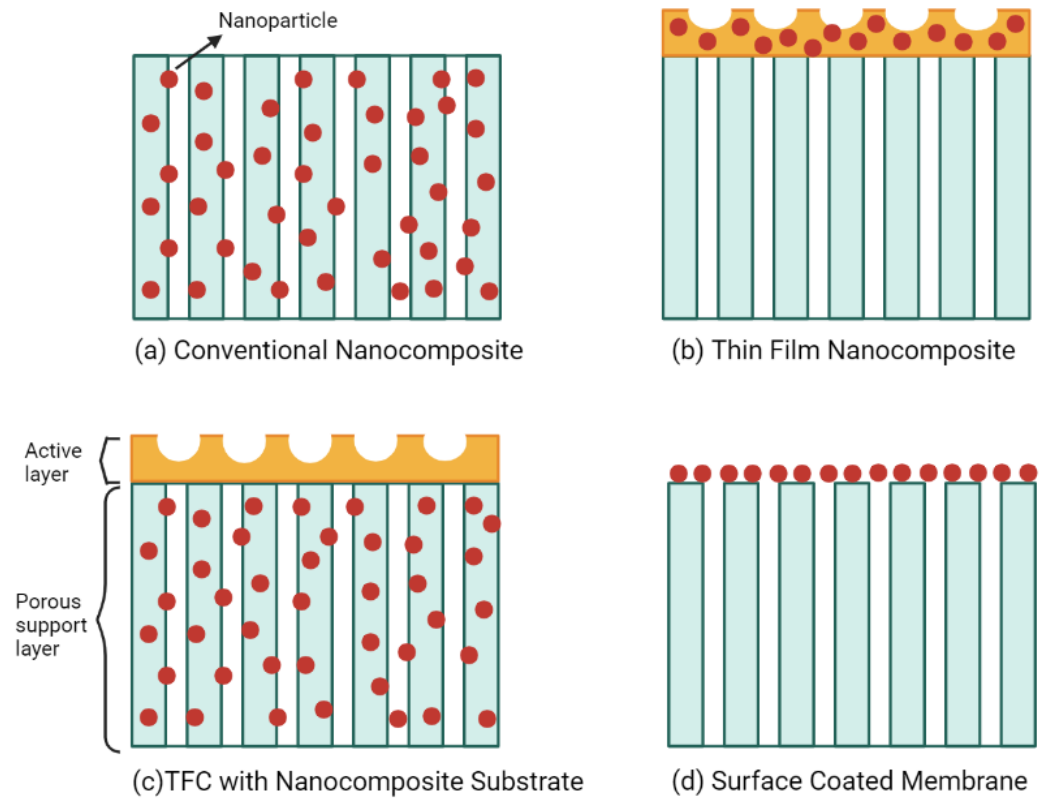


Figure 2.2 Nanocomposite membrane types

Since graphene oxide is not a free-standing material, it is used either by incorporating it into the polymer structure or by coating the surface. GO structures included in the polymer structure may not show the desired properties as well as the coating materials. The composite material prepared by coating is more developed and can exhibit superior performance [33].

Spin coating, dip coating, spray pyrolysis, EPD, drop casting techniques are used for graphene oxide thin film coating.

Dip coating, one of the liquid chemical thin film deposition methods, is the oldest commercially applied coating process. Today, membranes, protective coatings, sensors, superconducting layers, dielectrics, ferroelectrics, actuators, passivation layers, etc. It is used in various applications such as. Dip coating method is the method of depositing particles on the surface by pulling a layer from a liquid coating medium. Film production basically consists of three stages. Immersion and holding: The substrate should be kept in suspension for a certain period of time in order to obtain a good coating and to ensure full wetting. Thus, sufficient

interaction between the substrate and the coating solution is achieved. Deposition: The substrate is pulled upwards at a constant rate, at this stage, excess liquid will flow from the surface. Evaporation: The solvent in the suspension evaporates from the coated substrate and forms the thin film. This stage can be supported by drying. Afterwards, additional heat treatment can be applied to this coating, which is produced both to induce crystallization of functional oxides and to burn organic residues [34].

The spin coating process involves pouring liquid resin into the middle of a substrate and then rotating the substrate at high speeds. The centrifugal force caused by the high speed rotation initially enables the resin in the center to spread to the edges and consequently the formation of a thin film on the surface. Film thickness and properties vary depending on factors such as the surface tension of the resin, its viscosity, the percentage of solids it contains, acceleration, rotation speed, and the concentration of solution and solvent. Generally, volatile solvent is used so that the solvent can evaporate simultaneously with the process. Also, as the rotation speed increases, the film thickness decreases. The spin coating method can be used both in micro fabrication and in the production of thin films with thicknesses less than 10 nm [35]. Spin coating has several advantages such as the production of thinner films, easy handling and control of substrates and chemicals. Also, small changes in solution and spin-related parameters in this method can cause large differences in the thin film produced [36].

Electrophoretic deposition (EPD) can be defined as the storage of charged particles from a stable suspension medium under an electric current on the surface of an oppositely charged substrate. By using the EPD method, it can be ensured that the powdered material is deposited homogeneously on the electrodes. Once the pile is formed, the deposited electrode must be separated from the deposit. For EPD to be commercially applicable, the substrate must be easily separated from the deposit without degradation. This separation process can be performed more easily with careful and controlled drying in simple structures while complex sintering [37]. Electrophoretic deposition; It is a simple, fast, economical technique that can be applied at room temperature, the deposition rate and film thickness can be controlled, and the surface morphology can be changed by

changing the electrolyte concentration and electrochemical potential [38]. Aqueous solutions are generally used in this technique. This is because; It is easy, efficient, reusable, environmentally friendly, offers wide potential windows and has high conductivity compared to non-aqueous solvents. A stable suspension is required to obtain a homogeneous, effective coating [39]. It is divided into cathodic EPD and anodic EPD. There are basically two parameters that affect the EPD process. The first one is related to the suspension, the second one to the electrical conditions. In more detail, the conditions affecting the properties of the thin film; particle size, liquid dielectric constant, suspension conductivity, suspension viscosity, zeta potential, suspension stability, effect of deposition time, applied stress, solid concentration in suspension, conductivity of substrate [8].

In chemical spray pyrolysis technique (SPT), a solution is pulverized using a neutral gas such as nitrogen. In this way, they reach the substrate surface as very fine droplets. The components react in the substrate and form a chemical compound. Other components used in the process are determined to be volatile at the precipitation temperature, except for which deposit is desired. The main condition for obtaining quality thin film with chemical spray pyrolysis technique (SPT) is the optimization of preparation conditions such as solution concentration, spraying speed, substrate temperature. This optimization is the most important parameter as it controls the distribution and size of the droplets in the heated layers. Increase in the deposition efficiency and quality of thin films can be achieved with these atomization techniques. The film thickness depends on the amount of precursor solution sprayed, substrate temperature, distance between substrate and spray nozzle, concentration of precursor solution. The properties of the film produced depend on the carrier gas, spray rate, anion/cation ratio, cooling rate after deposition, substrate temperature, droplet size [40].

The drop casting method is an adjustable and easy precipitation method in which drying is carried out under conditions such as temperature and pressure, using small substrates. The thickness of the film produced by this method can be easily changed with the dispersion concentration and volume. In addition, the rate of evaporation and the degree of wetting of the substrate by the solvent used also

affect the film structure. Drop casting is an easily accessible, fast and relatively economical method for forming thin films on small substrates [41].

2.3 Environmental Applications of Graphene Oxide Composite Membranes

Graphene oxide is used in environmental fields by incorporating into the structure of various polymers due to its superior dispersion ability and unique chemical properties. Developing these composite membranes, which are used to remove various contaminants and dyes from water, is an area of interest for many scientists.

For example, Sui et al. [42] prepared PEI-GO membrane with amaranth acidic dye and high adsorption capacity for CO_2 gas. These results show promise in environmental applications such as greenhouse gas removal and adsorption of waste dyes. Xu et al. [43] designed a GO/TiO_2 filtration membrane to remove methyl orange (MO) and rhodamine B from water and for the MO solution. Provided an excellent filter efficiency of 100%.

Also, Graphene Oxide Membranes can be a solution for removing salt from seawater. For example, Wang et al. [44] designed a PEC-GO nanofiltration membrane for dye and salt removal from water. While it achieved excellent dye removal capacity of 99.5% for Congo red, it showed good nanofiltration properties of 92.6% and 43.2% for Mg2+ and Na+ ions, respectively.

Another area where Graphene Oxide membranes are widely used is the separation of mixed gases. For example, Huang et al. [45] developed a ZIF-8@GO membrane with the LBL (layer by layer) method. This membrane showed high hydrogen selectivity thanks to covalent bonds and capillary forces. The separation factors of H_2/CO_2 , H_2/N_2 , H_2/CH_4 ve H_2/C_3H_8 mixtures were found to be 14.9, 90.5, 139.1 and 3816.6, respectively. These results revealed that this produced composite membrane is a promising agent for purification by molecular sieving and hydrogen separation.

2.4 Eggshell Membrane (ESM)

Eggshell membrane (ESM) is a biomaterial that is considered waste but has unique properties. Thanks to these superior properties, it has been seen as a potential material to be used in a wide variety of applications and has begun to be widely studied. They have a wide range of uses in the field of nanoparticle synthesis, capacitors, batteries, fuel cells, solar cells, biomedical and biosensor[46].

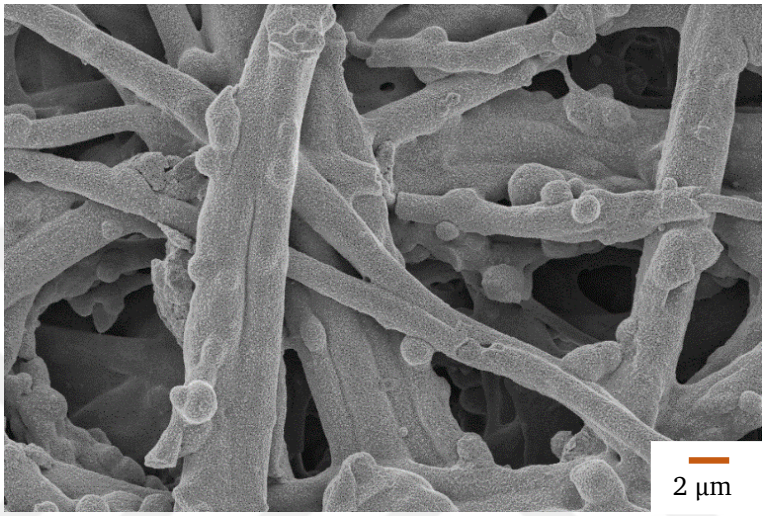


Figure 2.3 SEM images of the fibrous eggshell membrane

ESM can also be used as a natural biosorbent: Its contaminated water can be purified from a variety of undesirable types, including heavy metal ions or organic dyes. It has a high percentage of cross-linked protein fibers in its structure. The diameter of these fibers is 0.5-1.5 μm and there are pores with a size of 5 μm between the fibers. This porous structure is thought to allow the eggshell membrane to act as a selectively permeable material [47].

As seen in Figure 2.4, ESM has different usage patterns.

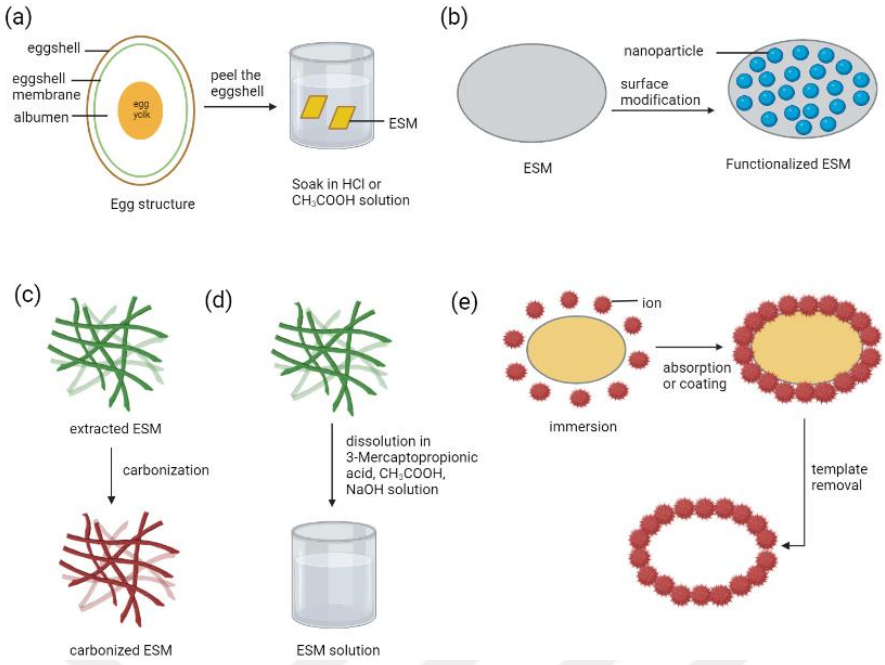


Figure 2.4 Various uses of ESM (a) Separation and preparation of ESM (b) ESM functionalization (c) Carbonization of ESM (d) ESM solution (e) Use of ESM as template

Eggshell membrane has different uses. The first is the mechanical separation of the ESM from the ES. The mechanically separated ESM is dipped in HCl solution to remove any remaining ES and finally dried at room temperature (Fig. 2.4a). The second use of ESM is the functionalization of its surface (Fig. 2.4b). Various properties of ESM are improved by the immobilization of various chemical components on the ESM. Another use of ESM is carbonization of ESM (Fig. 2.4c). Bare ESM is carbonized in grassy carbon discs in argon at 800 °C because it has low electrical properties. It is then activated in air at 300 °C. The resulting material exhibits superior electrical properties. Using ESM as soluble eggshell membrane protein (SEP) is another use (Figure 2.4d). The production of an aqueous solution of water-insoluble ESM is an important issue for ease of forming and size control as it contains high disulfide bonds. This problem is partially solved by soluble eggshell membrane protein (SEP), which is produced by treating the ESM with a special acid solution. However, SEP does not have exactly the same chemical properties as bare ESM [48]. Finally, the ESM can be used as a template (Figure 2.4e). ESM is used as a template to create hierarchical structures of metals or other molecules, thanks to their superior interlocking micro/nano structures. This

generated ESM template is often used to fabricate electrical devices and catalysts [49].

Table 2.1 shows the use of eggshell membrane in various adsorption studies.

Table 2.1 Comparison of the Use of Egg Shell Membrane in Various Adsorption Studies

ESM isolation	ESM usage	Material	Application	#
12 h HCl	ESM in powder form	MESM (Methyl Esterified ESM)	Microalgae adsorption	[50]
30 min %1 acetic acid	Creating the extraction column	GQD/ESM	SPE sorbent	[51]
1 h and 0.05 M acetic acid/NaOH	5 x 8 mm sections	Cu – Ag/MESM	Adsorption of heavy metals from wastewater and as a template	[52]
ESM HCl soaked in acid	Calcination at 400 °C for 2 h	CuO/ESM and ZnO/ESM	Organic pollutants, microorganisms, Congo red removal/as biopattern	[11]
	ESM in powder form	C-MgO-EMP	Wastewater treatment	[53]
30 min HCl	2 cm x 2 cm sections	AgNP/ESM	Adsorption and detection of acidic and basic dyes	[54]
diluted acetic acid	ESM powder was used (sieved to a particle size of -0.125 mm)	zeolitic imidazolate frameworks (ZIF)/ESM	BR18 dye and Cu^{+2} removal from wastewater	[55]
	Carbonized ESM used	CESM-CNT	Solar Water Treatment System	[56]
HCl	ESM used in powder form	ESM	Au adsorption	[57]
HCl/NaOH	used dried and shredded	ESM	Adsorption of Cr (VI), Cd (II) and Cu (II)	[58]
	ESM used in powder form	ESM	Cr (VI) adsorption	[59]
HCl	as a template	MgAl – Cl - LDH / ESM	As template for Cr (VI) adsorption & LDH coating	[60]
%10 acetic acid	ESM used in powder form	Tiol / ESM	Hg (II) adsorption	[61]

Table 2.1 Comparison of the Use of Egg Shell Membrane in Various Adsorption Studies (continued)

HCl	Dried, broken into small pieces	Tiol / ESM	Adsorption of heavy metals	[62]
HCl	In 0.5 x 0.5 mm pieces	PEI / ESM	Cu (II) detection	[63]
HCl/NaOH	ESM used in powder form	ESM	Adsorption of malachite green	[64]
HCl/NaOH	ESM used in powder form	ESM	Adsorption of the organic dye Eosin B	[65]
HCl/NaOH	ESM used in powder form	ESM	Congo red	[66]
HCl/NaOH		ESM	Azo dye Eriochrome T	[67]
HCl/NaOH	ESM used in parts	ESM	LAS biosensor	[68]

Liu et al. [58], investigated the adsorption of Cr (VI), Cd (II) and Cu (II) of dried and crushed ESM. It has been observed that optimum experimental conditions such as ESM dosage, adsorption time and temperature are different for each ion. Daraei et al. [59], made a review on the optimum test conditions for Cr (VI) of powder ESM. The effects of various events such as sorbent dosage, temperature, contact time, Cr (VI) concentration and pH on adsorption value were investigated using theoretical calculations. Maximum adsorption efficiency of 81.47%; 3.78 g dosage was obtained at 20 ° C temperature, 117.52 minutes contact time, 5.0 mg L^{-1} Cr (VI) concentration and 3.54 pH values. Abdollahi et al. [51], separated the ESM from the ES by soaking in 1% acetic acid for 30 minutes and used the GQD/ESM composite as a new SPE (solid phase extraction) sorbent in the extraction of OPP (organophosphorus pesticide) from aqueous solution. Various parameters such as sample loading flow rate, pH of the solution, sample volume and nano-sorbent amount, which have an effect on the extraction of organophosphorus pesticides in GQDS/ESM, have been investigated. It has been determined that the proposed method has a low detection limit of 0.006-0.32 ng mL^{-1}, a wide linear range of 0.05-100 ng mL^{-1} and a good linearity of $R2 > 0.997$. Thus, it has been concluded that the method can be successfully applied to determine OPPs in fruit juices and water samples.

He et al. [11], aimed to use the ESM both as a bio template and in the removal of organic pollutants, congo red and microorganisms in water. The ESM separated by soaking in HCl acid was dipped in copper nitrate and zinc nitrate solutions, dried at room temperature and collected in a crucible, then calcined at 400 ° C for 2 hours. As a result of the characterizations, it was determined that CZ-ESM (CuO-ZnO-ESM) nanocomposites show stronger antibacterial activity, catalysis and adsorption properties on microorganisms and organic pollutants compared to their separate components. The maximum adsorption capacity was found to be 775 mg g^{-1}. Besides, CZ-ESM nanocomposites have been found to have a good inhibitory activity against S. Aureus and E. coli bacteria. These superior performances are attributed to the combination release of Zn and Cu ions and the homogeneous distribution of CuO and ZnO nanostructures on the ESM.

Minimum et al. [53], investigated the usability of the C-MgO-EMP composite in textile wastewater treatment. The catalytic efficiency of C-MgO-EMP catalyst in TOC (total organic carbon) removal (mineralization) from textile waste water and degradation according to ADMI color unit was found to be 78% and 93%, respectively. High TOC removal from paint compounds was achieved with MgO ESM powder doped with C. Thus, it has been concluded that the C-doped MgO powder is a stable catalyst for the removal of stubborn compounds in waste water. Candido et al. [69], made a study on the use of AgNP/ESM in adsorption and fixation of acidic and basic dyes. The ESM was separated by soaking in HCl acid for 30 minutes, and by adding silver nanoparticles to its structure, it has been shown that it can be used as a low-cost and efficient adsorbent to remove MB and MO from aqueous solution. It has been stated that AgNP/ESM is a composite that can be applied in the detection of dyes with concentrations as low as 10^{-9} M.

Ishikawa et al. [57], studied heavy metal adsorption using ESM in powder form. It has been shown that ESM can adsorb gold ions in wastewater and thus its use in water purification is possible. Optimum pH was found to be 3. It was determined that the sorption rate increased with the shrinking ESM size. Adsorption values of Au (I) and Au (III) were found to be 147 and 618 mg g^{-1}, respectively. Then, the adsorption values for different metals were measured and 98% for Au (III)), 97% for Ag (I), 94% for Co (II), 17% for Cu (II), 15% for Pb

(II), Adsorption values of 4% for Ni (II) and 3% for Zn (II) were achieved. Based on these results, it was concluded that some ions were partially adsorbed and then desorbed by the ESM, some were almost not adsorbed and some were almost completely adsorbed.

3
EXPERIMENTAL METHOD

3.1 Materials Used

In the GO synthesis process, graphite powder, potassium permanganate, sulfuric acid, phosphoric acid, hydrogen peroxide and hydrochloric acid were used. Chemicals are reagent grade that do not require an extra purification process. Deionized water was used in all solutions. Polycarbonate membrane with 220 nm pore size was purchased from Sterlitech. Eggshell membrane was obtained from household waste. Egg shells were obtained from domestic waste. A cresol red dye with a molar mass of 382.43 g/mol was purchased from Sigma Aldrich.

3.2 Composite Membrane Production

3.2.1 Synthesis of Graphene Oxide via Modified Hummers Method

GO was synthesized by the modified Hummers method. 40 mL of concentrated phosphoric acid (H_3PO_4) was added to 360 mL of concentrated sulfuric acid (H_2SO_4) and mixed. The solution was placed in the oil bath to keep the temperature between 40 and 45 °C and stirred at 200 RPM. Then 3 g of graphite was slowly added to the solution. Then 18 g of potassium permanganate ($KMnO_4$) was added. The reaction mixture was found to be dark green in color. During these processes, the temperature was monitored to be between 40 and 45 °C. It was allowed to react for 16 hours. As a result of the reaction, it was observed that the mixture was dark purple and green in color. Then the mixture was cooled with 400 g ice.

Aliquots 3 and 5 of 3 mL of 30% H_2O_2 by weight were added. The color of the suspension was seen to change from dark purple to bright yellow with bright white spots. 7 hours were waited for this process. It was centrifuged at 3000 RPM for 45 minutes and washed with copious amounts of water. Glass rod was used to break up the lumps. Care was taken not to shake the centrifuge tube as GO could gel with water. It was then washed three times with 35% by weight concentrated HCl.

Glass rod was again used to break up the pellet and gently agitated. During this time, care was taken not to shake vigorously to avoid bubbles in the solvent. It was centrifuged at 3000 rpm for 45 minutes. It was washed three times with anhydrous ethanol. Finally, the GO solution was dried in a 90 °C oven for 24 hours to produce the GO powder and the GO solution produced using the modified Hummers method was sonicated for 3 hour to exfoliate the nanoparticles before coating.

The schematic representation of the modified Hummers method used for graphene oxide synthesis in this thesis is in Figure 3.1.

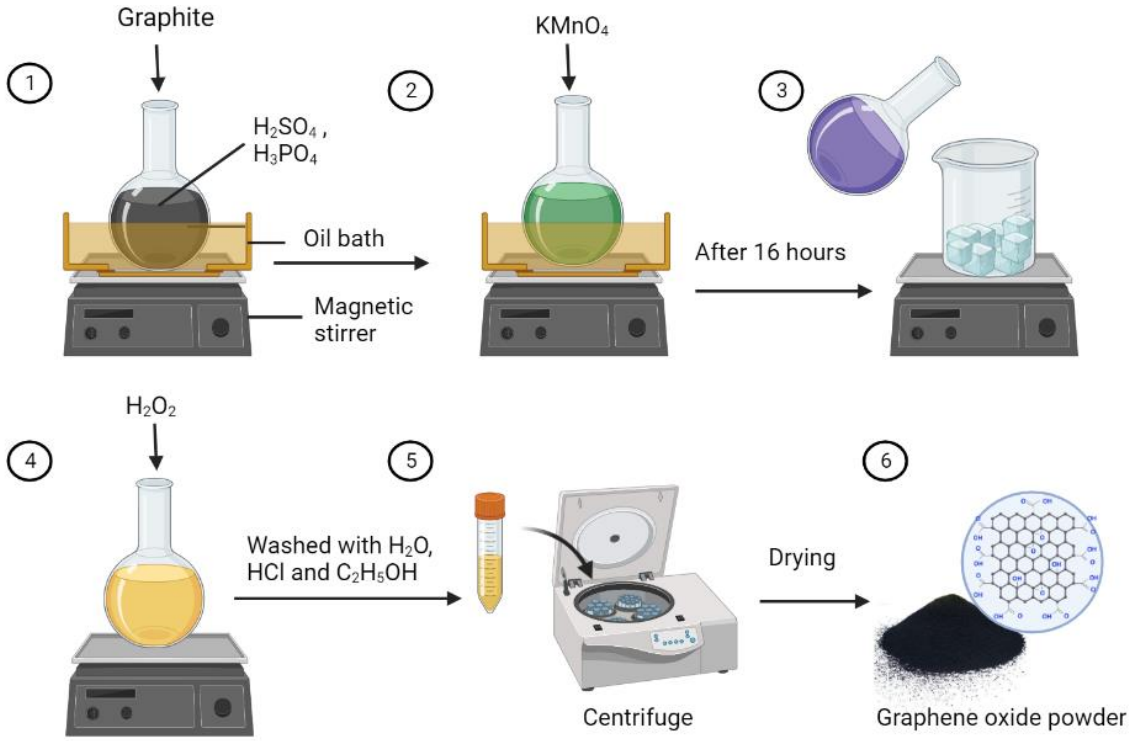


Figure 3.1 Schematic illustration for graphene oxide synthesis by modified Hummers method

3.2.2 Eggshell Membrane Preparation

Raw eggshells obtained from domestic wastes were kept for 1 day after being washed in tap water. Later, these eggshells were kept in DI water for 3 hours. After 3 hours, DI water was replaced with a new one and the same process was repeated 3 times. The eggshell membrane was easily separated from the eggshell by mechanical means without the need for any chemical treatment. Separated

ESMs were cut in 2 cm diameter for GO coating and testing in the existing U-tube assembly.

3.2.3 Composite Membrane Production via Drop Casting Method

The homogeneous GO solution produced by the modified Hummers method was sonicated for 3 hour to exfoliate the nanoparticles before coating. Then, 0.5 mg/ml 50 μL GO solution for ESM/GO1, ESM/GO2 and ESM/GO3 nanocomposite membranes, respectively; It was evenly coated on the ESM substrate using the drop casting method in 1, 2 and 4 layers.

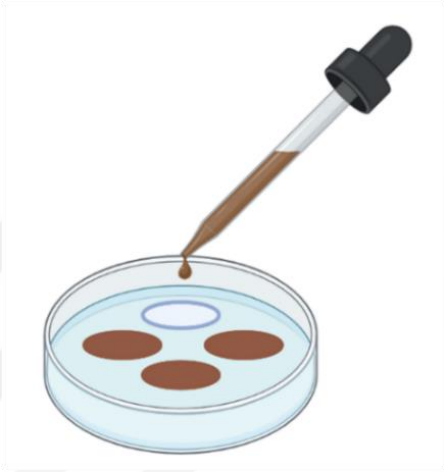


Figure 3.2 Drop casting method

After coating, the samples were dried under vacuum for 15 days to prevent crack formation on the membrane surface. The effect of vacuum drying on the coating performance of the membrane is shown in Figure 3.3.

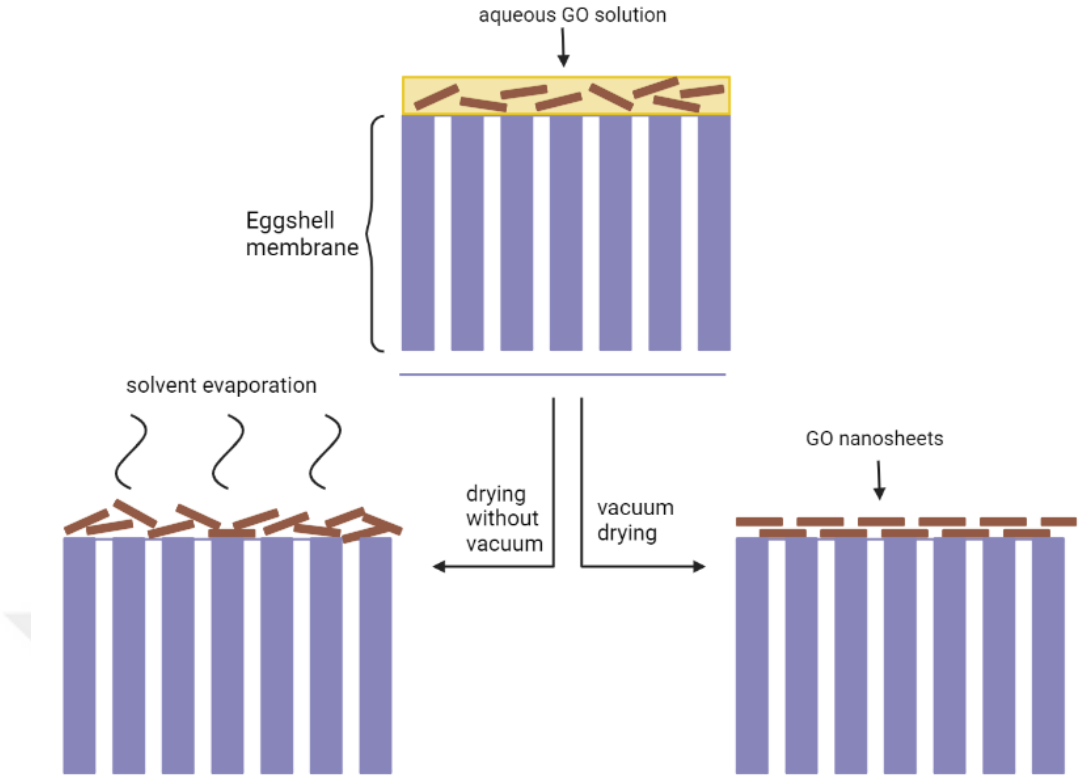


Figure 3.3 Vacuum and non-vacuum drying difference in drop casting method

3.3 Characterization Instruments

The morphology of the Graphene Oxide used was evaluated by SEM, and the GO/ESM camposite membranes produced were characterized by Filtration Test, SEM, UV-VIS, FTIR, Contact Angle measurement device.

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is a chemical analytical method that converts the vibrations of the infrared ray in molecules into a frequency spectrum that can be analyzed mathematically and enables material analysis at the molecular level by using these characteristic frequency values. In infrared spectroscopy, IR radiation is passed over the sample. While some of the emitted radiation passes directly through the sample, some of it is absorbed by the sample. The spectrum obtained here shows the transmission values. A specific spectrum is obtained for each sample and this spectrum forms a kind of fingerprint of the sample. In this study, Fourier Transform Infrared Spectroscopy (FTIR) method was used to examine functional groups in pure ESM and graphene oxide deposited ESM samples. FTIR measurements were made in in Ataturk University Eastern Anatolia High

Technology Application and Research Center (DAYTAM) Bruker VERTEX 70v model FTIR device with an absorption frequency between 400 and 4000 cm^{-1}.

3.3.2 Scanning Electron Microscopy (SEM)

In SEM, high voltage accelerated electrons interact with the sample and generate photon and electron signals scattered at different angles. The scattered electrons are collected in the detectors, after passing through the signal amplifiers, these signals from the sensors are converted into digital signals by processing with software. As a result, images are obtained. Backscattered electrons provide information about atomic number and atomic composition, while secondary electrons provide information about material topography. In this study, SEM measurements were made in Ataturk University Eastern Anatolia High Technology Application and Research Center (DAYTAM) Zeiss Sigma 300 model device to examine the surface morphology of membranes. Samples were gold plated before SEM measurement.

3.3.3 Contact Angle Measurement

Contact angle refers to the ability of a liquid to wet a solid material surface. The Contact Angle Measurement Device is an optical tensiometer device where the free surface energy, contact angle of the sample and surface/interface tension values can be determined with precise and easy methods. It gives information about the material surface depending on the shape of the drop formed by the liquid on the solid surface. In this study, hydrophilicity and hydrophobicity properties showing the wettability of membranes were measured in Ataturk University Eastern Anatolia High Technology Application and Research Center (DAYTAM) Attension Theta Flex model device.

3.3.4 Filtration

Filtration test was performed using the U-tube assembly. In this test setup, it is aimed to prevent the passage of unwanted dyes by using a semi-permeable membrane. The pre-prepared membranes were sandwiched between two 2 cm diameter adhesive aluminum sheets with a 1 cm diameter gap in the middle and placed between the O-rings. The membrane is tightly fixed to each other by a spherical sheaf clamp in the chamber between the two cylinders. Thus, leakage

from the U-tube assembly to the outside or from one channel to the other during the osmosis test is prevented. After the membrane is placed in the apparatus, one side of the cylinder is filled with cresol red dye with a concentration of 0.05 M and the other side with pure water. The cylinders are filled by tilting in all directions, thus preventing the formation of air bubbles around the membrane. The cylinders were filled with of 15 mL of solutions. After each experiment, the assembly was dismantled by draining all the liquid in the cylinders. The cylinders were separated and the membrane was removed. O-rings and cylinders were sonicated in soapy water and then rinsed with water and used after drying on a heater. The apparatus was kept in a magnetic stirrer during the filtration test so that the dye would not settle. In Yildiz Technical University Bioengineering Laboratory was used to examine the dye rejection performance of membranes.

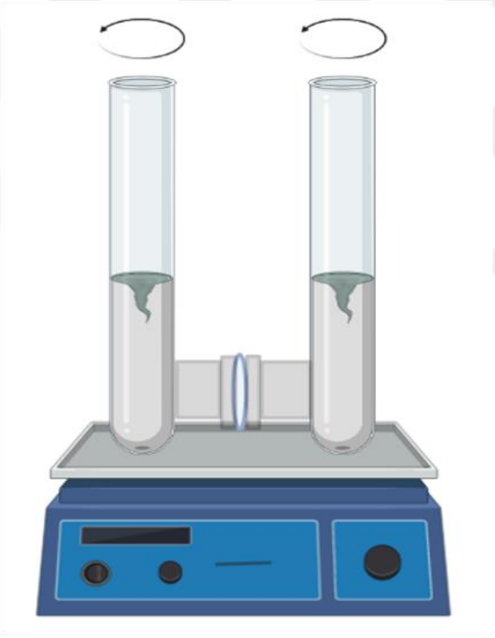


Figure 3.4 U-tube assembly used in filtration tests

3.3.5 UV-VIS Spectrophotometer

Ultraviolet and visible light (UV-Vis) absorption spectroscopy is based on the principle that the light intensity decreases after the beam emitted from a light source passes through a sample and reflects from its surface. The decrease in light intensity indicates the substance absorbed. Absorption is mostly caused by the excitation of bonding electrons in molecules. In this study, UV-VIS Spectrophotometer obtained from Yildiz Technical University Metallurgical

Materials Engineering Department was used to examine the absorption performance of membranes.

4
RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared Spectroscopy (FTIR)

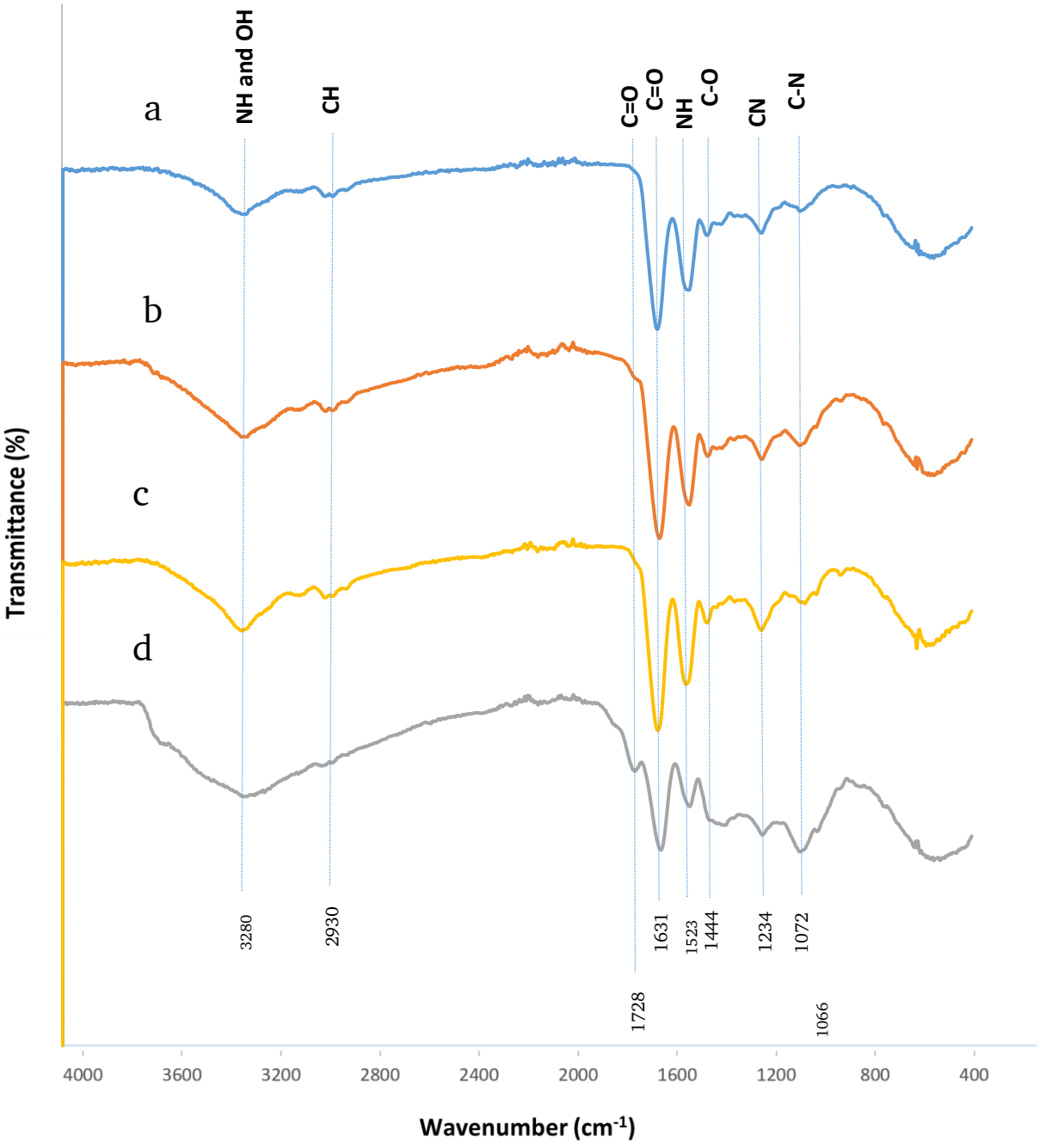


Figure 4.1 FTIR spectra for (a) ESM, (b) ESM/GO1, (c) ESM/GO2 and (d) ESM/GO3

FTIR analysis of bare and nanocomposite membranes produced in order to examine the functional groups in their structures and the vibration frequencies of various bonds was performed. The analysis results of the membranes are given in Figure 4.1. FTIR was studied in the range of 400–4000 cm^{-1} to investigate the surface properties of the ESM. As seen in Figure 4.1 peaks were observed at 3280, 2930, 1631, 1523, 1444, 1234, 1072 cm^{-1} positions for bare ESM. Characteristic peaks were observed in two different regions. The first region is between 3750 and 2800 cm^{-1}, and the second region is below 1700 cm^{-1}. The results of Fourier transform infrared (FTIR) spectroscopy analysis showed that the bare Eggshell Membrane exhibited absorption bands at 3371 cm^{-1} attributed to the stretching mode of the NH and OH groups, in agreement with the literature. The peak at 1631 cm^{-1} is attributed to the amide C=O stretching vibration. The peak amide NH bending at 1523 cm^{-1} corresponds to the peak C–O stretching at 1444 cm^{-1}, the peak amine CN stretching at 1234 cm^{-1}, and the peak amine C–N stretching vibration at 1072 cm^{-1}. In the spectrum shown in Figure 4.1, it is seen that the peak intensity at 3280 cm^{-1} increases with the increase in Graphene Oxide concentration. Also, with the addition of GO, it was observed that it gave a peak at 1728 cm^{-1}, which was not observed in bare eggshell. These are the characteristic peaks of GO. This shows that GO is well distributed. The band at 1728^{-1} cm represents the C=O vibration. Also, the broad band between 3000 and 3700 cm^{-1} corresponds to the presence of the O–H functional group on the graphene oxide surface. The first flat peak indicates the OH group of graphene oxide. It provides the material with hydrophilicity. Before the GO addition, this peak was steeper, but with the increase of the GO addition, it became broader, indicating that the material is more hydrophilic. There was a decrease in severity related to the functional groups' connections to GO.

4.2 Scanning Electron Microscopy (SEM)

The images obtained from the SEM analysis results of bare ESM and GO/ESM nanocomposite are shown in Figures 4.2. SEM analysis of the surface GO functionalized ESM was also performed to observe the effect of GO on the ESM surface.

The eggshell membrane (ESM) is a fibrous structure containing collagen in its structure between the egg and the eggshell, and the spaces between the fibers are highly porous [70]. The fibers in the eggshell membrane are in layers parallel to the eggshell. This fibrous structure can differ in size, direction, and fiber location [71]. Additionally, the SEM images revealed that the calcium carbonate crystals found in the eggshell structure were also found in the bare eggshell membrane [46].

Addition of GO positively affected the membrane morphology. GO nanoparticles made the porous structure of the bare ESM more compact and reduced the pore size. Thus, a composite with a morphological structure that can easily remove unwanted particles from the membrane surface was produced. Compared to the bare ESM, with the increase of GO content, the membrane became more hydrophilic and the morphological structure of the membrane tended to be flatter.

The rough structure of the bare ESM consisting of protein fibers allows a high rate of particles passage in the membrane. This may cause a disadvantage for the selective permeability of the membrane. However, with the addition of GO at low rates, the rough surface became a smoother surface and closed the gap-shaped defects.

As can be seen in the contact angle measurements, the contact angle value decreased from 92° to 35° with the inclusion of graphene oxide in the ESM structure. This may be evidence of the membrane surface becoming a flatter and hydrophilic structure.

Since the addition of higher concentrations of GO may form GO agglomerates in the membrane structure and wrinkles in the membrane layer, a high amount of GO was not added to avoid this defective structure.

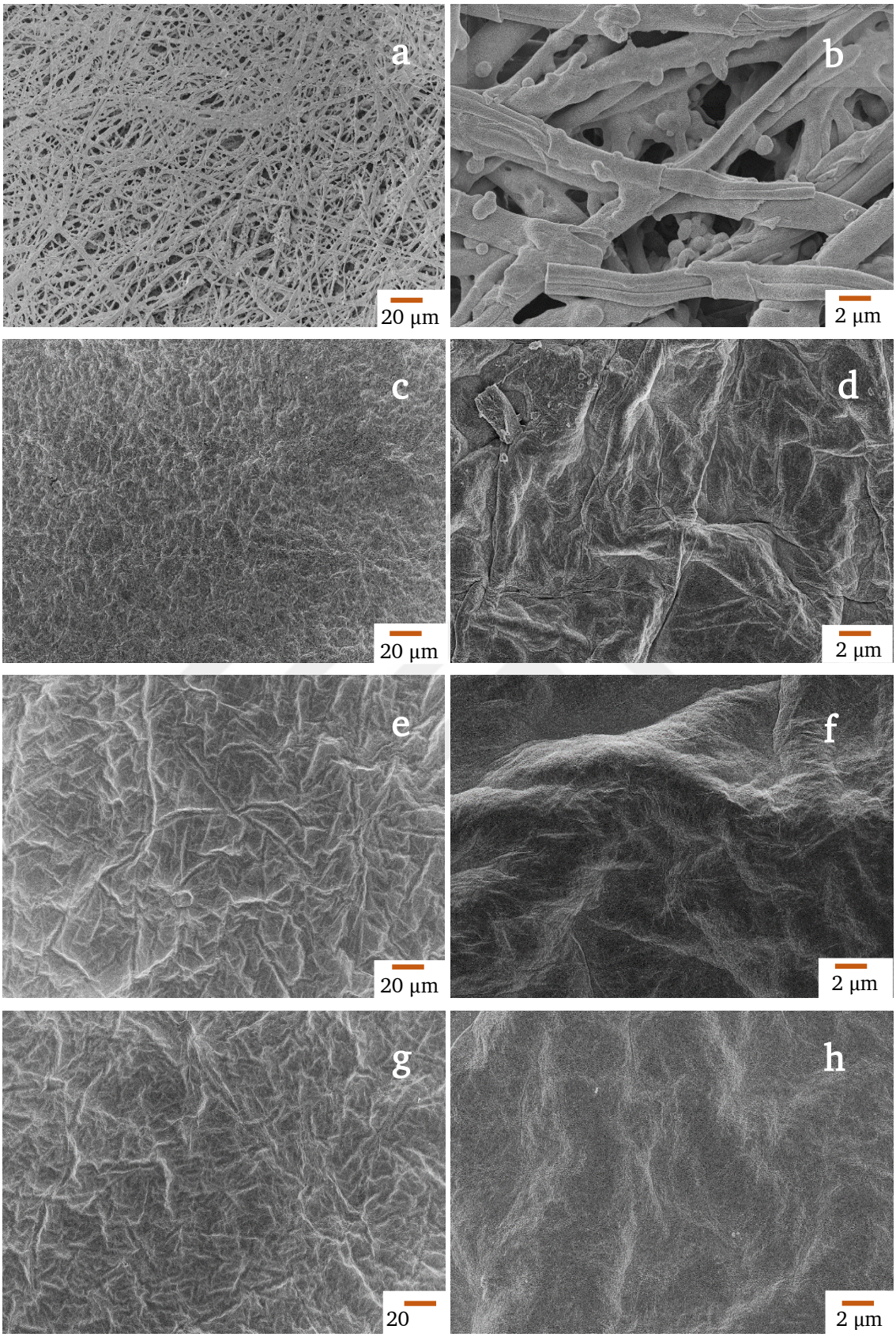


Figure 4.2 SEM images of the bare ESM and ESM/GO composite (a,b) ESM (c,d) ESM/GO1 (e,f) ESM/GO2 (g,h) ESM/GO3. The SEM images were taken at 250x, 3.00kx magnifications

4.3 Contact Angle Measurement

The contact angles of the produced bare and nanocomposite membranes were measured to examine the hydrophilicity and hydrophobicity properties. The measured contact angle values are given in the Figure 4.3.

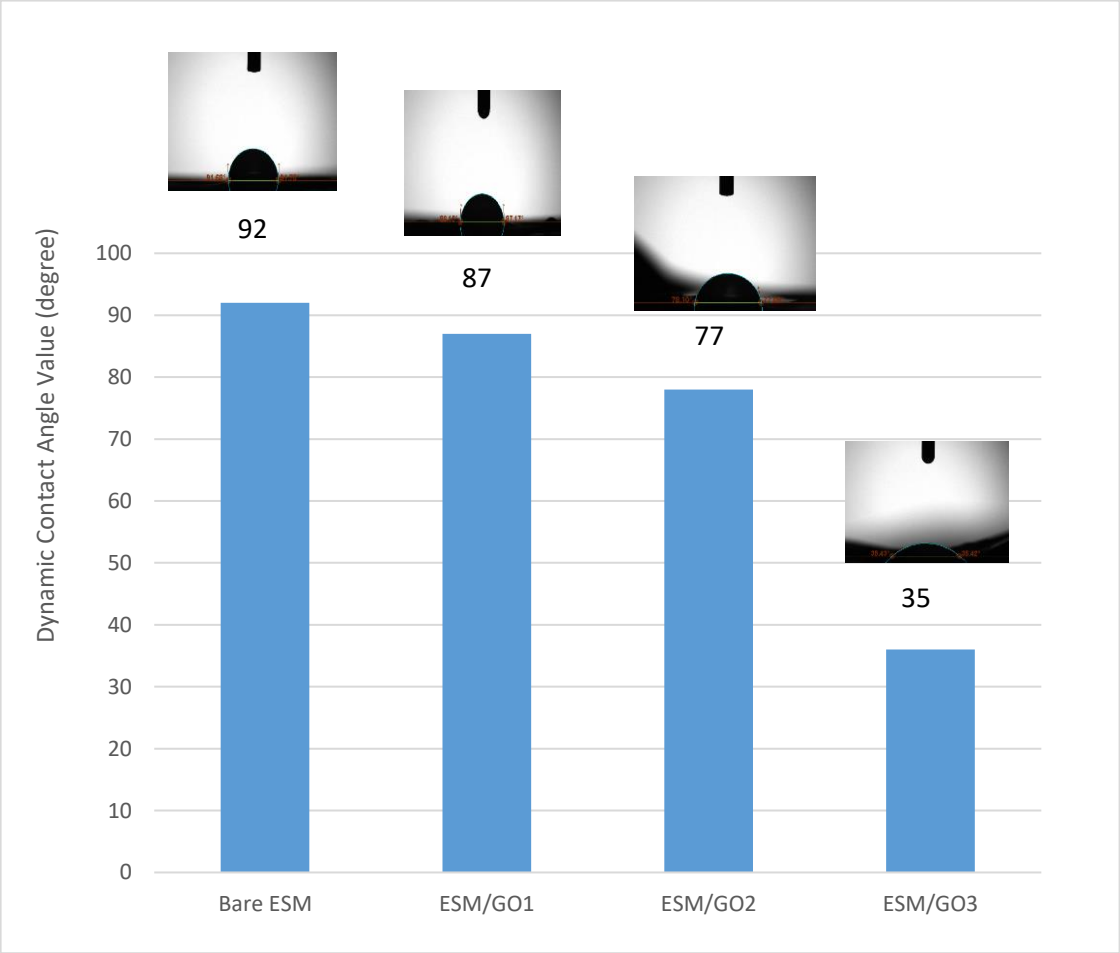


Figure 4.3 Dynamic contact angle values of pure ESM and ESM functionalized with GO nanoparticles

The contact angle of ESM/GO composites is less than 90°. ESM containing GO nanoparticles in different proportions have water contact angles of 87°, 77° and 35°, respectively. It can be said that as the nanoparticle ratio on the membrane surface increases, the contact angle of the water decreases and therefore the hydrophilicity of the ESM increases. On the other hand, the contact angle measurement of the bare ESM is 92°. This means that ESM is inherently hydrophobic.

The smaller the contact angle value, the greater the membrane hydrophilicity. There was a significant reduction in contact angle with the addition of GO to the structure of the ESM. That is, the addition of nanoparticles (GO) caused the membrane surface to become more hydrophilic. Graphene oxide nanoparticles dispersed on the surface of the ESM contain a high proportion of -OH groups. This may be responsible for the increase in hydrophilicity. Thus, it can be concluded that by incorporating graphene oxide into the ESM structure, the surface changes from hydrophilic from hydrophobic.

4.4 Filtration

Dye permeability was investigated to examine the effect of GO nanoparticles on ESM by U-tube filtration test. In this study, 50 ppm red food coloring was used. As a preliminary study, the dye rejection performance of a polycarbonate membrane with a pore size of 220 nm, which is frequently used commercially, was investigated. The tests were initially carried out using a single-layer membrane. However, it has been observed that even the smallest defects in the membrane can affect the test results and cause errors. For this reason, all filtration tests for bare PC, bare ESM, PC/GO and ESM/GO nanocomposite membranes were prepared by compressing 3 same membranes in succession between 2 adhesive aluminum. Thus, it was thought that the defects on the membrane surface would minimize the error in the test results. Then, the same filtration test was performed for the polycarbonate membrane coated with 4 layers of GO by drop casting method. The dye rejection performance of the PC/GO nanocomposite membrane was different from that of the bare PC membrane. It was observed that the addition of GO nanoparticles improved the dye rejection performance of the membrane and allowed less dye migration.

In the next filtration test, the dye rejection performances between ESM/GO nanocomposite and PC/GO nanocomposite produced by adding GO to the eggshell membrane instead of the polycarbonate membrane under the same conditions were compared. As can be seen in Figure 4.5 and Figure 4.6, ESM/GO has proven to show better dye rejection compared to PC/GO. This result can be attributed to the high adsorption ability of the eggshell membrane and the good surface

interaction resulting from the functional groups on its surface. It has also been proven that ESM can outperform commercially used membranes.

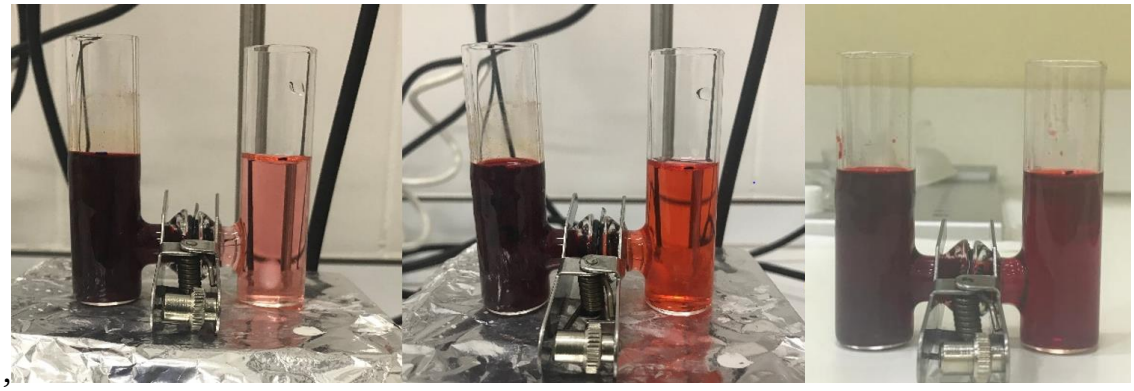


Figure 4.4 (a) Bare PC membrane after 10 minutes (b) after 1 hour (c) after 24 hours

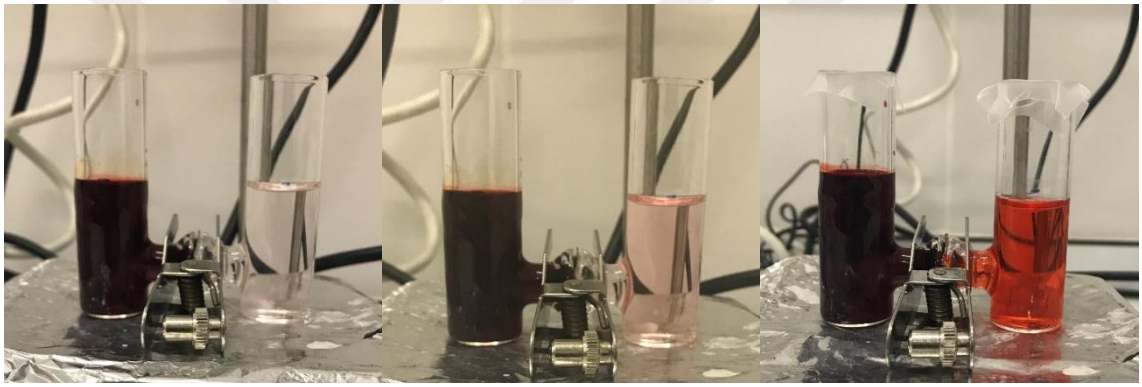


Figure 4.5 (a) PC/GO membrane after 1,5 hours (b) after 3 hours (c) after 24 hours

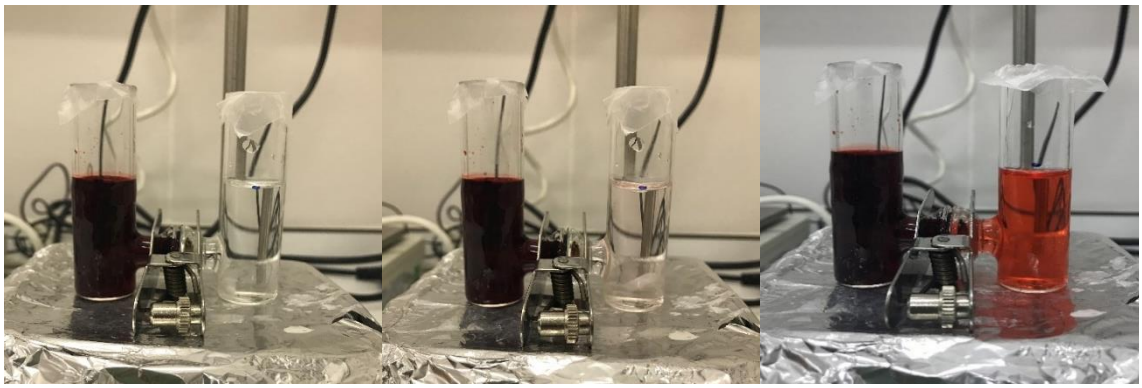


Figure 4.6 (a) ESM/GO membrane after 1,5 hours (b) after 3 hours (c) after 24 hours

A similar study was then performed with a different dye, the negatively charged cresol red dye. 0.05 M cresol red dye solution was used in the tests. Again, for the reason explained above, filtration tests were prepared by compressing 3 same membranes in succession between 2 adhesive aluminum. In these tests, the effect of adding GO at different rates to the eggshell membrane structure on the dye rejection performance of the membrane was investigated. Figure 4.7 shows samples of the ESM/GO1 membrane produced by adding bare ESM and a single layer of GO, taken from the U-tube assembly at certain time intervals. Considering the dye permeability of the ESM/GO1 membrane at the end of 24 hours; Even a single layer of GO coated eggshell membrane appears to have high dye rejection performance. In the coatings prepared with 2 layers and 4 layers GO, there was no color change in the samples taken even after 24 hours and a high impermeability of 99.9% was encountered. The dye rejection performance increased with the increase of GO deposited on the membrane surface. This is evidence that with the increase of GO, the porosity on the membrane surface decreases and there is a more compact membrane surface.

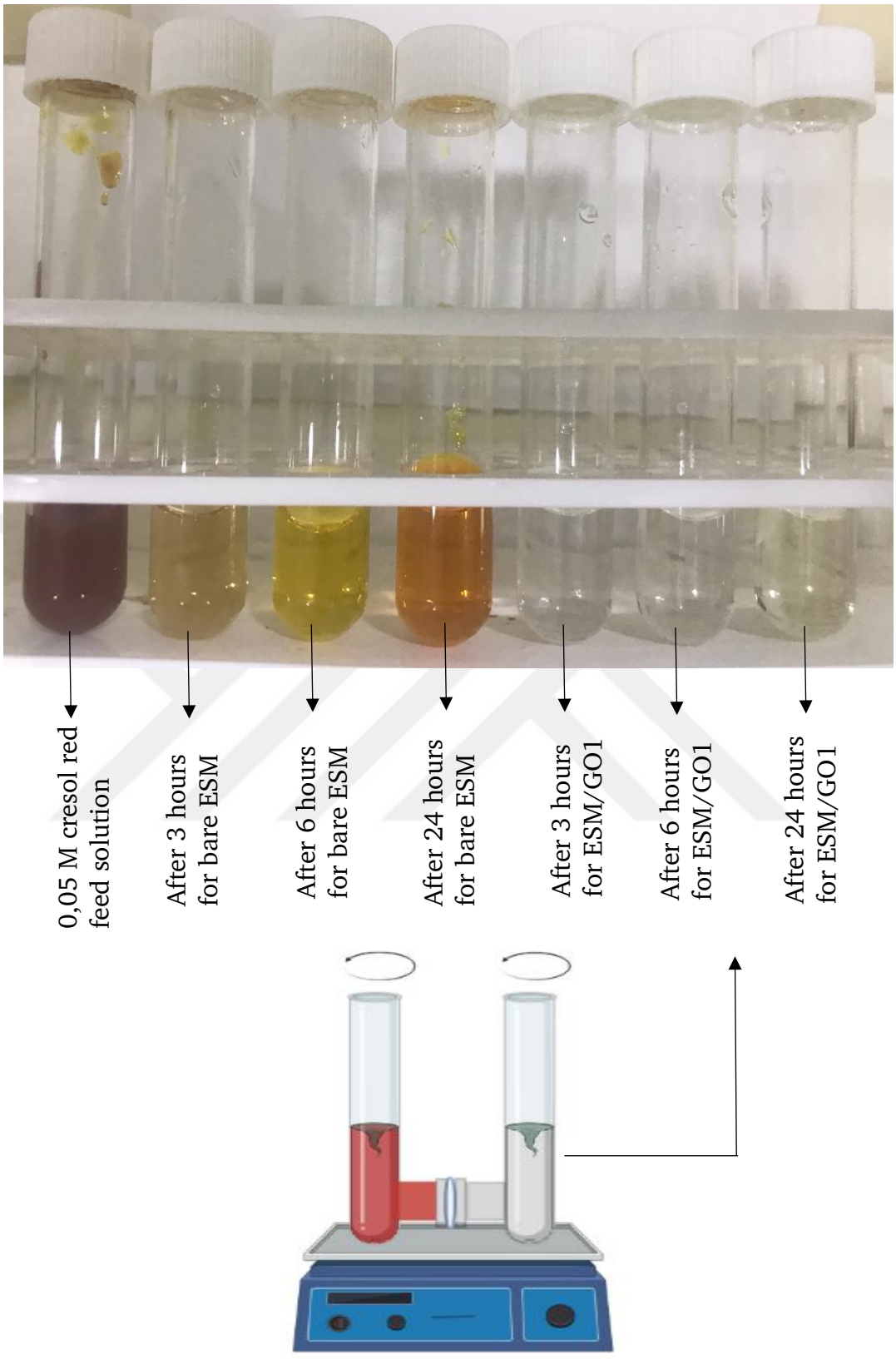


Figure 4.7 Samples taken from the u-tube assembly for cresol red

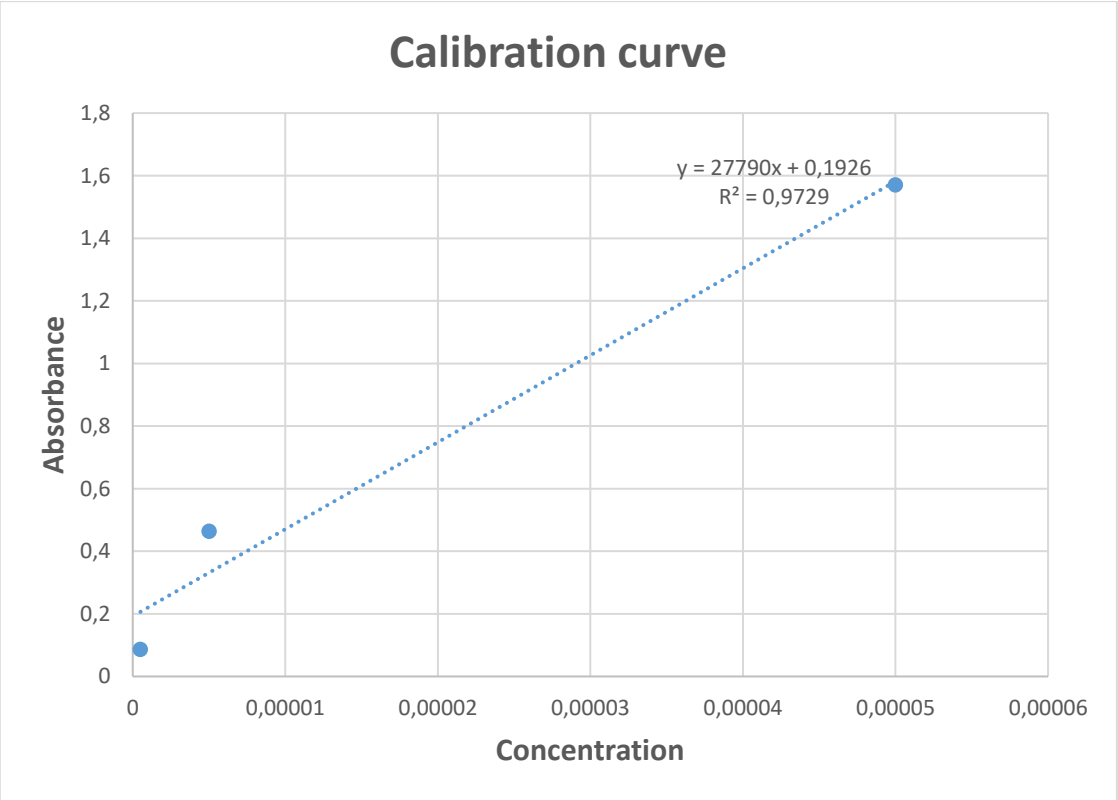


Figure 4.8 Calibration curve for cresol red dye

It was observed that the absorbance spectra for our samples at different concentrations in the UV device peaked at approximately 440 nm, similar to the literature. For this reason, cresol red standard solutions with different concentrations were prepared and measurements were taken at 440 nm, and as a result, a calibration curve was created. Then, the absorbance values of our samples at 440 nm were measured. With the created calibration curve; Concentration values were reached based on the absorbance values of our samples taken from the filtration test nozzle and whose concentrations are unknown.

Table 4.1 The absorbance and concentration values of the samples taken from the filtration test

Sample	After 3 hours for bare ESM	After 6 hours for bare ESM	After 24 hours for bare ESM	After 24 hours for ESM/GO1
Absorbance	0,563	2,435	2,538	0,198
Concentration	0,00001333	0,00008069	0,0000844	0,00000019

The schematic representation of the parameters that affect the dye rejection performance of the eggshell membrane functionalized with graphene oxide is in Figure 4.5.

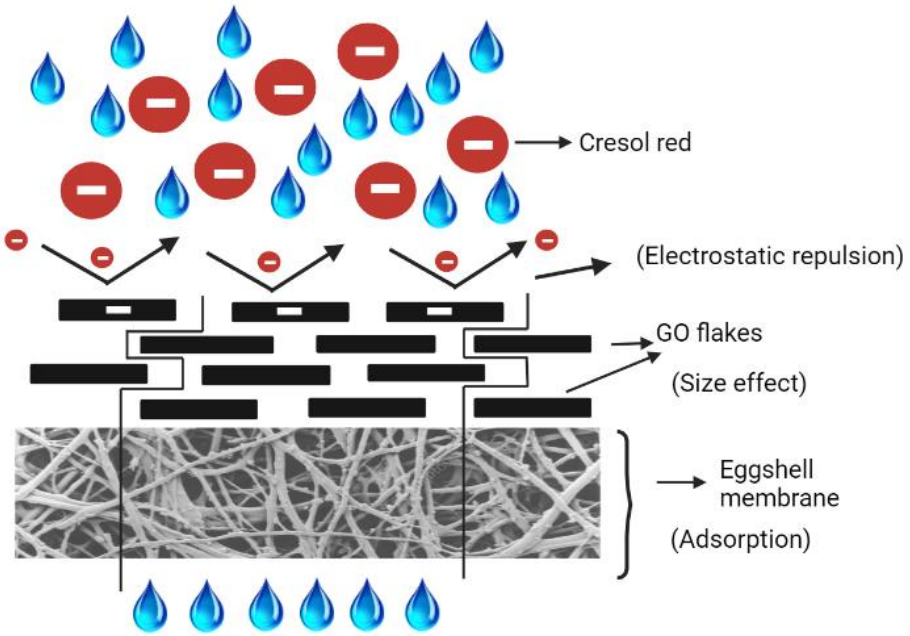


Figure 4.9 Membrane filtration mechanism of ESM/GO membrane

The image of the GO/ESM before it is used in the filtration tests and the bare ESM that has adsorbed dye on the surface after filtration is shown in Figure 4.6.

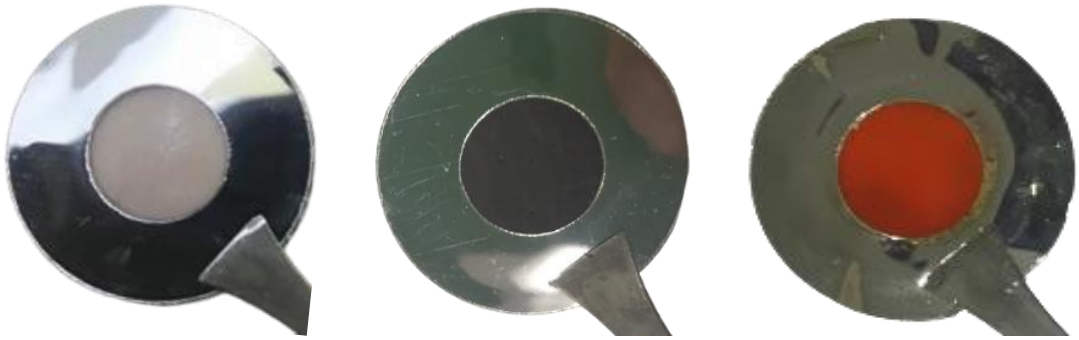


Figure 4.10 (a) Bare ESM before filtration test (b) GO/ESM before filtration test (c) Bare ESM after filtration test

4.5 Conclusion

This thesis was carried out to produce a waste eggshell membrane with high dye rejection performance using the drop casting method. The second aim of this study

is to investigate the effects of different graphene oxide nanoparticle ratios on eggshell membrane morphologies.

- GO nanoparticles were synthesized by the Hummer method, which is a simple and low-cost method.
- The eggshell membrane is easily separated from the eggshell by mechanical means without any chemical treatment.
- The synthesized GO nanoparticles were incorporated into the eggshell membrane to improve membrane hydrophilicity, morphological structure, and dye rejection performance.
- It was concluded that the dye rejection performance of the Bare ESM was lower, while the dye rejection performance of the ESM/GO nanocomposite membrane was higher. In addition, the dye rejection performance improved with the increase of graphene oxide ratio in the membrane, which means that the main aim of the thesis was achieved.

Other important findings from this study are given below.

- ESMs prepared with the addition of GO at different rates have different contact angle values.
- Bare ESM's surface has a contact angle value of 92°, while ESM/GO membranes have a contact angle of 87°, 77° and 35°, respectively. These results show that the membrane becomes more hydrophilic as the graphene oxide nanoparticle ratio increases.
- SEM images also revealed that the produced membranes have a flatter surface with the increase of the graphene oxide ratio, which also explains the decrease in the contact angle with the addition of graphene oxide.
- Dye rejection performance of the produced membranes; It is due to the combination of both chemical and physical remediation.
- Graphene Oxide particles with negative charge; While reducing the pore size of the membrane, it also has a repulsive force between it and the anionic cresol red

dye. This is another reason explaining the improvement in membrane performance.

The produced biocomposite membrane has shown that it has the potential to replace synthetic polymer membranes by increasing its efficiency through functionalization of the surface of the waste eggshell membrane.

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PUBLICATIONS FROM THE THESIS

Conference Papers

1. M. Muslu, M.E. Oruc, C.B. Ustundag, and H. Sadikoglu “Polycarbonate / Graphene Oxide Composite Membrane Production”, presented at the 20th International International Metallurgy & Materials Congress, Istanbul, June 2021.