ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

DESIGN, CHARACTERIZATION,AND PERFORMANCE TESTS OF NANOFIBROUS FILTER FOR REMOVAL OF VOLATILE ORGANIC COMPOUNDS (VOCs) BY PHOTOCATALYTIC OXIDATION (PCO) FOR AIRCRAFT CABIN AIR FILTRATION APPLICATIONS

M.Sc. THESIS

Arda Küçüksarı

Department of Aeronautical & Astronautical Engineering

Aeronautical & Astronautical Engineering Programme

Thesis Advisor: Assist. Prof. Dr. Hülya Cebeci

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

UÇAK KABİNİ İÇERİSİNDEKİ UÇUCU ORGANİK BİLEŞİKLERİN FOTOKATALİTİK OKSİDASYON YÖNTEMİ İLE GİDERİLMESİ AMACIYLA NANO FİBROZ YAPILI FİLTRELERİN ÜRETİMİ, KARAKTERİZASYONU VE FİLTRELERİN PERFORMANS TESTLERİ

YÜKSEK LİSANS TEZİ

Arda Küçüksarı
(511111105)

Uçak ve Uzay Mühendisliği Anabilim Dalı

Uçak ve Uzay Mühendisliği Programı

Tez Danışmanı: Yard. Doç. Dr. Hülya Cebeci
Tez Eş Danışmanı: Yard. Doç. Dr. Ali Kılıç

ŞUBAT 2015

Arda Küçüksarı, a **M.Sc.** student of ITU **Graduate School of Science, Technology and Engineering** student ID **511111105** successfully defended the **thesis** entitled "**DESIGN, CHARACTERIZATION AND PERFORMANCE TESTS OF NANO FIBROUS FILTER FOR REMOVAL OF VOLATILE ORGANIC COMPOUNDS (VOCs) BY PHOTOCATALYTIC OXIDATION (PCO) FOR AIRCRAFT CABIN AIR FILTRATION APPLICATIONS**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Assist. Prof. Dr. Hülya CEBECİ** İstanbul Technical University	.....
Co-advisor :	**Assist. Prof. Dr. Ali KILIÇ** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. İbrahim ÖZKOL** İstanbul Technical University	.....
	Assoc. Prof. Dr. İdris ÇERKEZ Bursa Technical University	.....
	Assist. Prof. Dr. Hüseyin AVCI Eskişehir Osmangazi University	.....

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Date of Defense : 10 February 2015

To my family,

FOREWORD

This thesis is the final section of my three years graduate degree in Aeronautical Engineering at Istanbul Technical University. This project is supported by Boeing Co. Global Technologies Division. The project was aimed to develop an advanced air filtration system to improve the air quality for cabin crew and passengers.
Firstly, I would like to show my special appreciation and gratitude to my supervisors, Assist. Prof. Dr. Hülya Cebeci and Assist. Prof. Dr. Ali Kılıç, for contributing valuable and inspring advices, and feedback on my works during the project term. I also thank to Assist. Prof. Dr. Hüseyin Avcı for his supports for developing of the filters during the studies. Moreover, I would like to thank TEMAG Laboratory, for giving me an opportunity to perform production and characterization of the filters in there, with the support of TEMAG Laboratory colleagues. Furthermore, I would like to thank Emine Canbay for helping me produce the filters and extra helps. I would like to thank Onur Ağma for his supports and helps in designing and drawing steps of the photocatalytic UV-LED reactor. Lastly, I would like to appreciate my special thanks to room 307 colleagues for always motivating and supporting me during my gradute studies.
While I am closing one chapter of my life and opening up a new one, I would like to thank my family for their support.

December 2014

Arda Küçüksarı
Metallurgical and Materials Engineer

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ABBREVIATIONS

APU : Auxiliary Power Unit
CAQ : Cabin Air Quality
CDC : Centers for Disease Control and Prevention
CO : Carbonmonoxide
CO_2 : Carbondioxide
DMF : Dimethylformamide
DMSO : Dimethylsulfoxide
ECS : Environmental Control System
EPA : Environmental Protection Agency
H_2O : Water
HEPA : High-Efficiency Particulate Air
IAQ : Indoor Air Quality
LED : Light Emitting Diode
MB : Methyleneblue
MFC : Mass Flow Controller
MM : Milimeter
MS : Mass Spectrometer
NF : Nanofiber
NIOSH : The National Institute for Occupational Safety and Health
NM : Nanometer
NP : Nanoparticle
PAN : Polyacrylonitrile
PCO : Photocatalytic Oxidation
PID : Photoionization Detector
PPB : Parts per Billion
PPM : Parts per Million
PP : Polypropylene
PPN : Peroxyacetyl Nitrate
PVA : Polyvinylalcohol
PVDF : Polyvinylidenefluoride
RHB : Rhodamine B
RPM : Revolution per Minute
SBS : Sick Building Syndrome
SVOCs : Semi Volatile Organic Compounds
TiO_2 : Titaniumdioxide
TPU : Thermoplastic Polyurethane
UV : Ultraviolet
VOCs : Volatile Organic Compounds
VVOCs : Very Volatile Organic Compounds
WHO : World Health Organization

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DESIGN,CHARACTERIZATION,AND PERFORMANCE TESTS OF NANO FIBROUS FILTERS FOR REMOVAL OF VOLATILE ORGANIC COMPOUNDS (VOC) BY PHOTOCATALYTIC OXIDATION (PCO) FOR AIRCRAFT CABIN FILTRATION APPLICATIONS

SUMMARY

Indoor air quality (IAQ) recently is an essential subject for people because of the amount of personal time, which is spent in indoor environment such as houses, offices, shopping malls and vehicles increases day by day. Therefore, IAQ affects human health, their efficiency and comfort.

Bacterias, viruses, dusts are some of the contaminants in the indoor environment. These pollutants usually include carbon oxides, nitrogen oxides and volatile organic compounds (VOCs), and other particulates. Volatile organic compounds are major effective chemical contaminants that people breathe in indoor environment.

For aircrafts, indoor air quality is called as Cabin Air Quality (CAQ) which is one of the most important parameters that affect passenger comfort in aircraft, especially on long duration and transatlantic flights. Because of the dynamic structure of aircrafts, cabin altitude, flight duration, temperature, pressure, cabin humidity and dehydration changes according to environmental conditions which affects the CAQ. Dusts, bacterias and viruses can be removed until a limited size from aircraft cabins by High Efficiency Particulate Filters (HEPAs) but gas filtration is a big challenge comparing to particulate filtration. VOCs are generally in gas phase because of their chemical properties.

VOCs are familiar indoor contaminants, which are emitted from different sources such as in-flight meal and drink services, combustion by-products, consumer products, construction materials of people in the cabin etc. The accumulation of excessive amounts of VOCs causes health problems for passengers such as headache, fatigue, tiredness, nausea, and illness. For this reason, the filtration of these VOCs in cabin is needed. There are several traditional pollution removal method in aircraft cabins. However, these contaminants are converted from the gaseous phase to the solid phase by these removal methods. This requires manually frequent cleaning or periodical exchange of the filter.

Photocatalytic oxidation (PCO) is a novel and promising method for the improvement of cabin air quality since the contaminants can be removed from the cabin and oxidize the contaminants to water vapor (H_2O) and carbon dioxide (CO_2) which are not harmful for human health by using a combination of semiconductor catalysts and light energy. Titanium Dioxide (TiO_2), which is the catalyst that is activated by UV light, is the most commonly used compound in PCO reactors.

Design, characterization, production and the efficiency tests of the filters against VOCs in photocatalytic oxidation process is the main topic of this study. Electrospinning method used for production of the filters with different polymeric materials. Titania was deposited onto the nanofibers(NFs) mat as catalyst by electrospraying which is a similar method of electrospinning. For activation of these filters UV light is required and for providing that UV-Lamps and UV LEDs (Light Emitting Diodes) were used as a novel technology. By varying the UV light intensity on the filters, efficiency analyzes were made. The reason of choosing UV LED instead of UV-Lamp is the advantages of LEDs.

In conclusion, cabin air quality is poor on newer model aircrafts because of the incorporation of recirculation systems and lower outside airflow. Therefore, CAQ is an important issue for aircraft manufacturers and airline companies in these days. High efficiency particulate air type filters (HEPA-types) are already included in recent aircrafts in order to remove particulates and biological particles from the recirculated air in the cabin. However, VOCs are still can not be removed from the cabin air by current filters. Consequently, PCO reactors must be developed and mounted in aircrafts for removing VOCs and increasing the CAQ in aircrafts.In this study, the photocatalytic capable NF based filters was designed, fabricated, tested and optimized to maintain a highly efficient cabin air filtration system using the PCO process.

UÇAK KABİNİ İÇERİSİNDEKİ UÇUCU ORGANİK BİLEŞİKLERİN FOTOKATALİTİK OKSİDASYON YÖNTEMİ İLE GİDERİLMESİ AMACIYLA NANO FİBROZ YAPILI FİLTRELERİN ÜRETİMİ, KARAKTERİZASYONU, GELİŞTİRİLMESİ VE FİLTRELERİN PERFORMANS TESTLERİ

ÖZET

Dünyamız artan endüstrileşme, yüksek nüfus artışı ve çarpık kentleşme gibi sebeplerden ötürü bir çok anlamda olumsuz durumla karşılaşmaktadır. Bu olumsuzluklardan en başta gelenlerinden birisi ise su kirliliği ve hava kirliliğini meydana getiren çevre kirliliğidir. Hava kalitesi sağlık açısından büyük öneme sahiptir, insanların çoğu zamanlarını geçirdiği ev, ofis, ulaşım araçları gibi kapalı ortamlarda dış ortamdakine göre daha düşük özelliklere sahiptir ve bu durum insan sağlığını, çalışma verimliliğini ve yaşam konforunu doğrudan etkilemektedir.

Dışarıdaki hava ortamından daha az sirküle olması ve daha durağan bir hava yapısına sahip olmasından ötürü, iç ortamlardaki hava kalitesinin dış ortam hava kalitesine göre daha düşük olmasına neden olan tozlar, virüsler, bakteriler, karbon oksitler, nitrojen oksitler ve organik uçucu bileşikler gibi birçok kirletici bulunmaktadır. Bu kirleticilerden kimisinin insan üzerinde ciddi bir etkisi olmaz iken bazılarının ölümcül etkileri dahi olabilmektedir. Kısmen daha az etkisi olduğunu söyleyebileceğimiz uçucu organik bileşikler ise insanların özellikle iç ortamlarda soludukları başlıca kimyasal organik kirleticilerdir. Özellikle hava yolu ile bulaşan bulaşıcı hastalıklar gibi hastalıkların önlenmesi amacıyla filtrasyon teknolojilerinde ciddi çalışmalar yapılmaktadır.

Kapalı bir ortam olan ulaşım araçları geçirilen zamanın azımsanmayacak derecede olduğu yerlerden biri olarak tanımlanabilir ve diğer taşıtlarda olduğu gibi uçak kabinlerinin hava kalitesi de doğrudan yolcu konforunu etkilemektedir. Uçak kabinindeki hava kalitesi; irtifa, basınç, uçuş süresi, dehidrasyon, nem ve yolcu sayısı gibi parametrelerden ve bunların yanında kabin içerisindeki çeşitli etmenlerden ötürü oluşan kirletici maddeler hava kalitesini etkileyebilmektedir. Özellikle uzun süreli uçuşlarda, kabin hava kalitesi yolcu ve kabin ekibini konfor ve sağlık açılarından kısa süreli uçuşlara göre daha fazla etkilemektedir.

Kirleticiler arasında en yoğun olarak rastlanan uçucu organik bileşikler (VOCler)'in yoğunluğu, uçak içerisindeki yemek ve alkol servisleri, yolcu eşyaları ve ürünleri, kabin içi yapı malzemeleri ile boya maddeleri ve dış hava gibi birçok biyolojik ya da yapay kaynaklar nedeniyle artar. Kabin içerisinde yüksek konsantrasyon VOClerin yüksek konsantrasyon seviyelerine ulaşması durumunda özellikle uzun yolculuklarda, yolcular ve kabin ekibinde halsizlik, baş ağrısı, yorgunluk ve bulantı gibi birçok sağlık problemleri görülmesi olasıdır. Bu olumsuz etkilerinden ötürü, VOClerin uçak kabini içerisinde uzaklaştırılması yolcuların ve kabin ekibinin konforu ve sağlığı açısından önemli bir noktaya gelmiştir.

Bu kapsamda bir çok akademik çalışma yapılmakta olup çalışmalar kapsamında geliştirilen filtreler VOCleri gaz fazından katı faza dönüştürerek sistem içerisinde hapsetme prosesine dayanan mekanizmalar geliştirilmiştir ve bu geliştirilen filtreler bazı yolcu uçaklarında kullanılmaktadır. Bu tipteki filtrelerin gazı depolama prensibine göre çalışmasından ötürü zaman zaman değiştirilmesi ve yenilenmeleri gerekmektedir ki bu durumda hava yollarının ve uçak üreticilerinin kaçınmak istedikleri bir durum olan ekstra iş gücü ve ek maliyetler getirmektedir.

VOCleri katalizör ve kullanılan katalizörün bant aralığına göre ultraviyole veya görünür ışık seviyesindeki, ışık yardımıyla zararsız olan karbon dioksit ve su buharına dönüştüren fotokatalitik oksidasyon yöntemi, kabin içerisindeki VOClerin temizlenmesi için en etkili ve ümit vaad eden yollardan biri olarak görülmektedir. UV ışık altında aktifleşen titanyum dioksit (TiO_2) hem zehirli olmaması, hem ekonomik olarak uygun olması hem de uygulamadaki kolaylık ve lojistik imkanlarının iyiliğinden ötürü fotokatalitik tepkimelerde kullanılan en verimli katalizörlerden birisidir.

Filtrasyon teknolojilerinde özellikle membranların üretiminde olduğu gibi fotokatalitik oksidasyon yönteminin kullanıldığı sistemlerde de ışık altında kalan alanı tanımlayan aktif yüzey alanı büyüklüğü verimliliği etkileyen çok önemli bir parametredir. Aktif yüzey alanını değiştirmenin en kolay ve en efektif yolu ise kullanılan fiber çaplarında değişiklik yapmaktır. Daha fazla verimlilik için daha yüksek yüzey alanının gerektiği düşünülecek olursa, fiber çapını küçültmenin en etkili yol olacağı söylenilebilir. Günümüzde ince fiber çaplarının talep edildiği durumlarda akla ilk gelen fiber yapısı nano ebattaki çaplara sahip olan nanofiberlerdir. Bu tip fiberlerin üretiminde çeşitli metodlar olup en genel olarak kullanılan yöntem kolaylığı ve ekonomikliğinden ötürü electrospinning yöntemidir. Electrospinning yöntemi ile nano boyutta fiberler üretmek mümkün olmakta ve istenilen yüksek yüzey alanı bu yöntem ile sağlanılabilmektedir. Üretilen bu filtrelere hava geçirgenlik, taramalı elektron mikroskobu (SEM) vb. gibi karakterizasyon testleri uygulanılarak, filtrenin morfolojik ve fiziksel yapısı hakkında bilgi sahibi olunulmuştur.

VOClerin fotokatalitik olarak ortamdan uzaklaştırılması için nano lif yapılı filtrelerin üretimi, filtrelerin karakterizasyonları, filtrelerin verimlilik testleri, reaktörün tasarımı ve geliştirilmesi bu çalışmanın ana konusunu oluşturmaktadır. Geleneksel floresan UV lambaların daha yüksek enerji seviyelerine rağmen, UV dalga boyuna sahip ışık yayan diyotlar (LED) yenilikçi, sağlıklı ve yüksek verimli ışık kaynağı olmalarından ötürü bu çalışmalar kapsamında ilk çalışmalarda geleneksel floresan UV lamba kullanılırken çalışmaların ilerleyen kısımlarında ki bu büyük bir bölümünü kapsıyor UV-LED teknolojisi tercih edilmiştir.

Electrospinning yöntemi ile yüksek voltaj uygulaması sonucunda üretilen nanofiberler (NF) filtrenin ana iskeletini oluşturmuşlardır. Filtrenin asıl işlevini kazanmasını sağlayan katalizörler yüksek yüzey alanı elde edebilmek amacıyla nano partikül olarak seçilmiş ve 2 farklı yöntem ile NF yapı üzerine biriktirilmiştir. Birisinde fiberlerin katalizör ile beraber üretimi ile katalizör olan partiküllerin NF içerisine gömülmesi metoduyla çalışılırken diğerinde prensipte electrospinning yöntemine benzer olan electrospraying ile NFler üzerine püskürtülmüştür. Bu kapsamda farklı miktarlardaki katalizörlerin filtre verimliliğindeki etkisini gözlemleyebilmek amacıyla farklı oranlarda katalizörler NFler üzerinde biriktirilmiştir. Çalışmalarımız kapsaminda literatürde de çok yoğun bir şekilde kullanılan ticari TiO_2 olarak adlandırılan ve bizim de kullandığımız Degussa P25'e alternatif olarak daha yüksek verimliliğe sahip olması hedeflenilen sol-gel yöntemi ile üretilmiş olan TiO_2 katalizörlerin de nanofiber yapı üzerinde electrosprayleme yöntemi ile biriktirilmesi yapılmıştır. Demir, nitrojen, ve demir ile nitrojenin birleşiminden meydana gelen co-doped sol-gel TiO_2 filtrelerin bant boşluklarının düşürerek daha yüksek verimlilik elde edilmeye çalışılmıştır.

Bu üretilen filtreler iki farklı nesilden meydana gelen ve bizim tarafımızından dizayn edilen reaktörün içerisine yerleştirilerek, konsantrasyonu kontrol edilebilir düzeyde VOC içeren gazlar gönderilerek test edilmiştir. İlk nesil olan reaktör içerisinde geleneksel fluoresan UV lamba kullanılırken, 2. nesil reaktör için düşük ışık yoğunluğuna sahip olan UV-LEDler ve daha sonraki çalışmalarda daha yüksek özelliklere sahip olan ve bir önceki nesil LEDler ile gerçekleştirilen testlere göre daha yüksek verimlilikle sonuçlanması beklenen UV-LEDler tercih edilmiştir. UV lamba ve birinci nesil UV-LEDler ile yapılan çalışmalar VOC kaynaklarının gaz fazından sıkıştırılmış olarak bulunduğu tüplerden sağlanırken ikinci nesildeki VOC kaynaklarımız sıvı fazdaki VOCler olmuştur. Bu sıvı fazdaki VOCler gaz fazına döndürülerek sisteme verilmiştir. Yine birinci nesil test sonuçları aktif karbonlar üzerinden analiz yapılırken, ikinci nesil UV-LEDler ile yapılan çalışmalar kütle spektrometresi (MS) cihazı üzerinden yapılmıştır. Böylece aslında 2. nesil UV-LED sistemi hem kullanım açısından hem de verilerin güvenilirliği açısından önemli bir gelişme noktası olmuştur.

Sonuç olarak, VOClerin yolcu ve uçuş ekibi üzerindeki etkileri göz önüne alındığında kabin içerisindeki VOC miktarını azaltmak, uçak üreticilerinin ve havayolu şirketlerinin önemli ve güncel bir sorunu haline gelmiştir. Yüksek Verimli Partikül Hava (HEPA- type) filtreleri günümüzde birçok uçakta kullanılsa da, VOClerin kabin içerisinden temizlenmesi konusunda herhangi bi yeterlilikleri kesinlikle yoktur. Bu durumdan ötürü, fotokatalitik oksidasyon yöntemiyle donatılmış filtrasyon sisteminin tasarlanması ve kullanılması bir gereklilik haline gelmiştir. Bu projenin temel amacı, uçak içerisinde kullanılmak üzere, nano fiber temelli filtrelerin araştırılması ve geliştirilmesi, filtrelerin yerleştirileceği reaktörün geleneksel lamba ve LED teknolojisi kullanılarak geliştirilmesi, VOClerin nano üretilen filtreler kullanılarak ultraviyole ışık altında fotokatalitik reaksiyonlar gerçekleştirilerek uzaklaştırılması ve bu filtrelerin optimizasyonu.

1. INTRODUCTION

Air pollution, caused by industrialization, unplanned urbanization, high population increase and unconscious consumption, is one of the most important environmental problem that threatens future of the world with it's livings. It is also air quality in indoor environment decreases as well. Home, office, factories, vehicles are the places where people mostly spend their time. Since air quality directly affects human health and comfort level, filtration studies have been accelerated for last few decades. Aircraft cabins are one of the most risky area amongst the indoor environments where indoor air change is not be performed directly. Cabin air quality is a big challenge because of the limitations and restrictions which are specified by international aviation organizations to protect human health against over dossages of contaminants. So, lots of studies focused on improvement of cabin air quality.

1.1 Motivation of Thesis

This thesis aims to develop a novel approach for cabin air filtration in aircrafts. Besides particulate filtering through HEPA filters, enhancing the cabin air quality through VOC removal is crucial for human and cabin crew. For this purpose, high surface area nanofiber filters are manufactured by electrospinning. The most common and effective semiconductor, TiO_2 is chosen as the catalyst material and deposited onto nanofiber through several methods for performance efficiency. A new light source as UV-LED is studied for the understanding of efficiency in VOC removal at laboratory scale VOCs such as ethanol, toluene and benze are chosen as target compounds for the filtration system.

1.2 Literature Review

According to World Health Organization (WHO) data, 2.4 million people die every year because of the air pollution. This topic is widely studied by private companies and the universities because of the importance and the economic capacity of filtration.

Since increased amount of personal spent time (around 80% of their time) in indoor environment, filtration studies are generally focused on indoor filtration applications. At the same time some studies showed that, indoor environment is much polluted than outdoor environment. VOCs are well known air pollutants emitted from cooking, construction materials, office equipment and consumer products.

Traditional pollution control method such as activated carbon transfers the gas phase of the contaminant to solid phase [1], however photocatalytic oxidation method is a promising method because of the pollutants can be oxidized to water vapor and carbondioxide. Since the promising advantages of PCO, this topic has been widely studied for the last few decades.

In the literature, PCO studies are made with traditional fluorescent UV lamps with 254 or 365 nm wavelength. Generally PCO studies were made by using 365 nm wavelength light source [2-5]. Because of the higher energy emitting of UV-C sources, there are also some studies made with 254 nm light sources. The reason of two different wavelength is analyzing the effect of wavelength energy on the PCO efficiency [6, 7]. Increasing importance of clean water sources and easier application, many researchers have been studying on water treatments by PCO [8]. Methylene Blue (MB) and Rhodamine B are the major contaminants of water treatment studies [9]. Although, PCO for air filtration is less studied topic by scientist, there are many studies made for VOC degdaration [10-12].

PCO studies demonstrated that, one of the most important parameter that influencing the filter performance against the contaminant is active surface area. Researchers consider this situation and studied with nano sized materials for improving the performance. Besides increasing the surface area through catalyst,increasing substrate surface area by nanotechnology is critical. NFs which can be produced by electrospinning as the most common and easiest method were thought to be an appropriate substrate. Because of the advantages of NFs, this fibers have been studied for tissue engineering, solar cells, batteries and for filtration technologies including water and air treatment.

Since LEDs were not able to provide enough light intensity for PCO applications, fluorescent UV lamps were a better choice for PCO. A novel study area has been opened for PCO systems after the development of high power LEDs which can

overcome the required light intensity values for activation of catalysts in the last decade. In recent studies, the UV-LEDs performance is studied for gas and water treatment [13-16]. These UV-LED researchs are especially focused on water purification [9, 17]. Some different studies were performed for investigation of the photocatalytic performances and comparasion of produced filters under illumination of UV fluorescent and LED lamps [6, 18-20].

Electrospun nanofibrous filters for PCO applications under illumination of various kinds of UV sources were examined in this thesis. The novelly of nanofiber filters and UV-LED application is also shown by literature survey.

2. AIR QUALITY AND VOLATILE ORGANIC COMPOUNDS(VOCs)

2.1 Description of indoor air quality

Indoor air quality (IAQ) is a term which refers to the quality of air within and around structures, buildings and habitats. It especially relates to the health and comfort of people who reside in these places. Therefore, indoor air quality has become a significant health and safety concern since people spend more than 70% of their time in indoor environments. These habitats are home, office, car, shopping centers, aircraft cabins, and so on. The level of contaminants in outdoor environment is absolutely less than the level of contaminants in indoor environment. Indoor air contaminants involve carbon oxides (CO and CO_2), nitrogen oxides (NO_x), volatile organic compounds and other particulates. VOCs are familiar indoor contaminants which are diffused from different sources such as cooking, combustion by-products, office equipment, and consumer products. Lastly, air quality in aircraft cabins and cars has also causer much concern because these vehicles are also typical indoor environments.

2.2 Cabin Air Quality

Compared with indoor air quality in various buildings, air quality in mobile cabin including train, bus, aircraft, and subway is also important [21]. Aircraft cabin environement differs in several ways from offices and homes, due to extremely high occupant density and the confinement of passengers to their seats for long periods of time [22]. The reported maximum VOC levels are comparable across the different transportation vehicles, with ethanol and acetone was encountered higher levels in aircraft cabin air [21].

2.2.1 Contaminants in cabin air

Jet engines, auxiliary power units (APUs) and air conditioning machines as well as from de-icing fluid, condensation, smog, fog and from the engine exhousts of aircraft,

including their own, whilst on the ground as well as other external environmental odours and contaminants. Contaminantion could also occur during the takeoff and landing stages of the flight. Except of these contaminants, occupants and materials in the cabin are the other reasons of contaminants. Besides of these, air ventilation systems can cause a build up of contaminants, spread of disease, a decrease in the quantity of oxygen and high carbon dioxide levels. Because of the cruising altitude of the aircraft, mixing ratio of ozone in the air which is around 500 - 800 ppb is much higher than most polluted cities in the world [23]. However, filtration of aircraft air decreases to less pollutant levels. The levels of contaminants in cabin air are shown in **Table 2.1**. CO (carbonmonoxide) gases are occurred because of the tobacco smokes which are the primary complain of cabin crew. Although tobacco smoke can be removed from the filtration system, CO gases can not be filtrated through these filters.

Table 2.1: Contaminants in cabin air [24].

Item	Average Measured (ppm)	ACGIH (ppm)	ASHRAE (ppm)
CO_2	600 – 1500	5000	1000
CO	0,6 – 1,4	25	-
Microbial Aerosols	Very low	-	-
Ozone	0.02	0.01	0.05
Particulates	40/175 RSP	10000 TSP	260 TSP
NO_2	Very low	3	
SO_2	Very low	2	
VOCs	1,8 – 3,2	1000	

Low contaminant levels in the cabin are due to the thight control outgassing of components used in the airplane furnishing and the effectiveness of the recirculation system to remove essentialy all microbials and particulates from the recirculated air.

2.2.2 Cabin air ventilation system

Commercial cabin air recirculation systems typically uses engine compressors to ensure circulation in the cabin. Most modern aircraft, an average of about 56% of the

outside air supplied to the cabin is vented out of the aircraft. For remaining air High Efficiency Particulate Filters (HEPA) are used for recirculating of cabin air [22].

Major recirculation generators of cabin air are engines. A modern turbofan engine has core and bypass sections. The core section is the power-generating part of the engine, whereas the bypass section is the main thrust-generating part, usually referred to as "fan". The core section is composed of three main sections. These are a burner section, in which fuel is added, compressor stages, and turbines stages where power is drawn out to drive the fan and the compressor. The core section catches only one fifth of the air drawn into the engine [24]. The flow chart of the air ventilation system, shown in **Figure 2.1**, illustrates the process of air ventilation in a commercial aircraft.

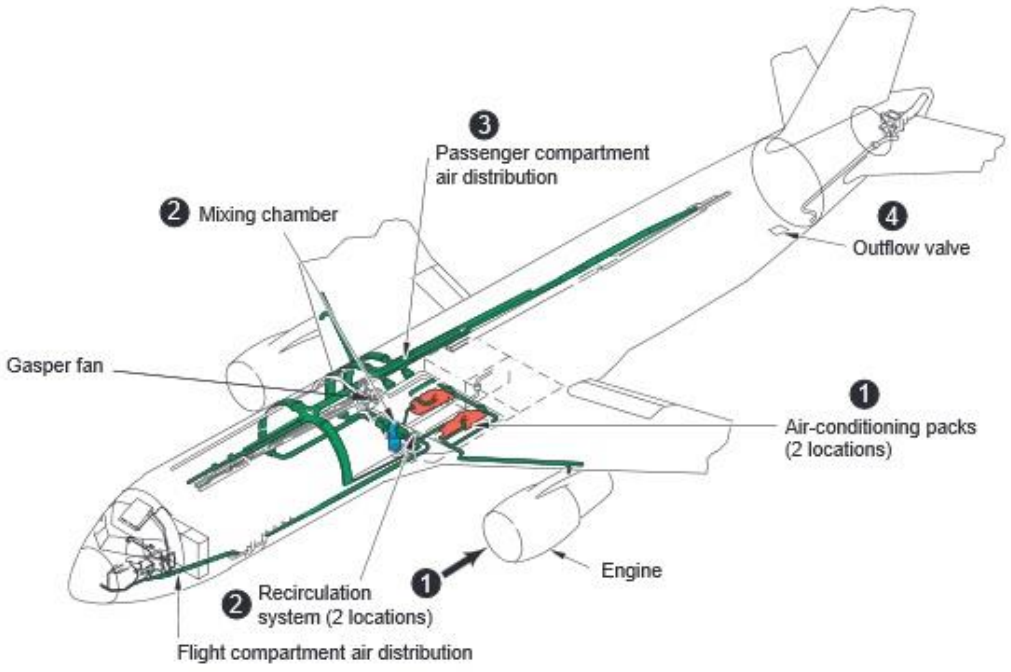


Figure 2.1: Schematic view of the cabin air ventilation system [24].

In the first step of the process, outside air continuously flows into engine, where it is compressed. Secondly, the compressed and hot air passes stops by an ozone converter before reaching the air conditioning units. Thirdly, outside air passes through cooling packs to a mixing manifold. Then, outside air, entering the mixing manifold is combined with recirculated air, which has been purged with high efficiency filters. This air consists of approximately 56 percent outside and 45 percent-filtered recirculated air. Air from the mixing chamber is then continuously delivered from overhead outlets directly into the cabin. Lastly, as outside air is delivered into the

airplane, an equal bulk of air from the cabin is evenly exhausted from the airplane cabin. Federal Aviation Administration (FAA) required 0.25 kg/min per person of outside airflow to cabins, corresponding to a volumetric flow rate of 3.5L/min per person at sea level [22]. Total cabin air is generally changed and filtered in every 3 to 5 minutes for typical aircrafts. This duration can vary according to aircraft model, size and ventilation properties. **Figure 2.2** demonstrates the air exchange rates of some different environments.

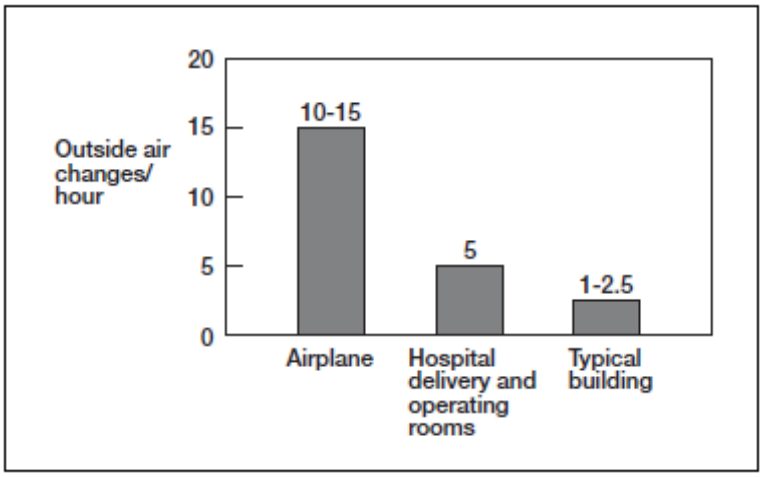


Figure 2.2: Air exchange rates in different environments [24]**.**

In conclusion, the designing of the cabin ventilation system provides air supply at one seat row and leaves at nearly the same seat row, minimizing airflow in the fore and aft directions. The potential of spreading passenger-generated pollutants is therefore reduced by controlling fore and aft airflow.

2.2.3 Environmental control system

Cabins of the aircrafts must be equipped with a system which controls the environment inside the cabins because of incapability of human being to such environment [25]. The system is called as Envrionmental Control System (ECS). Advanced technological systems such as ECS and Environmental Protection System (EPS) are used for vehicles which are used in different conditions such as space, air and sea. Sustainability of pressure, temperature, humidity, fire protection and recirculation system in the cabin was provided by ECS. Besides such goals of ECS, providing the enough fresh air and controlling heating/cooling to maintain the passenger and crew comfort are the two main goals of the system [25]. The air flow inside the cabin for freshing the air pattern is shown in **Figure 2.3**.

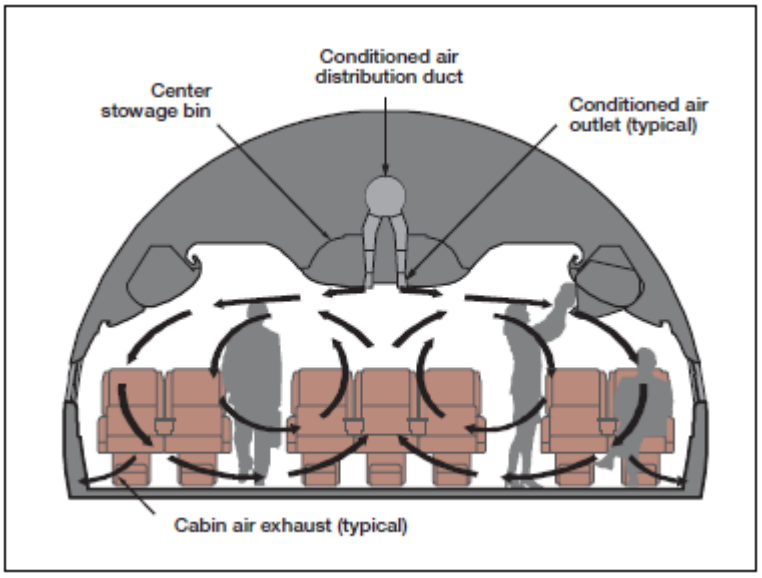


Figure 2.3: Typical main cabin airflow patterns [24].

Since the aircraft cabin is of a rather small/limited volume, in which passengers directly influence parameters of the cabin air quality and cabin environment, the control of an aircraft environment is much complex and complicated comparing to office and house environments.

2.3 Definition of VOCs

According to definition of the World Health Organisation (WHO), VOCs are referred as all organic compounds in the boiling point range of 50 – 260 ^{0}C [21]. VOCs are one group of air pollutants that degrade the air of the indoor and outdoor environment, and this pollutants exist widely in both indoor and outdoor environment [14]. VOCs represent the major part of indoor air contaminants and the sources of these organic compounds in indoor air are cooking, desks, carpets, paintings and ceilings [26]. Interior furnishing, cleaning products, building materilas and personal care products are the chemical sources which forms volatile organic compounds.

Organic compounds are divided into two main categories: polar and nonpolar compounds. Carbon and hydrogen, oxygen, sulfide and nitrogen are the ingredients of polar compounds. Nonpolar compounds measure as volumetric. Additionally, polar compounds easily interacts with metal and other surfaces since they are chemically reactive. A detailed classification of Indoor Organic Contaminants can be seen on **Table 2.2**.

Table 2.2: Qualification of indoor organic compounds .

Description	Abbreviation	Boiling Point Range (°C)	Example Compounds
Very volatile (gaseous) organic compounds	VVOC	<0 to 50-100	Propane, butane, methyl chloride
Volatile organic compounds	VOC	50-100 to 240-260	Formaldehyde, d-Limonene, toluene, acetone, ethanol (ethyl alcohol) 2-propanol (isopropyl alcohol), hexanal
Semi volatile organic compounds	SVOC	240-260 to 380-400	Pesticides (DDT, chlordane, plasticizers (phthalates), fire retardants (PCBs, PBB))

2.4 Sources of VOCs in Aircraft Cabins

Aircraft cabin environment is different in several ways from other indoor environments such as offices and homes, due to the extremely high occupants intensity and the confinement of passengers to their seats for long periods of time for long distance flights [22]. The reported maximum VOC levels are comparable across the different transportation types, aircraft cabin air is the place where highest amount of ethanol and acetone were observed in [21]. The exposure level of VOCs in the cabin air is significantly dependent on the sources and emission rates. Structural materials and household cleaning products make the significant contribution to the VOC amounts in the cabin air. In the aircraft cabin environment, human bioeffluents are the another major VOC source [22]. VOC levels in the cabin air are also related to period of the flight. In the beginning of the flight at the runway, after the intake of the passengers VOC levels are high for dichlorobenzene, methylene chloride, limonene because of using of cabin cleaning chemicals. During the meal and beverage serving, VOC levels increases for some specific VOCs such as ethanol.

2.5 Effects of VOCs on Human Health in Aircrafts

Volatile organic compounds are the major pollutants in indoor air. A lot of investigations have been carried out for measurement of the indoor air concentrations of VOCs all around the world. From these investigations it is found that a greater number of VOCs in indoor air has higher concentrations than outdoor air [21]. This pollutants doesn't impact only air quality it also significantly influence human health [21]. Photochemical oxidants such as ozone and peroxyacetyl nitrate are possible products of VOC emissions. Tropospheric ozone, formed in the presence sunlight from NO_x and VOC emissions , is toxic to humans, damaging to crops and is implicated in the formation of acid rain [27]. Many VOCs are known to be toxic and these are considered as carcinogenic [7]. There is a close relation between VOCs and the sick building syndrome (SBS), which is one of many terms used occupants to describe symptoms of reduced comfort of health [21]. A long term exposure to VOCs can cause acute and chronic health problems. According to EPA researches, these health problems can be listed as; eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system are the other part that might be affected by VOCs [28]. In addition to this, low concentrations of volatile organic compounds cause asthma and other respiratory diseases. High concentration of its also have narcotics effects on the central nervous system [29]. Some organics can cause cancer in animals; some VOCs are suspected or known to cause cancer in human. For instance, benzene is evaluated as carcinogenic substance in the classification by the EPA; carbon tetrachloride, chloroform, vinyl chloride, ethylene bromide are also classifed as at cancer risk [28].

The effect of several VOCs on cancer is shown in the following **Table 2.3**. While Level A is being described as "carcinogenic", B2 is explained as "likely to be carcinogenic" and C is defined as "which is possibly carcinogenic". As one can see, benzene is the carcinogenic volatile organic compound.

Table 2.3: Toxicity qualification of some VOCs [29].

Chemical	Cancer Factor (mg/ kg/ day)$^{-2}$
Benzene	A
Toluene	-
Ethyl Benzene	-
Xylene	-
Carbon Tetrachloride	B2
Chloroform	B2
Vinyl Chloride	C
Methyl Chloride	B2
Ethylene Dibromide	B2

2.6 Current Filtration Technologies in Aircraft Cabins

Practical air cleaning technologies for particles are widely avaible, typically consisting of fibrous filters installed in incoming outdoor air and recirculated air streams. Filtration of particulates are done by HEPA filters. However, air cleanining technologies for VOCs are less developed and surprisingly little has been published regarding their effectiveness and practicality when used in heating, ventilating and air conditioning systems of commercial buildings. Carbon adsorbents in current aircrafts.

2.6.1 HEPA-Type filters

Filtration of particulates and biological particles from the recirculated air is done by high efficiency particulate air type filter (HEPA). These are composed of fibers which randomly arranged. The fiber materials are usually fiber glass around 2μm diameter. HEPA filters are advantegous for aircraft applications because of their high capturing efficiency of bacterias from 10^7 m^3 of flow as a very high amount of air during their typical 5000h use [30]. 70 m^3 air flows thorugh every square centimeter of filter media

on the life of a typical HEPA filter [30]. These filters has a minimum efficiency of 94 percent to 99.97 percent against 0.3 μm size particles [24].

True-HEPA filters are another type which are more developed compared to traditional HEPA filters. These kind of filters are generally used in aircrafts and the efficiencies of that kind of filters are 99,999% against 0.3 μm particulates. If it is considered that the bacterias are generally around 1 μm and viruses are around 0.2 – 0.3 μm, these filters are enoughly capable to remove all of the viruses and bacterias from the aircraft cabins. Fiber diameter, face velocity, filter thickness are the primary reasons influencing the filter performance. For filtration of small particles can pass through the pores HEPA filters are designed for filtrating such particles and pollutants by using three different filtration mechanisms;

- Direct Interception
- Inertial Impaction
- Diffusional Interception

Direct interception is a result of porous structure for removing the particulates which are bigger than the pores of the filter. Another mechanism which is inertial impaction can remove particulates smaller than pore sizes. Density of these particles are higher than air. Thus, these high density particles deviate from the air flow path and impact on the solid surfaces or walls of the pores where they adhere [24]. Brownian motion is the fundamental of diffusional interception. Very small particles in the range 0.1 μm and below can be removed efficiently. The schematic view and the filtration mechanism of the HEPA filter is illustrated in **Figure 2.4**.

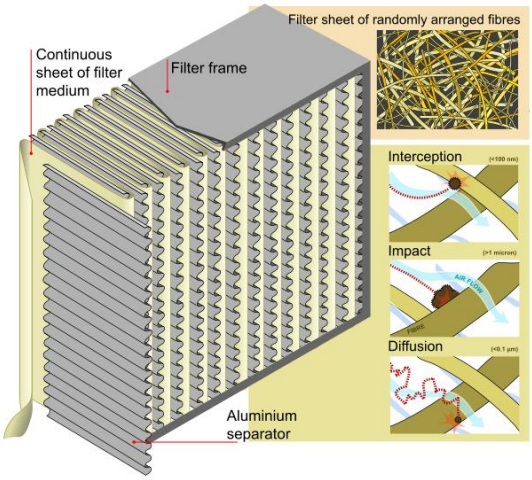


Figure 2.4: HEPA-type filter schematic view.

HEPA filters are used for such applications;

- Biomedical
- Hospitals
- Vacuum Cleaners
- Aircrafts
- Motor Vehicles

Some of the applications of HEPA filters are showed in **Figure 2.5**. For some applications these filters were used with UV light for killing off the live bacteria and viruses trapeed by the filter media. Because of importance of spread of airborne bacterial and viral organisms, these filters are especially used in hospitals and health institutes.

Figure 2.5: Applications of HEPA filters.

2.6.2 Activated carbon filters

Beyond the HEPA filters, activated carbon filters can remove some different contaminants that HEPA can not demonstrate. An activated carbon filter sample is demonstrated in **Figure 2.6**. Activated carbon is a well-known process for removing various organic contaminants and organic carbon in general [31]. It is also most commonly used physical adsorbent for removal of VOCs from air streams. They are most commonly applied as a powdered feed or in a granular form in packed bed filters. Amount of carbon and residence time of air are the key parameters that determining the performance of VOC removal. In case of an air stream with multiple VOCs, a significant fraction of carbon becomes saturated with VOCs, higher molecular weight VOCs can drive previously sorbed lower molecular weight VOCs back into the air stream which resulted as breathing of unhealthy air for passengers.

Figure 2.6: Activated carbon filters.

Activated carbon filters are used in water and gas purification, air filters used in gas masks, medicine, sewage treatment and metal extraction applications. Gas purification applications are against oil vapours odour and other hydrocarbons. Any activated carbon filter media is not used in any aircraft for VOC purification except Boeing 787. For that aircraft, activated carbon filters are preffered for VOC removal that forms from the engine.

2.7 Future Filtration Technologies in Aircraft Cabins

Future filtration technologies are especially focused on reduced weight, extended service life, reduced maintenance costs and higher efficiency for removing of contaminants without any addition of chemicals. Catalytic converters, photocatalytic oxidation, plasma oxidation and particulate filtration methods are promising mechanisms for filtration technologies. Removal of VOCs from aircraft cabins can be achived by using photocatalytic oxidation (PCO), an efficient, promising and economic method [32]. Photocatalytic oxidation was used for removing of VOCs under UV light as cabin air filtration method.

2.7.1 Photocatalytic oxidation(PCO) and removal of VOCs by PCO

As an alternative approach to improve the indoor air quality and well-being of occupants, a technology of ultraviolet photocatalytic oxidation (UV-PCO) [33]. This method is also becoming very popular due to reduce building energy consumption in the recent years. Clean Air Act of 1990 regulated the emission of volatile organic compounds by industrial processes in the United States, which has created a strong

incentive for research in this area in both the academic and industrial communities involved in innovative sustainable environmental research [3].

The treatment of VOC vapours at source generally entails the construction of a treatment facility requiring a large land area which is not appropriate for vehicles and small places [34]. To reduce treatment costs, it is important to: (i) smaller emission control facilities in order to minimize construction cost and minimize required lands, (ii) facility should be operated at ordinary temperatures and pressures, and (iii) avoid formation of secondary pollutions [34]. Among the advanced oxidation processes developed to meet the ever-stricter antipollution legislation required by the pressure for environmental protection, photocatalytic oxidation shows much promise for the purification of contaminated wastewater containing organic pollutants and the removal of air contaminants [3]. Photocatalytic oxidation for toward VOC treatment has been studied for several years and these studies developed PCO systems [26].

2.7.2 Definition of PCO

The use of photochemical conversion and photocatalytic oxidation technology to remove organic hazardous chemicals has attracted considerable interest in recent years [35]. Among different air treatment methods, PCO is a strong candidate because of its high effectiveness, low air flow resistance lack of any requirement for reactivation [22]. The destructive removal of trace contaminant from polluted air and water by using various photocatalytic reactor systems has been intensively studied [36]. PCO provides significant advantages for the removal of pollutants associated with poor IAQ [37]. Nevertheless, only some particular molecules with photochemical activity could be degraded through photolysis, and a large number of VOCs were still hard to be processed but it has been accepted that the photocatalytic processes has a potential ability to degrade most of organic pollutants[35]. Nano - Semiconductor catalysts and ultraviolet light are commonly used for converting of organic compounds in indoor air into non harmful and odorless constituents such as water vapor and carbon dioxide [38]. This air treatment method can be operated at low temperatures and it can be very selective in radiation absorption [14]. Researches indicates that almost any organic pollutants and many of the inorganic pollutants produced by electrical, agricultural, textile, electronic, petrochemical, metallurgical and many other industries can be completely destroyed or seperated from the environment [14].

Various catalyst have been developed for PCO applications. These catalysts are commonly metal oxides or sulphides, TiO_2, ZnO, ZrO_2, WO_3, CeO_2, Fe_2O_3, Al_2O_3, ZnS and CdS [38]. All of these semiconductors have different band gap values and this is the primary parameter that affecting the required wavelenght and performance of the catalyst. The band gap of these semiconductors are shown in **Figure 2.7**. A perfect photocatalyst is defined by its capability to simultaneously cling two reactants that can be reduced and oxidized by a photonic activation over an effective absorption. Thus, TiO_2 is the most significant and popular catalyst. Titanium dioxide has been a popular photocatalyst for the treatment of organic pollutants in water and air and it has been widely used as a catalyst for the photocatalytic oxidation systems activated by UV light in recent years [14] [39]. Actually titanium dioxide is the most widely used photocatalyst for air and water purification systems and researchs.

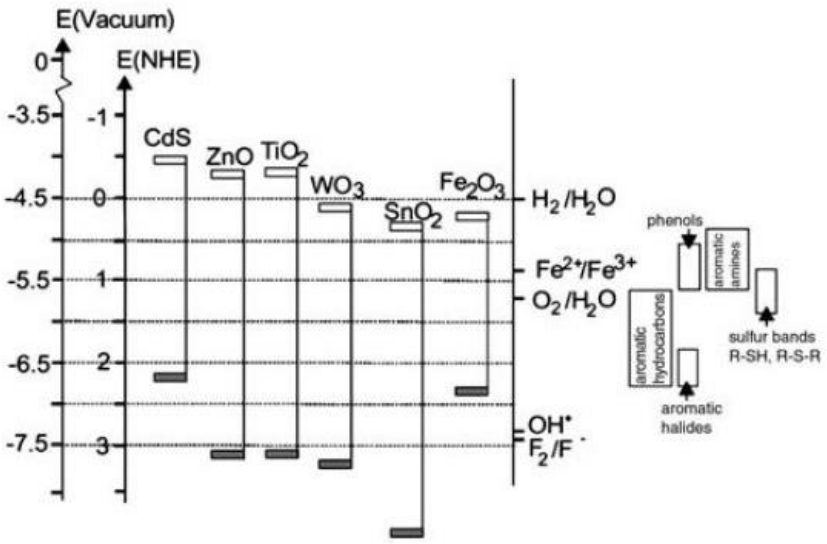


Figure 2.7: Band gap values of semiconductors [21].

2.7.3 Mechanism of PCO

Unlike conventional air purification technologies such as filtration and sorption, which only transfer indoor contaminants to another phase, VOC can be oxidized to carbon dioxide (CO_2) and water (H_2O) [40]. Most PCO reactors use nano-titania (TiO_2) as the catalyst that is activated under UV light. Schematic view of PCO reaction that occurs on TiO_2 surface is given in **Figure 2.8**. PCO reaction occurs at the surface of catalyst illuminated by light.

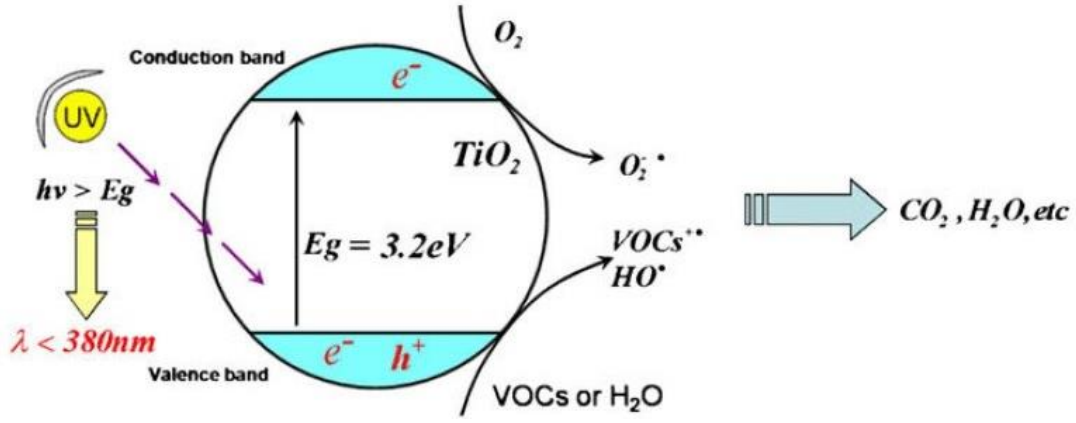


Figure 2.8: Schematic view of VOC degredation on TiO_2 surface [38].

As shown in **Figure 2.8** photons supplied from light source are totally adsorbed by the catalyst [33]. An electron in an electron-filled valence band (VB) is excited by photo irradiation to a vacant conduction band (CB), and this exciting leavs a positive hole in th VB [38]. These electrons and positive holes drive reduction and oxidation reactions, respectively, of compounds adsorbed on the surface of the photocatalyst [38]. The activation equation can be written as;

$$TiO_2 + hv \rightarrow h^+ + e^-$$

h^+ and e^- are powerful oxidizing and reducing agents, respectively. After this reaction, oxidation and reduction reactions occurs. These reactions can be expressed as;

$$h^+ + OH^- \rightarrow OH^* \text{ (Oxidation Reactions)}$$

$$e^- + O_{2(ads)} \rightarrow O_2^{-(ads)} \text{ (Reduction Reactions)}$$

Hydroxyl radical (OH^*) was formed by chemically transforming of organic compounds. Net reaction of VOCs can be explained as shown below;

$$OH^* + VOC + O_2 \rightarrow nCO_2 + mH_2O$$

As can be seen from the reactions occurred during PCO method, by-products are carbondioxide and water vapor. A schematic view of PCO mechanism can be seen on **Figure 2.9.**

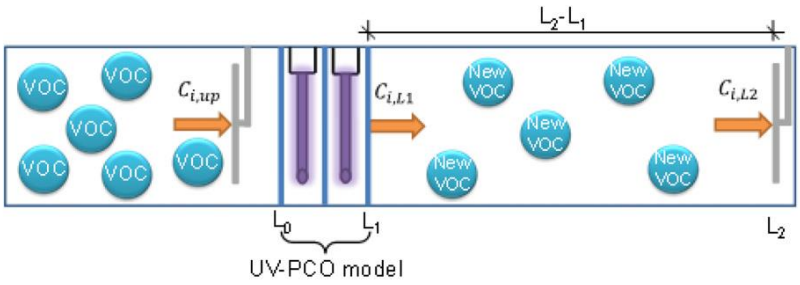


Figure 2.9: Schematic view of PCO reaction [33].

The reaction rate increased with increasing light intensity, as the heterogeneous photocatalytic reaction depends on the irradiation of

The Langmuir-Hinshelwood (L–H) model has been widely preffered to formulate the rate equations for the PCO reaction and decomposition or conversion efficiency (η) was calculated from the equation as shown below;

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$

where C_0 is the initial concentration of contaminant and C is the concentration of contaminant at time t.

Photocatalyst lifetime is potentially important in process economics because of its maximum run times between catalyst regeneration or replacement [38]. Catalyst activated by light is used during reactions and as a result of these reactions, the catalyst material loss its active sites and the loss of these active sites is called as deactivation. There are couple of reasons of deactivation. Firstly, generation of reaction residues may be adsorbed onto the catalyst surface and block the active sites. Secondly, some species may photopolymerize on the surface. Particle materials may change the catalyst surface by blocking pores.

2.7.4 Parameters in PCO reaction process

Efficiency results of the PCO reactions are directly influenced from ambient conditions and process parameters. Because of the importance of illumination for PCO, light source and intensity are can be assumed as the primary factor. Besides light source and intensity, pollutant concentration, humidity and temperature are the other parameters. Ultraviolet source and light intensity was studied for PCO efficiencies of the produced nanofibrous filters.

2.7.4.1 Pollutant Concentration

The optimum point of the contaminant concentration usually maximizes the PCO reaction rate while the other conditions remain stable. This optimum point is the maximum level of contaminant which is removed completely by PCO filtration. Over that point, total amount of the catalyst will not be enough for removing all of the VOCs because of the capability of the catalyst is limited.

2.7.4.2 Ultraviolet source and intensity

Since UV sources are the primary components of the PCO reaction processes, the intensity and wavelength of the UV light has a significant effect on the PCO reaction rate. Titanium dioxide can be activated under 380 nm wavelenght supplied from any light source. Intensity of the light directly affects the reaction rate. PCO efficiency is influenced positively with increasing light intensity.

2.7.5 Illumination under UV light

Ultraviolet light has wavelength below 400nm. Ultra Violet lightening systems are divided into two main categories. These are; traditional UV lamps and as a new technology UV light emitting diodes (LEDs). For photodegradation of VOCs UV-light irradiation acts as a dramatic energy provider [6]. It is expected that the decomposition efficiency and the operation costs for a photocatalytic system may be markedly improved through the improvement of UV light utilization [41].

Titaniumdioxide (TiO_2) is the primary and an effective catalyst in PCO applications. However, this type of catalyst merely demonstrates high catalytic activity under UV illumination at wavelengths of 340 – 388 nm [42]. This makes the UV radiation as main light source for PCO. It is aimed to the development of advanced catalysts for visible light applications. Therefore, some attepts have been made in that way such as developing of TiO_2 by some modification methods. The most typical modification techniques involve depositing noble metals, doping transition metals ions, combining with semiconductors and modifying with other substances [35].

2.7.5.1 UV Lamp

Traditional UV light sources can be classified as two categories;

- Incandescent sources
- Gas discharge sources

UV emissions of the former depends on the filament temperature which is usually around 2700 ^{0}C. Hence, filament lamps are very unproductive. For gas discharge lamps, the inner space of the lamps are filled with a gas which provides a fairly low ionization energy, sufficient vapor pressure, be inert and its lowest excited state must be at such a level that the resonance radiation appers at UV wavelength [19]. The reason of using mercury in UV-Lamps is fulfilling all of the requirement. However, EPA specified mercury as one of Hazardous Air Pollutants (HAPs) which can damage the brain and kidneys [19].

For gas charge UV light sources, the number of effective photons per input energy is not high due to the high quantum energy and/or wide spectrum, and it is very difficult to improve their Wall Plug Efficiency (WPE) which is defined as the optical power per electric power input [19]. So, efficiency of these lamps are pretty low.

Another problem of that light sourece are toxic effect of mercury which increasingly becoming controlled or banned by government safety and environmental regulators. They are also fragile, relatively short lifespan of thousands of hours compared to 50000 hours of UV-LEDs and instability of the output power. Traditional UV-Lamps are also instable for providing the output power.

2.7.5.2 UV-LED

Light Emitting Diodes (LEDs) are a new lighting technology and they are being commercially avaible since 2003. UV-LEDs are semiconductor p-n junction devices which are made up of gallium arsenide (GaAs), gallium arsenide phosphide (GaAsP), gallium phospide, or indium gallium nitride (InGaN) [43]. The toxicity of GaN is not stronger than copper and zinc so UV-LED is regarded as a safer alternative to mercury UV-Lamps [19]. Since long life expectancy of 50000 hours which is about 5 times that of Hg-vapor lamps, high robustness, minimum heat generation, good linearity of the emitted light intensity with current, suitability for operation in a pulsed regime at high frequencies, and are easily protable, it has a great potential to become a suitable light source.

With recent developments, there is great potential for the UV-LED to become a fertile light source for photocatalytic applications instead of mercury lamps. Furthermore, the next generation of photocatalytic systems needs a flexible, lightweight, and easily portable reactor, and the usage of energy efficient sources instead of classical ultraviolet excitation source. Because of these situations, UV-LED has been studied in PCO systems for degradation of severalxenobiotics, formaldehyde, bisphenol, and chlorophenol in contaminants waste streams [42].

2.7.6 Illumination under visible light

Photocatalysis with sunlight or room light has the potential to be a beneficial technology for environmental filtration systems. The commonly used PCO catalyst, TiO_2 which exhibits high catalytic activity in UV-light span is an effective catalyst in photocatalytic oxidation [32]. However, TiO_2 has lower efficiency under visible light region. Thus, using of these light sources for PCO applications is a still big challenge for indoor filtration because of the low fraction of UV light in indoor and vehicle applications.

Usually, there are three preparation ways for shifting the catalyst activating region from UV to visible area; doping TiO_2 with transition metal ions; doping nitrogen into TiO_2 and utilizing sensitizing dyes [38]. Doping with transition metal ions decreases the band gap and extends light adsorption of the material into the visible region. Coupling of catalyst with a small band-gap semiconductor or doping with transition metal ions such as V, Cr, Mn, Fe, Co, Ni, N or Cu extends light absorption into the visible region by shifting the band gap of the primary catalysts [38].

3. NANO FIBROUS FILTER PRODUCTION AND CATALYST DEPOSITION METHODS

3.1 Electrospinning

Electrospinning is a method in which nanofibers (NFs) are uniaxially stretched from a viscoelastic solution [44]. Since electrospinning is quite versatile and cost-effective comparing to other methods for producing functional NFs from variety of materials including polymers, polymer blends, suspensions, emulsions, sol-gels, non-polymeric systems, metal oxides and composite structures, this method has gained growing interest in the past decade [45]. Because of the high surface area, rigid and flexible structure and high porosity, the produced NFs by electrospinning is widely used for different purposes such as drug delivery systems, nanosensors,, micro/nano electronic devices, scafolds for tissue engineering and filtration media [46]. High-performance filters to chemical and biological sensors and protective clothing applications has been studied on nanoscale surface texture because of their small mesh allows trapping of very small particles [44] . High surface area is required from the substrate which is also inert material for maximizing the photo activity of the catalyst and the filter [34]. Electrospun NFs have high specific surface area with a distinctive nanoscale surface texture. This method is a result of the influence of an electrostatic field on the prepared viscoelastic solution for the formation of ultrathin fibers [45] . The diameter of the NFs can be varied from tens to hundreads of nanometers according to polymer solution and study parameters. A schematic view of electrospinning process can be seen in **Figure 3.1**.

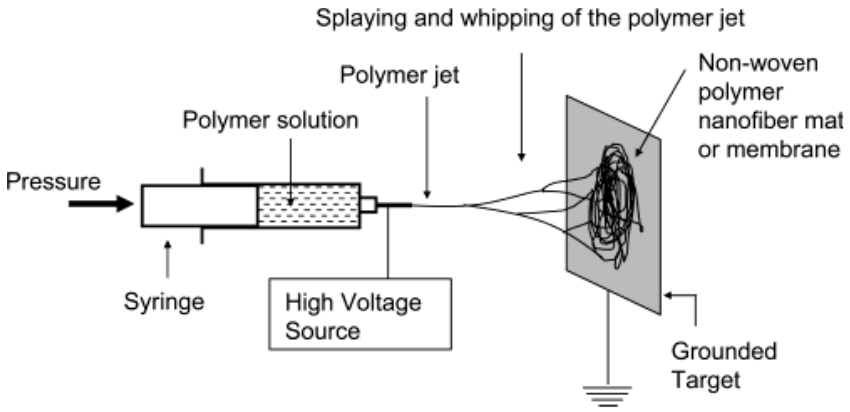


Figure 3.1: Schematic representation of electrospinning process [47].

For electrospinning procedure a high voltage is applied to the solution such that at a critical voltage depending on the viscosity of solution, the repulsive force within the charged solution is higher than its surface tension and as a result of that charged solution force a jet would erupt from the tip of the spinneret to grounded collector surface [44].

Electrospinning parameters have an important factor on controlling the properties of electrospun NFs. Especially fiber diameter is influenced from the study parameters such as solution viscosity and conductivity, applied voltage, feeding rate, distance between tip and collector and ambient humidity [44]. Solution viscosity and feeding rate depending on the concentration of polymer in the electrospinning solution has negative effect on NF diameter. On the contrary conductivity, applied voltage and distance between tip to collector has positive effect on decrease of NF diameter.

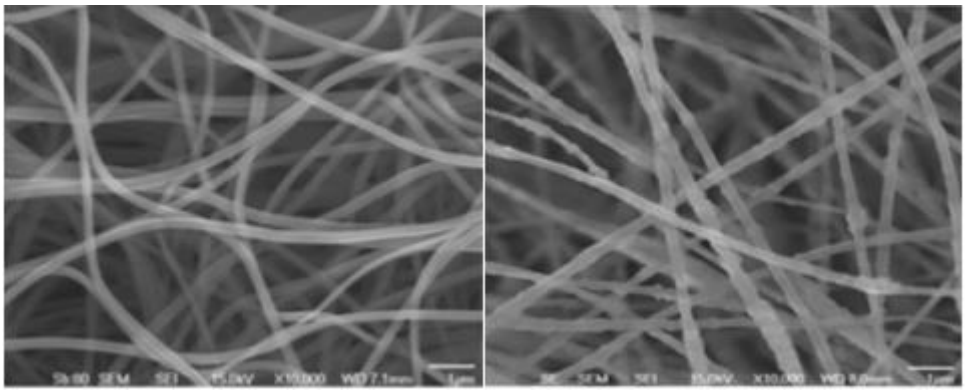
3.2 Catalyst Deposition Method

One of the most important parameter influencing the performance of the filter is catalysts deposition method. Distrubition and dispersion of the catalysts on the NF surface must be homogenous without agglomeration for maximizing the performance of the media for PCO application. Even though there are some methods, embedding and electrospraying methods are the most common methods for deposition of catalysts in the literature.

3.2.1 Fixed catalyst system

Fixing the catalyst in the NFs by embedding it onto TiO_2/polymer solution is widely used in literature. According to this method, catalyst nanoparticles(NPs) are dispersed

in the polymeric electrospinning solution and this solution is used for electrospinning. As a result of this process, these NPs are deposited inside the NFs. SEM images of embedded TiO_2 NPs onto NFs are shown in **Figure 3.2**.



(a) **(b)**

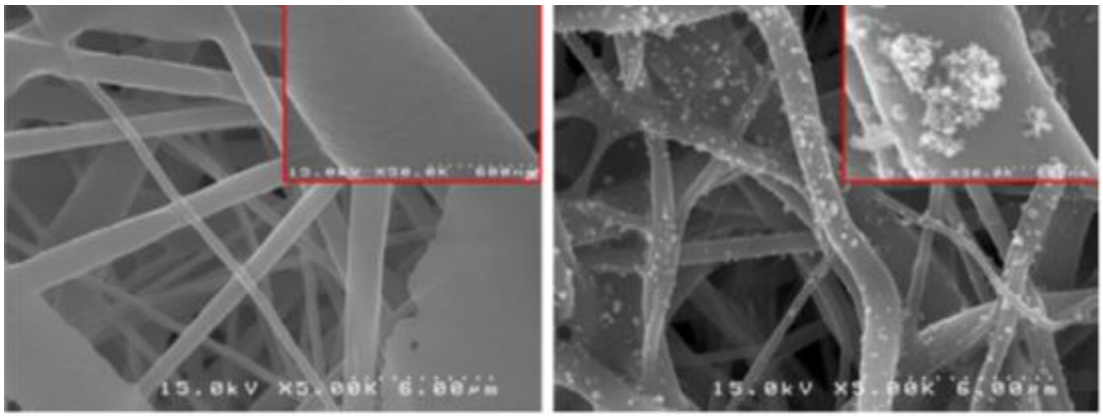
Figure 3.2: a) NF structure **b)** Embedded catalysts in the NFs [48].

Deposited catalyst NPs can be seen as beads in the NFs and these catalysts are agglomerated and deposited under the surface of NF which is a disadvantage for produced media. When TiO_2 is embedded in NFs, the light intensity which is adsorbed by the catalysts decreases enormously. Another disadvantage of this method is the agglomeration of TiO_2 which decreases the active surface area per each catalyst particle. Since PCO performance is highly related with surface area and TiO_2 distribution; fixed catalyst system through embedding is not preferred. Besides embedding, electrospraying is developed for next steps of the project. Performance of the catalysts are negatively affected from these disadvantages. Because of these undesired circumstances, instead of embedded method, electrospraying method was developed for next steps of the project.

3.2.2 Electrospraying system

Electrospraying is a technique closely related to electrospinning. It is a low-energy, low-cost material processing method. Electrospraying is a well-known technique of liquid atomization by employing electrical forces [49]. Atomization of the meniscus of a liquid flowing out from capillary nozzle concludes as fine droplets and these droplets are electrically charged [49]. The electrically charged droplets follow a trajectory to the nearest grounded surface where nano or microscale particles and coatings are collected thiny and uniformly on [50]. There is an application of high

electrical forces to lower viscosity liquid comparing to electrospinning solution. SEM images as shown in **Figure 3.3** were taken from a literature that is studied on the electrospraying of TiO_2 NPs onto polyvinylidenefluoride (PVDF).



(b) **(b)**

Figure 3.3: a) PVDF NFs b) TiO_2 electrosprayed NFs [50].

According to literature studies, distrubition and dispersion of the catalysts along the NFs by electrospraying method are much more homogenous and less agglomerated compared to embedded method. Since the direct interaction of catalysts with the light and higher active surface area achieved through electrospraying , higher performance is expected to achieve in PCO reactions.

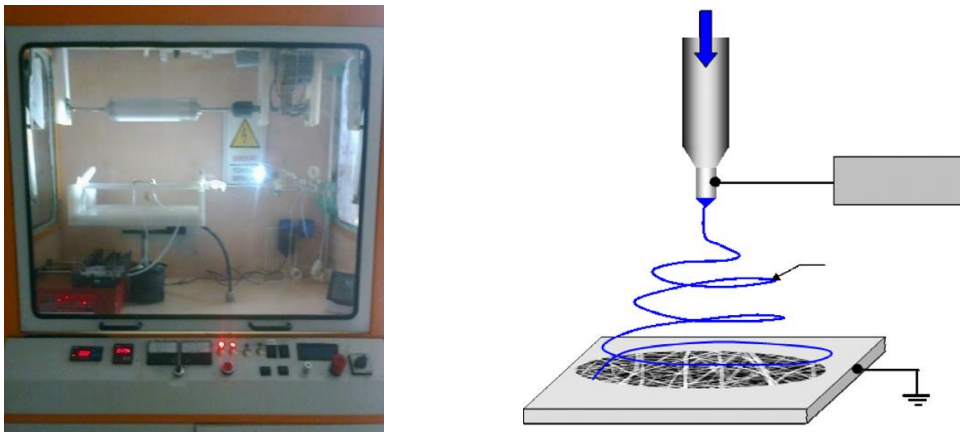
4. FABRICATION OF NANO FIBROUS FILTERS

4.1 Nanofiber (NF) Production by Electrospinning

In this study, NF mat as filter material was produced by electrospinning method. The reason of preference of NF material was its high surface area which is one of the most important parameter effecting the photocatalytic. For electrospinning studies 20 mL HSW Norm-Ject brand syringes was used with a 8mm brass diameter needle. During these studies, different voltage values, feeding rates and distances between tip with collector were studied because of the varying viscosity properties of each solution. However, rpm value of the collector was always same for orientation of the fibers.

Polypropylene (PP) nonwoven was choosen and used as the substrate for produced NF mat due to unflammable property and easily supplyability from TAC company.

During electrospinning studies two different machines were used in which **Figure 4.1** shows a home built system by former laboratory members of TEMAG.



(a) **(b)**

Figure 4.1: a) Home-built machine **b)** Schematic view of process [44].

Several polymers are capable of using for electrospinning process such as;

- Polyvinylalcohol (PVA)
- Polyacrylonitrile (PAN)
- Thermoplastic polyurethane (TPU)

These polymeric materials were tested for nano fiber production. Distilled water, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were used for dissolving and preparation of polymeric materials for electrospinning solution.

Electrospinning studies were firstly performed on aluminium foils as shown in **Figure 4.2**. Small pieces of aluminium foils were cut for collecting the produced NFs during optimization studies of electrospinning parameters. After the characterization studies were performed by scanning electron microscope (SEM), the optimized parameters for NF production was choosen as procedure. SEM characterization helped to select the proper polymeric material for fabrication in this study.

Figure 4.2: A view from electrospinning study.

4.1.1 PVA based

For the early studies it was focused on the fabrication of NFs as PVA based. PVA based NFs were produced by electrospinning. PVA was preferred because of it's untoxicity and dissolibility in water. Preparation of PVA solution for electrospinning can be seen as below;

- Mixing of PVA in distilled water with a concentration of 12 wt%
- Homogenous distrubition of PVA in distilled water at 80 ^{0}C for an hour
- Cooling down to ambient temperature

This solution was electrospun onto aluminium foil to examine NF formation. Electrospinning parameters for PVA NF production were studied for optimization. Although there were many studies for obtaining NFs, observation of NF formation was just for one study as shown the parameters below;

- Applied voltage 24 kV
- Tip to collector distance 150 mm
- Feeding rate 0,3 mL/h
- Collector speed 200 rpm

During this studies 1 wt% of TiO_2 (Degussa P25) was added to electrospinning solution and electrospun onto PP non-woven spunbond. TiO_2 NPs dispersed in the electrospinning solution were embedded in the produced NFs. The electrospinning parameters for this study were;

- Applied voltage 20 kV
- Tip to collector distance 150 mm
- Feeding rate 0,5 mL/h
- Collector speed 200 rpm

SEM images of pure and TiO_2 embedded PVA NFs are demonstrated in **Figure 4.3** and **Figure 4.4** respectively.

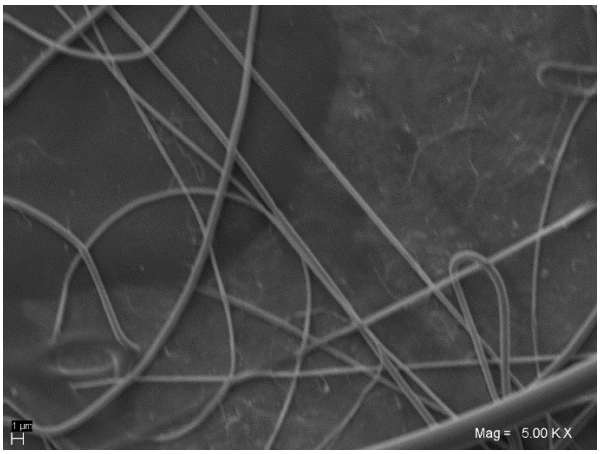


Figure 4.3: Pure PVA NFs.

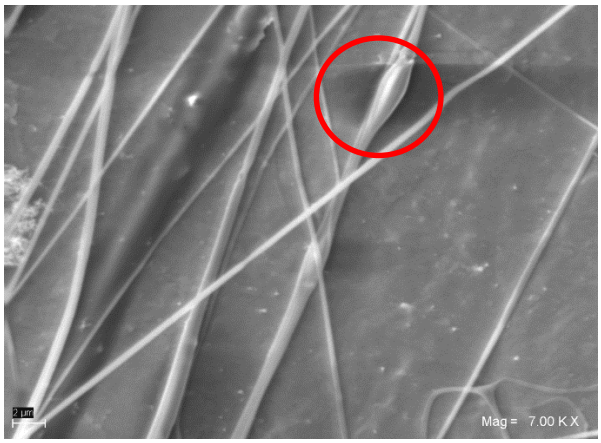


Figure 4.4: Embedded TiO_2 nanoparticles are demonstrated as red circle NFs.

4.1.2 PAN based

PVA based electrospinning studies showed us that PVA can be dissolved in water very well but it's electrospinnability was not appropriate for the studies. Since unsuccesful experiments with electrospun PVA NF, it was necessary to focus on another polymeric material. Thus, polyacrylonitrile (PAN) was begun to be used. PAN was dissolved in DMF without any additive. For one of the studies made with PAN, Degussa P25 addition was made with a concentration of 1 wt%. Pure PAN NFs were produced according to following procedure.

- 13 wt% PAN dissolved in DMF at 85 ^{0}C for 90 minutes
- Cooled down to ambient temperature

Cooled down PAN solution was electrospun for formantion of NFs. Electrospinning parameters of this solution are shown as below;

- Applied voltage 20 kV
- Tip to collector distance 15 mm
- Feeding rate 1,5 mL/min
- Collector speed 200 rpm

NF formation during electrospinning process with the parameters as shown above were observed and these parameters were accepted as appropriate parameters for such concentration level of PAN. NFs produced with that parameters were characterized in the SEM and showed in **Figure 4.5**.

Instead of electrospraying of TiO_2 solution, TiO_2 NPs were dispersed in the electrospinning solution at 1 wt% similar to PVA solution. TiO_2 NPs were embedded and formed beads where they existed in the NF is shown in **Figure 4.6**. With the

similars reasons of embedding TiO_2 in the polymer would decrease PCO efficiency, the next steps of TiO_2 deposition was focused on electrospraying.

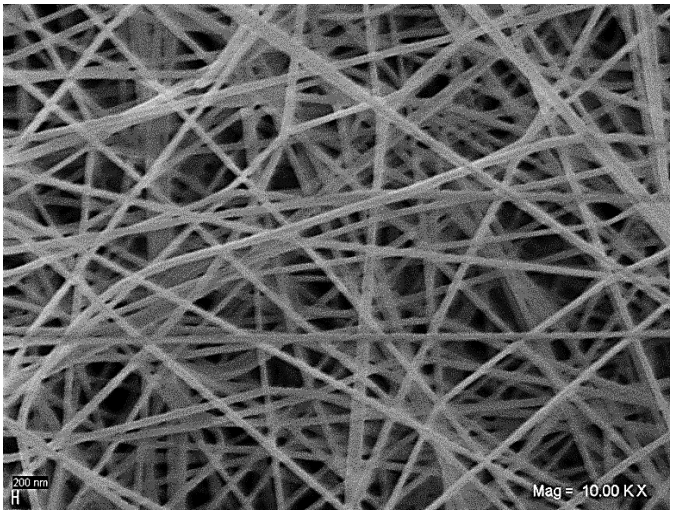


Figure 4.5: Pure PAN NFs.

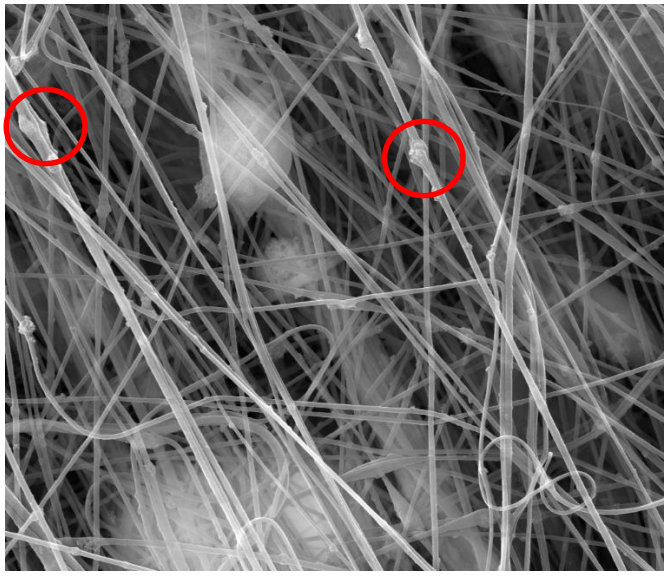


Figure 4.6: PAN NFs with embedded TiO_2 nanoparticles.

4.1.3 TPU based

Thermoplasticpolyurethane (TPU) is a resilient elastomer that has a wide range of applications such as coatings, sealants, transdermal patches, and catheters [47]. According to previous studies done with PVA and PAN it was necessary to change the polymeric material for obtaining higher performance from the fibers with better elasticity. From the literature, thermoplastic polyurethane (TPU) was chosen as the proper polymeric material for electrospinning. TPU is a class of polyurethane plastics with many properties, including elasticity, transparency, resistance to oil, grease and

abrasion. Used TPU which is called as C95 with high electrospinnability, good viscosity and high mechanical properties was supplied from BASF.

Some additives were made for improving the performance of solution during electrospinning. Sodium chloride was added 0,03 wt% of total weight for increasing the conductivity which affects electrospinning performance of solution. By addition of sodium chloride applied voltage for electrospinning was required. Ethyl acetate with 13 wt% was added to electrospinning solution for achieving a more viscous phase. The main chemical forming the NFs is polymeric material. For required NF formation, TPU was added to solution as 13 wt% of total solution. DMF was used 74 wt% of the total solution as solvent. The applied procedure for NF formation is summarized below in **Figure 4.7**.

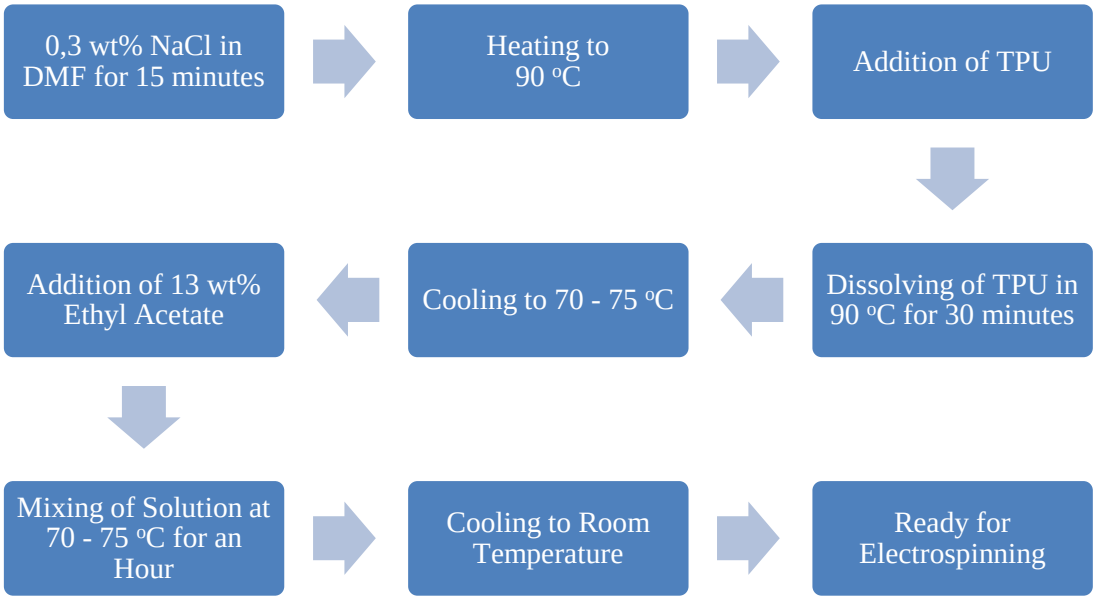


Figure 4.7: Production flow chart of TPU electrospinning solution.

The solution at ambient temperature was ready for electrospinning process aimed NF production as shown in **Figure 4.8**. The prepared solution should be stored in a dark area to avoid colour changes in the solution from visible light, which can effect the chemical structure of the solution.

Figure 4.8: 13 wt% TPU as electrospinning solution.

NFs were produced according to following electrospinning parameters;

- Applied voltage 24 kV
- Tip to collector distance 150 mm
- Feeding rate 0,65 mL/h
- Collector speed 200 rpm

Collector was horizontally moved for distrubition of NFs for wide area and obtaining bigger filter media. This movement was automatically controlled by automotion system. Dimensions of the filters were 44 cm height and 18 cm width. According to these dimensions, total filter area was 792 cm^2, two filter sample could be obtained for each produced electrospun media.

As it was mentioned in the literature part, one of the most important property of NFs is it's diameter. TPU concentration has decreased from 13 %wt to 10 wt% for decreasing the fiber diameter during electrospinning procedure which is crucial for enhanced surface area. And this 3 wt% of the solution was fulled by DMF. Since the viscosity of the solution changed, it was necessary to optimize the study parameters one more time. Three different voltage values and two different feeding rates were applied. By decreasing the polymer content, average diameter was changed and 10 wt% of TPU study optimization studies are given in **Appendix A-1**. As a result of these studies, it was observed that the best result was obtained from 25 kV and 0,7 mL/h feeding rate. This prepared solution was electrospun onto PP surface under same parameters applied for 13 wt% TPU. Thinner diameter NFs varying between 150 with 300 nm were obtained which can be seen in **Figure 4.9**.

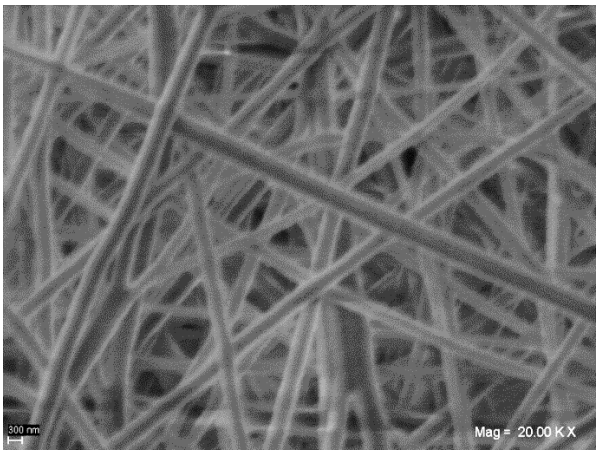


Figure 4.9: SEM image of 10 %wt TPU electrospun nanofibers.

Another development study during electrospinning studies was changing the DMF with another solvent because of its high toxicity on human health. DMF is the most common solvent used for electrospinning applications due to its high ability to dissolve polymeric materials easily and fastly. As nano fiber formation during electrospinning and preparation of polymeric solution, this solvent vaporizes and it is directly breathed by human. According to literature researches, Dimethylsulfoxide (DMSO) was found as a very similar solvent with DMF withouth toxicity for human health. Since DMSO is less toxic compared to DMF, some studies were done with DMSO instead of DMF by applying same parameters. During formation of NFs, some flow problems were happened but for obtaining the result of the DMSO study the process was continued for two hours.

After two hours of electrospinning, the produced NFs were investigated under SEM and the image is illustrated in **Figure 4.10**. According to these images it can be said that, the diameter of the nanofibers with DMSO solvent were thicker compared to DMF and also some bead formations were occurred. This result demonstrated that, the concentration of polymer in DMSO solvent was higher and concentration of polymer should have been decreased for achieving a better results.

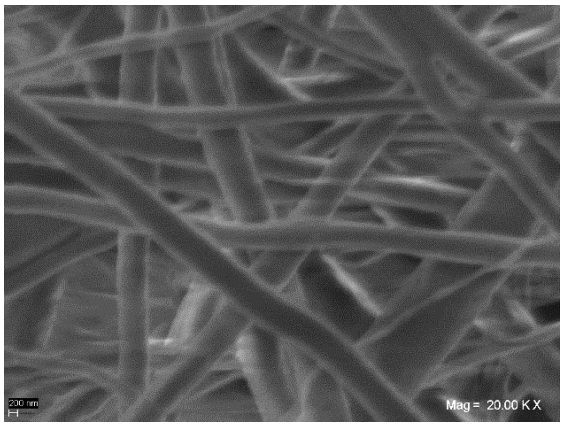


Figure 4.10: SEM image of electrospun TPU NFs with DMSO.

4.2 Deposition of Catalyst onto NFs by Electrospraying

Deposition of catalyst with good adhesion and distribution onto NFs is crucial to achieve a good performance of VOC degradation. Electrospraying was used to deposit both modified and unmodified (Degussa P25) onto NF surface. Details of electrospraying is explained in this section.

4.2.1 Degussa P25 as catalyst

A very widely used semiconductor for photocatalytic studies titaniumdioxide (TiO_2) was chosen as the primary NPs for deposition onto NFs. Degussa P25 was chosen as a commerical product which had 21 nm diameter supplied from Sigma-Aldrich.

For obtaining high efficient filters, these TiO_2 nanoparticles(NPs) must be distributed homogenously on the NFs without any agglomeration. Since agglomeration decreases the active surface area which decreases performance of the filters, electrospun nanofibrous filters were covered with TiO_2 NPs by using a method similar to the electrospinning method, which is called as the electrospraying. TiO_2 NPs were sprayed onto NFs directly and left for drying.

Homogenous and effective TiO_2 NPs distribution is a key factor in achieving high efficienct degradation capability. Many studies were performed with different solvents and different concentrations of TiO_2 in the solvent. Aluminium foil was used as a test bed for optimization studies of TiO_2 electrospraying parameters.

In the first studies the solvent for dissolving of TiO_2 was chosen as methanol because of its fast evaporation in air and capability to dissolve TiO_2 easily. So during electrospraying, methanol directly evaporated because of high applied voltage and it’s

high vaporization characteristic. Methanol and TiO_2 was mixed without any heat treatment for 12 hours and electrosprayed onto produced electrospun NF mat. This electrospraying duration was varied for required amount of TiO_2 on NF mat. Monolayer structure and sandwich structure were researched as two different filter type for obtaining the best performance. Schematic view of these structures are given in **Figure 4.11**.

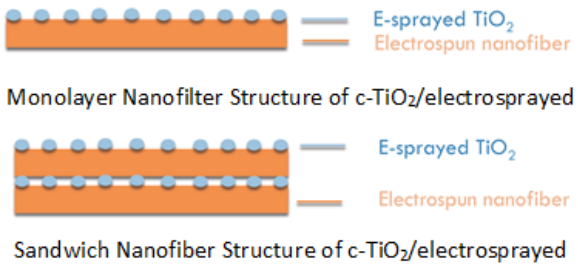


Figure 4.11: Schematic view of monolayer structure and sandwich structure.

Monolayer structure has one layer of nanofiber structure and the catalysts were deposited above of this layer. Monolayer structure studies were varied by electrospraying process durations such as 20, 40, 60, and 180 minutes were performed with Degussa P25 for investigating the effect of deposited amount of the catalysts on the filtration performance. According to deposition durations these fabricated filters were coded as "e" for electrosprayed onto nanofiber mat and "number" for defining the electrospraying durations like e-20 for 20 minutes of electrospraying, e-40 for 40 minutes of electrospraying, e-60 for 60 minutes of electrospraying, and e-180 for 180 minutes of electrospraying.

Besides mono layer, sandwich structure was developed by performing two layer of nanofiber and two layer of deposited catalyst. Production process of sandwich structure is shown in **Figure 4.12**.

Figure 4.12: Schematic of fabrication of sandwich structure.

Sandwich structure production process was consisted of two hour of electrospinning and forty minutes of electrospraying. In this study, 20 minutes of electrospraying of 0,5 wt% TiO_2 solution was performed after an hour electrospinning of NF surface, 60

minutes of electrospinning was done after completing the first layer and the last layer was accomplished by electrospraying of TiO2 solution for 20 minutes afterward. Although this sandwich structure filter had the same amount of TiO_2 with e-40, amount of TiO_2 on the surface of filter was equal to e-20.

With changing deposition durations, total amount of catalyst on the filter was changed too. Amounts of TiO_2 in the filters for changing deposition durations are given in **Table 4.1**.

Table 4.1: TiO_2 amounts in the filters for varying deposition durations.

Filter Type	TiO_2 in Filter (mg)	TiO_2 in Filter (mg/cm^2)	TiO_2 in Filter (%)
e-20	1,47	0,008	0,5
e-40	2,94	0,016	1
e-60	4,41	0,025	1,5
e-180	13,23	0,074	4,5
Sandwich	2,94	0,016	1

After long optimization studies, electrospraying of Degussa P25 was done according to following parameters;

- Applied voltage 25 kV
- Tip to collector distance 7 cm
- Feeding rate 2,2 mL/h
- Collector speed 200 rpm

4.2.2 Modified TiO_2 as catalyst

TiO_2 has a great interest in metal oxide semiconductors due to the wide bandgap, but low efficiency under irradiation in the visible light and undesirable recombination of the electrons and holes are the main disadvantages of the pure TiO_2. Therefore, for enhancement of the photo activity of TiO_2 numerous dopants have been reported. One of the methods is activation of TiO_2 under visible light by doping catalyst with different materials through chemical routes such as sol-gel process. In this study, modified photocatalysts such as , Fe-doped, N-doped, and N-Fe co-doped TiO_2 were successfully prepared via sol-gel method through hydrolysis and polymerization of

titanium tetraisopropoxide in 2-propanol. During these sol-gel studies, any Degussa P25 was not used as catalyst. Sol-gel preparing method is showed in **Figure 4.13**.

Figure 4.13: Sol-Gel preparation process.

By modificating or doping of TiO_2 the band gap of the catalyst was shifted to visible wavelength range which requires less light intenstiy for overcoming the band gap energy value compared to Degussa P25. In other words, the modified catalyst demonstrates higher activity under the same light intensity value applied to Degussa P25 catalyst because of the less band gap energy.

These modified TiO_2 sol-gels were electrosprayed onto TPU NF mat. Since the viscosity and density values of the electrospraying solution were changed, optimizing the electrospraying parameters was required. After optimization studies, electrospraying parameters were selected as;

- Applied voltage 27 kV
- Tip to collector distance 15 cm
- Feeding rate 2,2 mL/h
- Collector speed 200 rpm

As electrospinning and electrospraying studies, horizontal movement was applied for homogenous spreading of the catalysts onto entire surface of NF mat.

4.3 Morphological and Physical Characterization

Before application of filters to VOC removal analyzes, it was necessary to make some test for observing the filter properties as morphological and structural. The produced filters were nanofibrous filters consisting of NPs and NFs. Thus, these produced filters were not able to examined by eye and required developed analyzing method for understanding the morphological and physical properties of the materials. This characterization studies were also used for optimization researchs. Scaning Electron Microscope (SEM), Air permeability tests and Brunauer-Emmertt-Teller (BET) tests were used for characterization of the samples.

4.3.1 Morphological characterization of the filters (SEM)

SEM is a type of electron microscope which produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample and this interaction produces signals which draws surface topography and structure. SEM images were taken in the TEMAG Laboratory.

Because of the importance of distrubition and dispersion of TiO_2 on the surface of NFs optimization of electrospraying parameters were studied for obtaining higher efficient filters. Six different optimization studies were done for 20 minutes by changing the applied voltage and distance between tip and collector onto aluminium foils which were examined in the SEM as shown in **Figure 4.14**.

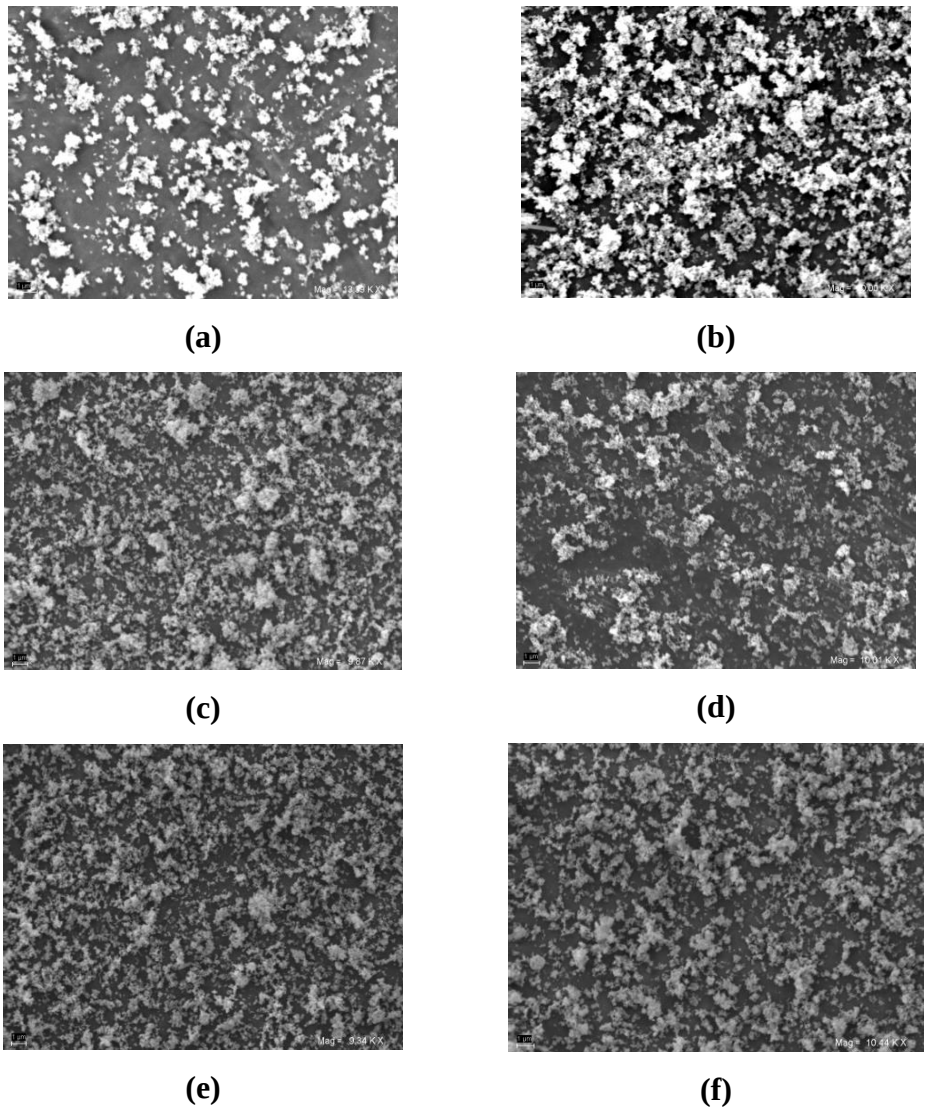
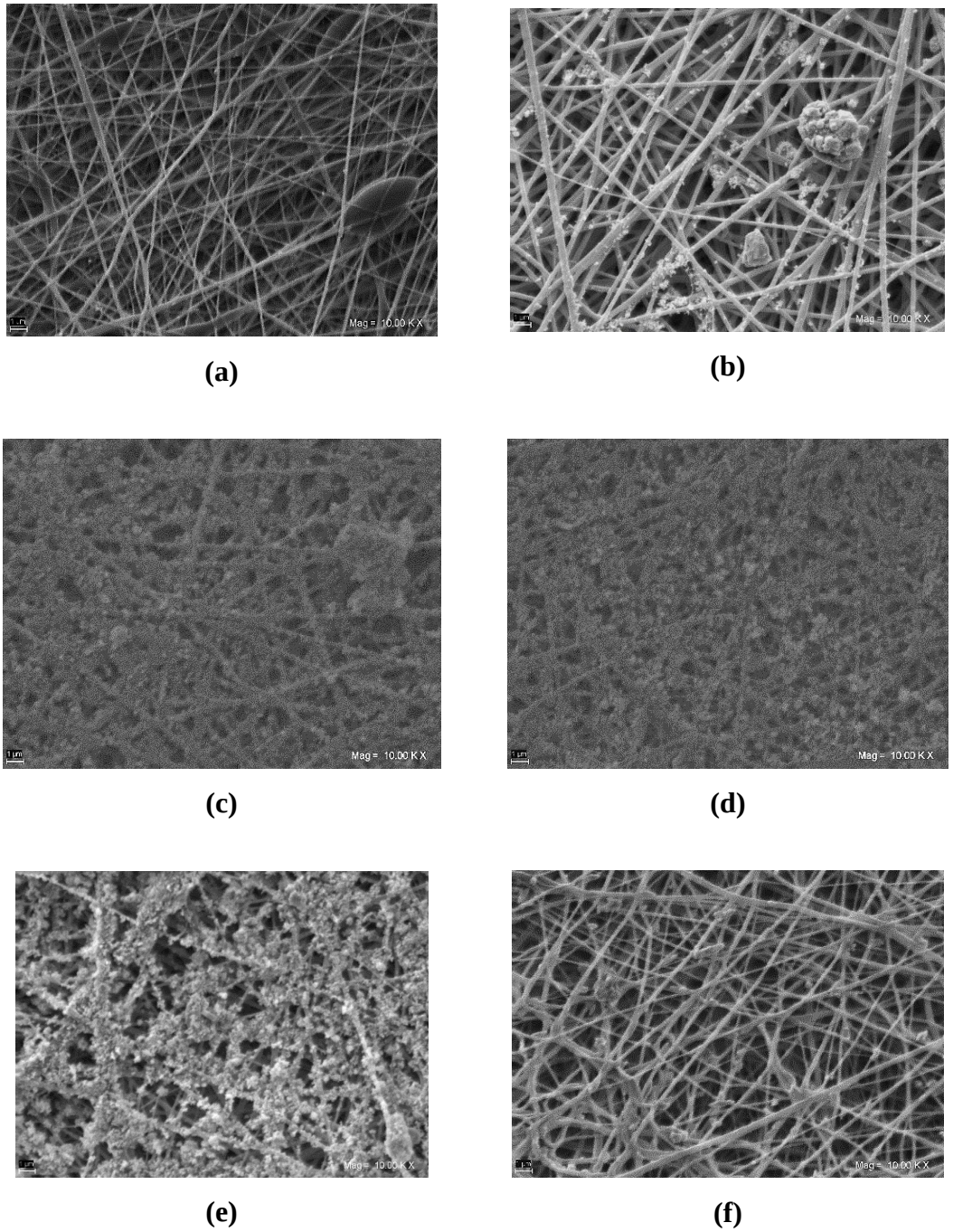


Figure 4.14: Electrospraying optimization studies **a)** 20 kV - 7 cm **b)** 25 kV - 7 cm **c)** 30 kV - 7 cm **d)** 20 kV - 12 cm **e)** 25 kV - 12 cm **f)** 30 kV - 12 cm.

Even though high amounts of agglomeration of the catalysts were observed on the SEM, 25 kV applied voltage and 7 cm distance between tip and collector were choosen as the parameters for further studies. After optimization of electrospraying parameters were conducted, electrospraying of nano particles onto NFs were made for different durations as demonstrated in **Figure 4.15**. Reason of changing the total electrospraying durations were for analyzing the effect of TiO_2 amount on PCO efficiency.



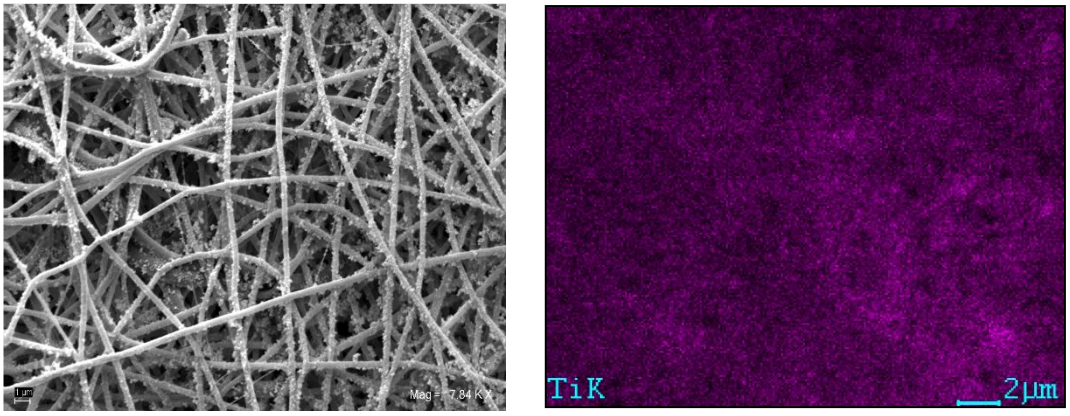
(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 4.15: SEM images of produced filters **(a)** Pure TPU NF **(b)** e-20 filter **(c)** e-40 filter **(d)** e-60 filter **(e)** e-180 filter **(f)** Sandwich Filter.

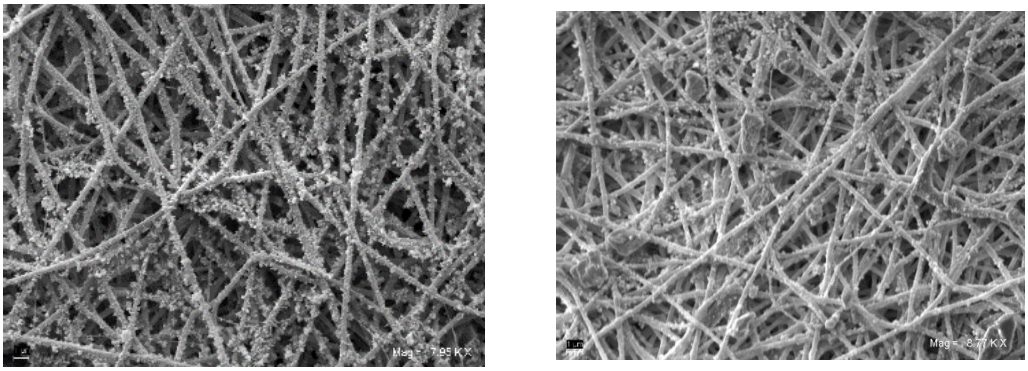
Although, e-20 and e-40 seems like the best results, all of these filters except pure NFs were performed in the reactor against VOCs. High agglomeration can be seen on e-60 and e-180 filter due to the long duration of electrospraying. The best TiO_2 distrubition result from the electrosprayed filters were accepted as e-40 filter and for this filter EDX Mapping analyze was conducted as can be seen in **Figure 4.16**.



(a) **(b)**

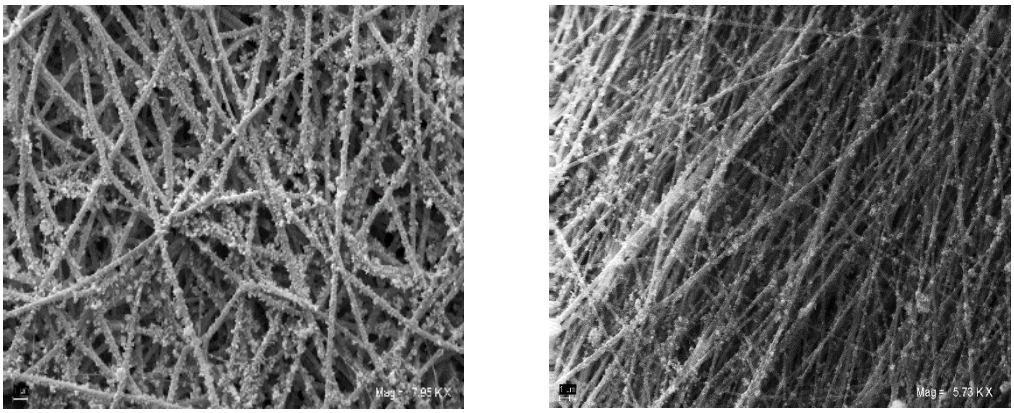
Figure 4.16: **a)** e-40 filter SEM image **b)** e-40 filter EDX mapping image.

For analyzing the adhesion property of NPs and NFs to each other and substrate, two different tests were applied to filters. Firstly, these filters were immersed in the distilled water and magnatically stirred under 0.04 Pa for 30 minutes. The SEM images for this study is demonstrated in **Figure 4.17**. Another adhesion test was applied under high air flow. This test was under 12 m/s air flow speed and continued for 5 minutes. Air flow test is showed in **Figure 4.18**.



(a) **(b)**

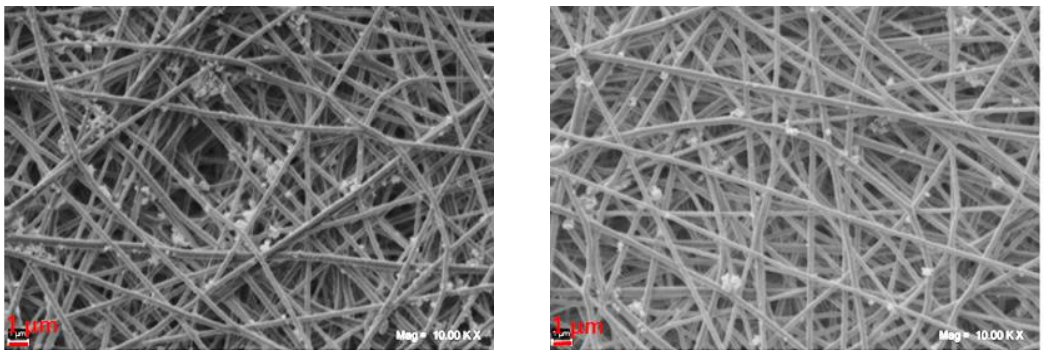
Figure 4.17: Adhesion property test with water **a)** Before **b)** After.



(a) **(b)**

Figure 4.18: Adhesion property test with air **a)** Before **b)** After.

According to these adhesion property tests, it can be said that, these TiO_2 NPs were stable on the surface of NFs which were not influenced for both tests. It was also studied on the effect of PCO reactions on the morphology of filter by examining the SEM images of the samples before the reaction and after the reaction as demonstrated in **Figure 4.19.**



(a) **(b)**

Figure 4.19: Effect of PCO reaction on the structure of the filter
a) Before the reaction **b)** After the reaction.

These SEM images prove us that, TiO_2 distribution and dispersion was not affected from UV illumination. NFs were still stable and any deformation was not observed.

4.3.2 Physical characterization of the filters (Air Permeability)

For physical characterization of the filters, air permeability tests were done for analyzing the air permeability property of the filters which is an important parameter for filtration applications. Air permability analyzes were done according to EN-ISO 9237 standart by using PROWHITE AIRTEST II machine as shown in **Figure 4.20**.

Figure 4.20: Air permeability test device.

Two measurements were done on the nanofibrous filter, and it was taken the average value of these measurements. Besides the nanofibrous filters, it was also performed only NF structure. Results of these studies are shown in **Table 4.2**.

Table 4.2: Air permeability properties of produced filters.

Filter	1st Measurement (mm/s)	2nd Measurement (mm/s)	Average Value (mm/s)
Only NF Structure (30 min)	53	55	54
Only NF Structure (1h)	17	19	18
Only NF Structure (2h)	16	18	17
e-20	19	22	20
e-40	31	25	28
e-60	15	32	23
e-180	9	29	19
Sandwich	25	28	27

As it can be seen from **Table 4.2** electrospun 2 hours of NF production were resulted as an air permeability property around 22 mm/s. For understanding the effect of NF

thickness on the air permeability property, it was also studied on production and testing of an hour and 30 minutes electrospinning. Air permeability properties were same for NF structure which was electrospun for an hour and 2 hours. However, NF structure formed from 30 minutes of electrospinning demonstrated that air permeability values increased from twenties to fifties. This corresponded to more than double times of 1 hour and 2 hour studies.

In addition to these measurements, HEPA filters were tested too. HEPA filters are widely used as particulate filters in typical aircrafts for cabin air filtration. These tests were done for understanding and creating a reference point for air permeability tests of the produced filters. Couple of measurements from different sides were done on the HEPA filter in order to examine the distrubition of glass fibers among the filter was homogenous or not. It was obtained that the fiber structure was very homogenous among the filter and air permeability values were same at every side of the filter. 75 – 76 mm/s were the air permeability of HEPA filters which was so close to 30 minutes electrospun NF mat air permeability value.

4.3.3 Characterization of specific surface area (BET)

BET was used as the method for determination of specific surface area. BET theory is a method that explains the adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of the material. Two samples were characterized according by BET. These samples were e-20 and e-60 filters. The characterization results are given in **Table 4.3**.

Table 4.3: BET results of the nanofibrous filters.

Sample Code	Electrospraying Time (min)	TiO2 Content (%)	Surface Area	Structure
e-20	20	0,5	849 m^2/gr	Mono
e-40	40	1	Tbd	Mono
e-60	60	1,5	821 m^2/gr	Mono
e-20	40	1	Tbd	Sandwich

As BET tests, e-20 and e-60 filters demonstrated similar surface area properties which were around 820 – 840 m^2/gr. This value is a quite good property as surface area and these test will be done for the rest of the filters.

5. TESTING OF NANO FIBROUS FILTERS FOR REMOVAL OF VOCs

5.1 Purpose and Design of Experimental Study

Meal services, bioeffluents, cleaning agents, and painting materials used in aircraft cabin expose Volatile Organic Compounds (VOCs) in the aircraft cabin. Especially for long duration flights, these VOCs has several effects on crew and passenger comfort and health. The environmental control system with HEPA filters in aircrafts does not have an ability to remove the VOCs with the current technology. The purpose of this chapter is to introduce a home-built VOC test system with UV-LEDs and to investigate the photocatalytic performance of nanofibrous filters with TiO_2. VOC test system is built to integrate either UV-Lamp and UV-LEDs to the photocatalytic reactor as a light source to study both of the light sources applicability. Several parameters such as light intensity, VOC type and concentration etc. were investigated and reported in a detailed fashion in this chapter.

5.2 VOC Test Sytem

The preliminary studies within the home-built VOC test system is performed with UV-lamp due to the well established literature on several VOCs with this light source. The 1st generation UV-lamp experimental set-up used in VOC removal tests were a home-built system and it is shown in **Figure 5.1**. There were two gas tubes at the experimental set-up. One of these tubes, which is labelled as (1), was used as diluent gas such as nitrogen or dry air and as VOC source, smaller gas tubes comparing to carrier gas were used which is labelled as (2). These tubes were certificated and purchased commercially for ethanol, benzene and toluene by varying concentrations. To control the speed of flow through in the test set-up, mass flow controllers (MFCs) were integrated to the system and labelled as (3, 6 and 9). Sensitivity of the MFCs were 50 mL/min and flow speed can be varied from 50 mL/min to 10 L/min. Mixing chamber was used to mix the diluent gas and VOC source in a desired VOC

concentration. For inhibiting adhesion of VOCs on the inner surface of mixing chamber, it was made of aluminium which is similar to VOC gas tank tube. Mixing chamber's volume was around 4 liter and it can resist until 7 – 8 bar pressure values. 3 photoionization detectors (PIDs) were used for analyzing the carbondioxide and VOC concentrations during the tests. One of the PIDs was carbondioxide sensor which is labelled as (8) and the others were the PIDs which are labelled as (5, 10) and also reffered as VOC sensors. Photocatalytic reactor is labelled as (7) demonstrates the region which the photodegradation of VOCs occur under UV source. The performance tests were performed in the reactor to investigate the efficiency of nanofiber filters.

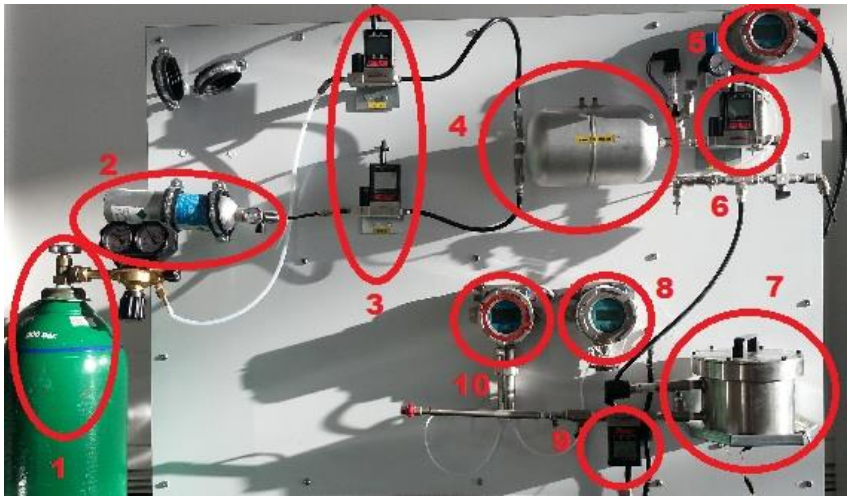


Figure 5.1: 1st generation experimental set-up.

Four traditional fluoroscent UV lamps with 365 nm wavelength were used in the test system as light source, and these light sources can be seen in **Figure 5.2**. These lights were controlled from the software and it was applicable to turn on the required number of the lights for changing the study parameters.

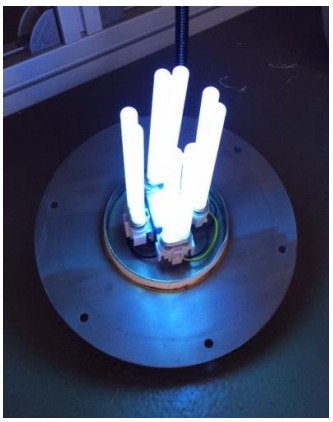


Figure 5.2: Traditional fluorescent UV lamps used in 1st generation reactor.

The PCO activity measurements were investigated with a standard recipe for the effectiveness. The basic steps of the test procedure are listed as below:

- Purging the lines with nitrogen to remove possible VOC contaminants and other pollutants
- VOCs was provided from current concentrated source tank
- VOC was mixed with diluent gas in mixing chamber
- Flowing & Mixing until reaching to desired VOC concentration value in mixing chamber
- Flow into the reactor at set flow rate
- Waiting for adsorption of VOCs without in a dark period
- UV illumination was begun, and PCO reactions were started
- Out from reactor
    - To VOC sensor
    - To CO_2 sensor
    - To sampling tubes (Active Carbon)

Since VOC gases tend to react with polymeric based materials in which those would directly affect the tests and performance analyzes. Since inhibiting such undesirable reactions, the materials for the connections and the parts were choosen as non reactive materials with VOC gases such as teflon material. These teflon materials were covered with stainless steel against any leakage that might occur on the teflon material. Aluminium was choosen for mixing chamber but reactor was produced by stainless steel.

Active carbon sorbent tubes were used as the sampling tubes shown in **Figure 5.3**. Active carbon tubes adsorbs the gases inside the carbons by transfering the gas phase into solid phase. Then these solid phase of VOCs were exposed to some chemical processes and delivered to GC/FID analyzer. The analyzer mesurements give us the total amount of PCO performance of the nanofiber filters.

Figure 5.3: Active carbon sorbent tubes for sampling.

The UV-Lamp study is performed to establish the VOC test system applicability for testing such a system at required properties. Then a UV-LED VOC test system is studied. Since aircraft cabins undergo large vibrations and needs several hours of lifetime the system needed to be re-designed with a light source which is more aircraft environment friendly and also reliable and efficient. UV-LEDs which does not have any mercury as a hazardous air pollutant, and long lifetime (more than 50K hours) posses a unique alternative light source.

The home-built test system is re-designed and built with UV-LEDs which is referred as 1st generation UV-LED test system. In this test set-up only the light source and photoreactor was changed but then the 2nd generation test system is built in a automated and controlled way.

In 2nd generation UV-LED system, some additional technologies was added to system such as an in-situ monitoring VOC detection system. The specific parts of the new test set up can be mentioned as the mass flow controller (MFC), VOC generator and mass spectrometry (MS). 2nd generation UV-LED system is shown in **Figure 5.4**. MFC was used for controlling the speed of dry air. Speed directly affects the concentration rate of VOC in the system. MFC could be arranged to 1 lt/min as maximum flow rate.

Figure 5.4: 2nd generation UV-LED system built with an in-situ VOC generation and detection system.

A VOC generator is designed and built which can use liquid sources of VOC and the liquid VOC source was transferred to gas phase by the effect of high flow rate of diluent gas. The system allows to feed two different VOCs in the reactor and which can be used as either to test two VOCs simultaneously in the system or can be used as one VOC and one humidity generator. To obtain concentration levels of VOCs in parts per million (ppm), VOC liquid was sent to system very slowly, and transfers to gas phase by evoporation. VOC containing diluent gas was sent to reactor from a special line which was appropriate for varying the temperature of inner side of connection for inhibiting the condensation of the VOC gas.

Mass Spectrometry (MS) was used to understand the degradation mechanism and rate of VOCs in the photoreactor. This device was ordered and shipped from Harrington company which is a product of United Kingdom. MS instrument performs the VOC detection analysis during the photocatalytic degradation during active and passive modes and this helped to understand the kinetics of the degradation mechanism as well. The instrument uses 12 mL/min gas from the system for analyzing the results under vacuum environment. A turbo pump was integrated into MS with an addition of external pump to apply vacuum inside of the MS. External pump was the main starter of pumping and then after a limit point turbo pump was functioning. Gas measurements for inlet and outlet concentrations were done by MS. Gas firstly entered

to the reactor and then the flow continued to MS from outlet of the reactor. Because of existence of the reactor, gas samples were taken from the outlet of the reactor. In the beginning of sending of VOC including gas to the reactor, the outlet was opened as well for releasing the gas filling the reactor. Since adsorption may occur on the filter media, it was waited for the stabilization of the system. After balancing of the system for ensuring the stability of the system, waiting duration was extended, and this stabilized value was assumed as inlet value of the system which was the initial concentration of the VOC. According to PCO process, after pressuring the reactor and waiting for a while for demanded illumination time or continuously flow, as soon as outlet flow was opened after PCO reactions, MS analyzes were begun. The VOC value taken from outlet was estimated as final concentration. Comparasion between outlet value and inlet values give us the performance results of the filter. The flow chart of the process is given in **Figure 5.5**.

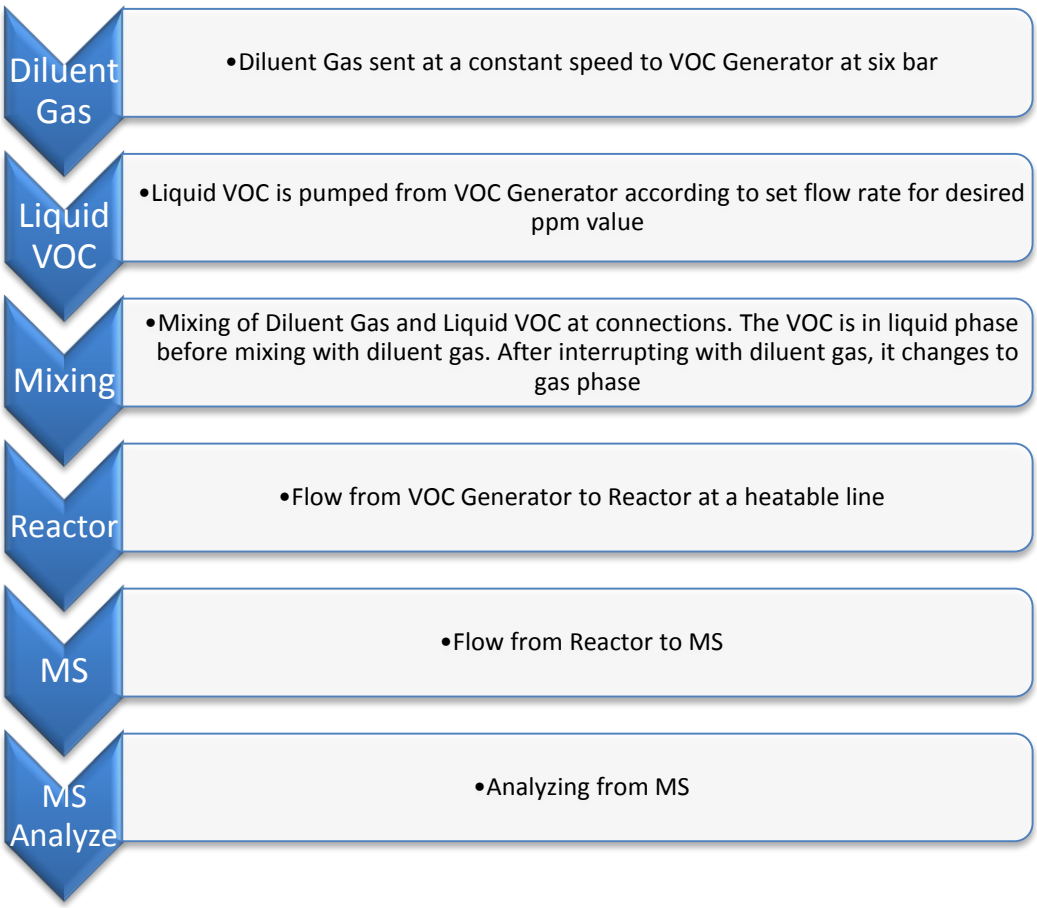


Figure 5.5: Flow chart of 2nd generation UV-LED system.

Simulating the aircraft environment requires circulating the air through reactor continuously. For air circulation, an air pump was supplied and connected to test system as demonstrated in **Figure 5.6**.This pump was connected to inlet and outlet of the reactor which works as a trasnfer pump and air from outlet was vacuumed and then pumped into reactor from inlet hole. The circulation rate can be varied from two to ten cycle in ten minutes.

Figure 5.6: Circulation pump.

The effectiveness of circulation pump through any leakage was checked with two studies without any filtration study.

5.3 Reactor Design With Various Light Sources

For improving the performance of the system and obtaining more efficient photodegradation , the system was developed by changing the light sources. The studied photoreactors can be listed as below:

- 1st generation UV lamp reactor: 4 UV lamps with 9,2 W total output power were used in a circular stainless steel photoreactor
- 1st generation UV-LED: 56 UV-LEDs with 19 mW maximum output power per each
- 2nd generation UV-LEDs: high power, efficient 24 UV-LEDs with 600 mW maximum output per each in a circular stainless steel photoreactor

5.3.1 1st Generation UV-lamp reactor

This reactor was designed for using of traditional fluorescent UV lamps with a cylindiric geometry which has its cap at the bottom.UV-Lamp reactor was designed with the following dimensions of 22x18 cm. and total volume of the reactor was 7,5 liter. A support for filter was mounted in the reactor which allowed to a nanofibrous

filter with dimensions of 45x18 cm with a surface area of 756 cm^2. These filters were attached to the supports. The support for filter media is shown in **Figure 5.7**.

Figure 5.7: Support for nanofibrous filter.

In the beginning silicon based material was used for covering the electricity connection of the lamps. During the performance tests, VOC concentration increased with time and the reason of that was understood as VOC emission from silicon material. So, this silicon based material was removed and changed the connection system by covering this area with teflon material which was not reactive with the gases. There were two propes in the reactor for measuring the instant pressure and temperature simultaneously.

Four fluorescent UV lamps in the reactor with a total power of 9,2 W, and it was also avaible to use desired number of lamps by controlling the software. Inlet and outlet position of the reactor which is illustrated in **Figure 5.8** was designed for letting the entire of concentrated air flew through the filter.

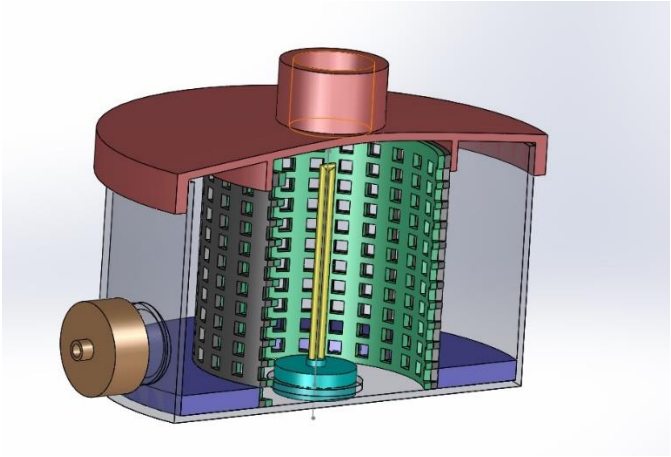


Figure 5.8: Traditional fluorescent UV lamp reactor.

5.3.2 1st Generation UV-LED reactor

For competitiveness in filtration industry, next generation photocatalytic systems needs to be more flexible and energy efficient instead of classical ultraviolet (UV) excitation sources due to their low efficiency, harmful side effects, difficulties in operating conditions, shorter lifetime and broader spectral wavelength. To overcome difficulties related with classic UV excitations sources, UV-LEDs are promising devices which can be made up of gallium arsenide (GaAs), gallium arsenide phosphide (GaAsP), gallium phosphide (GaP), or indium gallium nitride (InGaN) covered with resin. Higher efficiency and minimal harmful effects compared to UV fluorescent lamps are attractive from the reactor design perspectives. Especially photocatalytic oxidation reactors proposed to use in aircraft cabin environment needs to be designed compact, efficient, chemically and biologically stable and serve for long operation hours. Considering the LED prices drop in the market in the last few years, especially UV-LEDs with high powered options would be a good option to fluorescent lamps used in photocatalytic systems.

From this perspective a new photoreactor with UV-LEDs were designed and built from stainless steel with the following dimensions:.

- Diameter of base 17 cm
- Height 13.4 cm
- Diameter of Cover Cap 19.5 cm

Especially for gas studies one of the most challenging part was leakage at the system. Leakage controls were done which was also including harsh condition applications for ensuring the reliability of the reactor and connection parts. The reactor was subjected to totally 7 bar pressure gas for 72 hours. For realiability another control by filling the reactor with 5 bar pressure gas was also performed. As a reliability test approximately 8 lt of dry gas was filled into reactor and kept the system for overnight. According to these both controls no decrease on pressure was obtained and reactor was checked as controlled and reliable to use. The elctrical connection of the UV-LEDs to electric source was achieved by using board system

The air flow inside the reactor was from an inlet and outlet which were parallel to each other. Inlet was over the outlet and between this hole, filter material was located as shown in **Figure 5.9**. Distance between inlet and outlet was 30 mm.

Figure 5.9: Inlet (upper) and outlet (lower) of the reactor.

For first generation UV-LED reactor 96 UV-LEDs which consist of Indium, Gallium and Nitrogen were ordered and shipped from Hong Kong. As a UV-A light source UV-LEDs had 365 nm wavelength and provide enough energy for activation of TiO_2. The connection of UV-LEDs to board was performed with proper materials which will not cause any VOC generation. The board that UV-LEDs were custom made in our laboratory which also allows to vary the number of UV-LEDs during filtration studies. The initial studies were performed with 40 UV-LEDs and due to lower efficiencies it was increased to 56 eventually. A detailed image of 1st generation UV-LED reactor system is demonstrated in **Figure 5.10**.

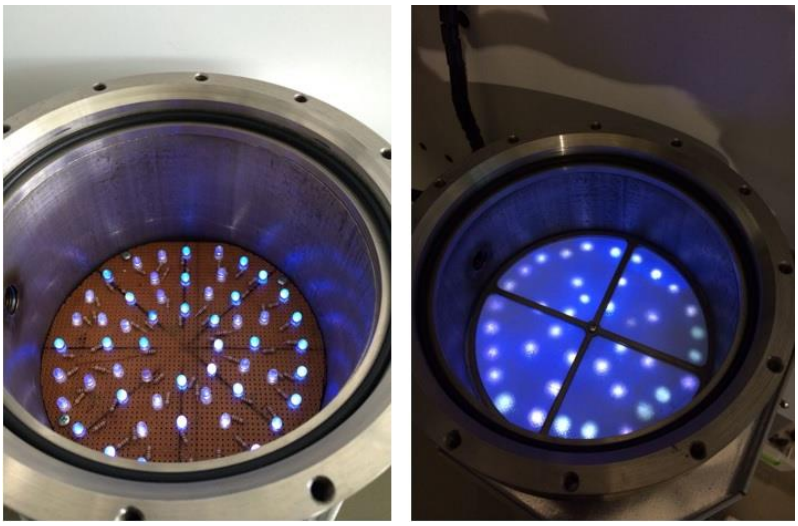


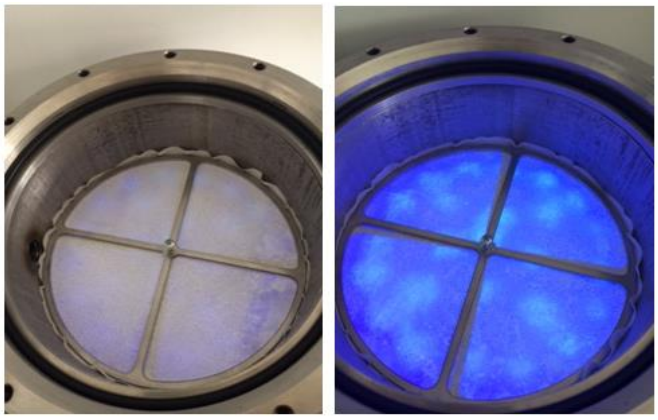
Figure 5.10: 1st generation UV-LED reactor system.

5.3.3 2nd Generation UV-LED reactor

1st Generation UV-LED studies proved that the achieved total power as 1,1 W was not enough for high efficiency. A new type of UV-LEDs from Nichia, Japan was found to be appropriate from literature surveys. Newly achieved UV-LEDs were efficient and high power compared to previous generation used in this study. With the same photoreactor these new 25 UV-LEDs were integrated. Electrical board had same dimensions with the previous LED system for avoiding change of the reactor.

These UV-LEDs were mounted on a board consists of aluminium composite material which was inert material. This board was located on the same place just like 1st generation reactor. Difference from previous board, there was not any holes on the board. Totally 25 UV-LEDs were mounted on this board. Since the location of the light sources directly affected the illuminated place of the filter, location of these light sources were so important. Every side of the filter must be illuminated to obtain the highest efficiency from the filter. On the other hand these areas must be illuminated homogenously on the filter. For this distrubition some calculations were made and according to these calculations, best places for UV-LEDs were decided.

Another problem lived in 1st generation studies was applied light intensity couldn't be varied. It was thought that for 2nd generation system, if it was possible to vary the applied light intensity, this could bring us an advantage by varying the light intensity which was another parameter for improving and optimizing the performance of the filter. The difference between minimum and maximum applied powers for 2nd generation UV-LEDs is shown in **Figure 5.11**.



(a) **(b)**

Figure 5.11: a) minimum light power **b)** maximum light power.

1st generation and 2nd generation UV-LED light sources were compared according to their illumination properties by changing the distance from LEDs. The measurement results are listed as shown in **Table 5.1**.

Table 5.1: Illumination properties of 1st and 2nd generation UV-LEDs.

Distance (cm)	1st Generation UV-LED Illuminated Radius (cm) / Area (cm^2)	2nd Generation UV-LED Illuminated Radius (cm) / Area (cm^2)
0,5	0,11 / 0,03	0,86 / 2,3
1	0,22 / 0,15	1,73 / 9,4
1,5	0,33 / 0,34	2,59 / 21,1
2	0,44 / 0,6	3,46 / 37,6
2,5	0,55 / 0,95	4,33 / 58,9
3	0,66 / 1,36	5,2 / 84,9

The illuminated area for farer studies made with UV-LEDs extends for 2nd generation UV-LEDs. Eventually, larger area under illumination has both of negative and positive effects on filter performance. Shorter distance studies

Although there is higher light intensity for smaller areas in shorter distances, it is expected . However, shorter distance from LEDs resulted in higher light intensity on the filter for the small pieces. As a result of this high light intensity this small areas were activated faster than farer studies.

Heating is the most serious problem of the UV-LEDs which influences life span of them. Besides life span of the LEDs, it also influences the temperature profile inside the reactor. Reaction kinetics occurred during PCO are very sensitive to temperature changes and elevated temperatures. If the reaction kinetics have influence due to this thermal gradient change, oxidation tests would not demonstrate the accurate properties of the filter. Temperature measurements in the reactor were studied as shown in **Figure 5.12** . These calculations were performed by holding thermocouple probe tip close to light sources for 15 minutes. This thermocouple could measure temperature instantly, thus it continiously could record the data as well. Temperature decrease from open top of the reactor was hindered by covering the top with a polymeric material. To simulate realistic conditions and investigate the temperature profile in the reactor a thermocouple was placed at 20 mm distance from the filter.

Figure 5.12: Temperature profile inside the reactor by a thermocouple.

Calculations were performed for three main light intensity levels containing 60 mW as minimum, 300 mW as mid-point and 600 mW as maximum which are corresponding to 1st level, 5th level and 10th level, respectively. Changes of reactor temperatures with changing power levels according to time are listed and showed in **Table 5.2**.

Table 5.2: Temperature changes depending on applied power.

Duration (Min.)	1st Level	5th Level	10th Level
0 – 1	25,9 – 27,0	27,9 – 30,3	29,8 – 41,4
1 – 2	27,3 – 28,3	31,2 – 33,2	44,6 – 52,5
2 – 3	28,6 – 29,3	33,6 – 34,6	54,6 – 59,1
3 – 4	29,5 – 30,0	34,9 – 35,7	60,6 – 63,6
4 – 5	30,2 – 30,6	35,9 – 36,4	64,6 – 66,5
5 – 6	30,7 – 31,0	36,7 – 37,1	67,0 – 68,5
6 – 7	31,1 – 31,4	37,3 – 37,6	68,9 – 70,2
7 – 8	31,5 – 31,7	37,8 – 38,1	70,5 – 71,6
8 – 9	31,8 – 32,0	38,2 – 38,5	71,9 – 73,0
9 – 10	32,1 – 32,3	38,6 – 38,9	73,3 – 74,4
10 – 11	32,4 – 32,6	39,0 – 39,2	74,7 – 75,5
11 – 12	32,6 – 32,8	39,3 – 39,6	75,8 – 76,6
12 – 13	32,9 – 33,0	39,6 – 39,9	76,8 – 77,6
13 – 14	33,1 – 33,3	39,9 – 40,2	77,8 – 78,5
14 - 15	33,3 – 33,3	40,3 – 40,6	78,8 – 79,9

Temperature changes were feasible for 1st level and 5th level studies. In the end of 15 minutes for 1st level studies, temperature was 10 ^{o}C higher than initial temperature value of the reactor which can be acceptable. The temperature values were stable and no increase was observed after 14th minute. Because of application of higher power, temperature increase was faster than 1st level during 5th level studies. Thus, temperature increase maintained for a longer duration and temperature increase was being observed even after 15 minutes. However, temperature increase trend was quiet low after 15 minutes. 10th level was the highest applicable power from LEDs. The temperature increase was dramatic in initial 15 seconds compared to 1st and 5th level studies. Temperature was approximately 80 ^{o}C and increase rate was observed as 1 ^{o}C/min during 15th minute of the test. Since the increase rate at 10th level was very high, this power was not applicable for PCO studies. The high levels of powers (such as more than 8th level) were not studied during filtration in this study.

5.4 VOC Removal Tests

In this section, the efficiencies of the produced filters with different properties were analyzed against ethanol, toluene and benzene. The properties of the filters were changed according to amount of catalyst loading, structure, and catalyst type.
1st generation fluorescent UV lamp, 1st generation UV-LED and 2nd generation UV-LED systems were performed for analyzing the effect of light source on performance of the filters within the VOC removal tests.

5.4.1 Performance tests of 1st generation UV-lamp system

Totally 4 UV lamps with maximum output power of 9,2 W were used during 1st generation fluorescent UV lamp studies. Ethanol, toluene and benzene were tested by using e-20 filter type under the same parametric values. The electrospraying duration created variable TiO_2 content over the NFs which would be expected to have an effect on the degradation capabilities of the catalyst. The initial concentrations of ethanol, toluene and benzene which could be reffered as low concentration were around 0,5 – 2 ppmv. The VOC containing gas was sent to the reactor after concentrating of the diluent gas with VOC in mixing chamber according to desired concentration level. PCO reactions were performed in the pressurized reactor with contaminated gas and the results which can be seen in **Table 5.3** were taken after 10 minutes from the

beginning of the reactions. These tests were performed by GC-MS analysis using adsorbent tubes as introduced in the previous sections.

Table 5.3: Performance tests of filters under UV-Lamp illumination.

VOC	Initial Concentration (ppm)	Efficiency (%)
Ethanol	10	93
Toluene	10	70
Benzene	10	55

Ethanol, toluene and benzene were removed from the reactor with varying efficiencies in 10 minutes. Although toluene and benzene were filtrated from the system, the highest removal rate was observed for ethanol because of the easily degradable chemical structure of ethanol.

5.4.2 Performance tests of 1st generation UV-LED system

UV-LEDs were begun to be used as light source for PCO applications because of their stability, long life span and non-toxicity. 1st generation UV-LEDs were mounted on the new generation reactor with smaller volume and the filters were tested with e-20, e-40 and e-60 against ethanol and toluene concentrated gases. Insufficiency of 40 UV-LEDs for the primary studies, number of LEDs were increased to 56 for improving the light intensity and increasing efficiencies of both filters and the system in the further studies.

5.4.2.1 Ethanol removal studies

Filters were tested under the illumination of 40 UV-LEDs from 20 mm away for 40 minutes. The filters chosen for performance tests were e-20 and e-40 and the removal efficiencies of the filters are demonstrated in **Table 5.4**.

Table 5.4: Removal efficiencies of the filters against ethanol (40 UV LEDs).

Filter	Initial Concentration (ppm)	Reaction Time (min)	Removal Efficiency (%)
e-20	1,06	40	28 (increase)
e-40	0,5	40	26

As can be seen on **Table 5.4**, final concentration of ethanol concentration was increased 28% according to initial concentration for e-20 study which might be a result of condensation of ethanol gases inner surface of the reactor. Disappearence of 26% of ethanol concentration taken from inlet was obtained during e-40 filter study. PCO efficiencies were considerably unsatisfactory due to insufficient illumination of 40 pieces of UV LEDs. Whereas the number of UV-LEDs had been changed during the optimization of the reactor; the dimensions of reactor, fabrication method of the filters, and process of the experiment had remained same.

The same performance tests against ethanol were repeated for the filters that used in previous study after optimizing the system by increasing the total number of UV-LEDs to 56. Homogenous distribution of light with higher intensity for illuminating the entire filter was achieved by increasing LED number. The tests were performed with e-20, e-40 and e-60 filters and they were illuminated with a distance of 20 mm from the LEDs. Removal efficiencies of the filters are shown in **Table 5.5**.

Table 5.5: Removal efficiencies of filters against ethanol (56 UV LEDs).

Filter	Initial Concentration (ppm)	Reaction Time (min)	Removal Efficiency (%)
e-20	2,388	40	89
e-40	0,5	40	34
e-60	0,5	40	14

Although total amounts of TiO_2 were higher for e-40 and e-60 compared to e-20, highest degradation of ethanol was achieved from e-20 filter due to agglomeration NPs at 40 and 60 minutes of electrospraying which has a negative effect on the total active surface area. Inhibition of agglomeration can enhance the performance of the filters with higher TiO_2 content. Consequently, performances were improved by increasing the number of UV-LEDs for both e-20 and e-40 filters as a result of higher light intensity.

5.4.2.2 Toluene removal studies

The same tests which were studied for ethanol were also performed for toluene as well in the same manner with same filters and test parameters. Toluene experiments were directly begun with 56 pieces of UV-LEDs.

The filters were exposed to UV illumination from 20 mm away for 40 minutes for low concentration levels which are detailed in **Table 5.6**.

Table 5.6: Removal efficiencies of filters against toluene.

Filter	Initial Concentration (ppm)	Reaction Time (min)	Removal Efficiency (%)
e-20	2,388	40	89
e-40	1,061	40	34
e-60	2,388	40	34

According to the studies, e-40 and e-60 filters had the same efficiency which was around 34% against toluene after 40 minutes. In ethanol removal tests, e-20 filter had the highest efficiency compared to e-40 and e-60 filters as obtained from toluene removal study as well. The reason of decreasing the efficiency for higher TiO_2 loading was estimated as formation of agglomeration of the NPs that decreases the total active surface, similarly observed in ethanol degradation.

5.4.3 Performance tests of 2nd generation UV-LED system

High power UV-LEDs were preffered as light source for PCO applications because of their higher properties compared to 1st generation UV-LEDs. A wider range of filters

deposited with Degussa P25 TiO_2 or modified TiO_2 were performed in 2nd generation UV-LED system against ethanol and toluene under different conditions.

5.4.3.1 Ethanol removal studies

Because of the intensity and importance of ethanol in the aircraft cabin environment, ethanol was mostly preferred for all of the produced filters. Catalyst type, deposited amount of catalyst and the structure were changed for understanding the effect of filter properties within ethanol removal tests. The light sources were arranged 15 mm away from the filter for each study which was performed for 10 minutes in a pressurized reactor without any flow.

After the system upgrade to a continious monitoring of degradation through MS and VOC supply supply by generator the efficiency tests were performed at higher concentrations of VOCs.

First tests were performed for analyzing the effect of amount of TiO_2 loading on filter efficiency under illumination of LEDs for 10 minutes as a batch type test with 4th level power which is corresponding to 240 mW arranged output power per each as shown in **Table 5.7** and **Figure 5.13**. Initial concentrations were arranged around 240 ppm and dry air was setted as carrier gas during the studies.

Table 5.7: Ethanol removal performance of TiO_2 loading amount.

Filter Type	Initial Concentration (ppm)	Removal Efficiency (%)
e-20	245	19
e-40	248	9
e-60	231	6
e-180	237	4
Sandwich	243	7

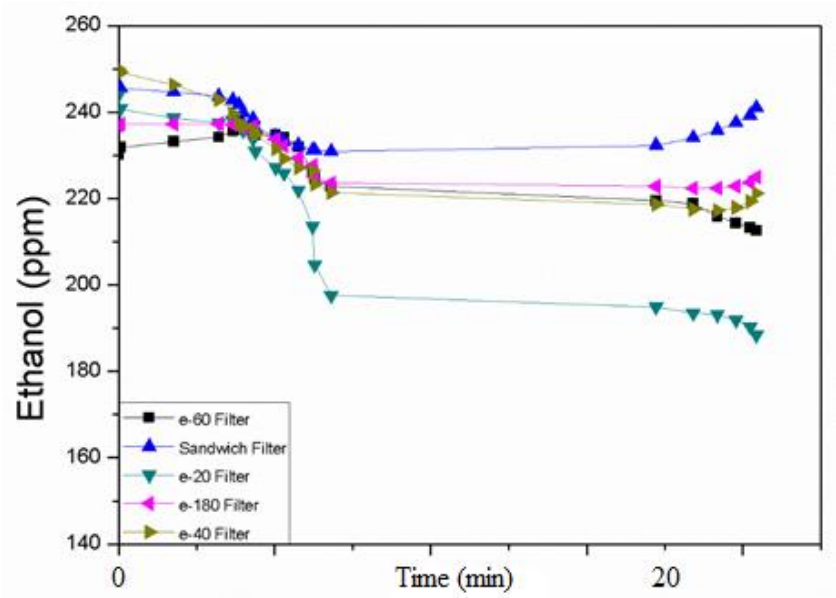


Figure 5. 13: Ethanol removal performance by changing TiO_2 loading amount.

Filters demonstrated different efficiency values which varies between 4% to 19% for equal test durations. e-20 filter removed the highest amount of ethanol from the system compared to other filters. Obtaining highest efficiency from the lowest catalyst loading were the results of agglomeration and non homogenous distrubition of the TiO_2 NPs which decreases the active surface area. Consequently, this study proves the importance of active surface area on the PCO applications. Performance of the filters for higher amounts of catalyst loading can be improved by inhibiting the agglomeration of NPs.

In literature studies made with PCO and UV-LED, the contaminated gases were exposed to light for longer durations which were around several hours. In this study, 260 ppm and 190 ppm concentration levels were setted for ethanol and toluene, respectively and e-60 filters were tested for 5 hours in a batch type reactor. Performance tests of the filters are shown in **Table 5.8** and **Figure 5.14** as table and graph form.

Table 5.8: VOC removal performance tests of e-60 filter for longer duration.

Filter Type	Target VOC	Initial Concentration (ppm)	Removal Efficiency (%)
e-60	Ethanol	260	48
e-60	Toluene	190	28

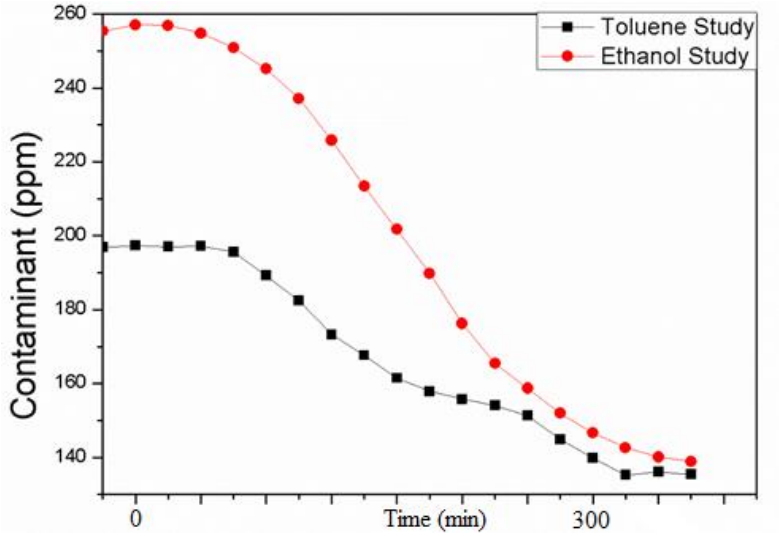


Figure 5. 14: Long duration studies of e-60 for removal of ethanol and toluene.

The same filter can perform with varying efficiencies against different VOCs due to changing chemistry and structure of the each VOC under the same conditions. Final concentration of the ethanol was almost half of the initial concentration after 5 hours of PCO test. Even though, the same filter was tested against toluene as well, degradation level of toluene decreased to 28%.

Another study was analyzing the performances of doped TiO_2 deposited filters between each other, they were not only compared with each other but also compared with filters which were deposited with Degussa P25 as catalyst. Since the doped filters were arranged for comparing with e-60, 60 minutes of electrospraying were done for production of modificated TiO_2 containing filters. Distance between filters and the LEDs which were setted for 240 mW output power per each was arranged as 15 mm and 2 bar pressurized reactor with concentrated gas around 230 ppm were illuminated for 10 minutes. The more explanatory information about the tests can be seen in **Table 5.9** and **Figure 5.15**.

Table 5.9: Comparison of catalyst against ethanol under same PCO conditions.

Filter	Initial Concentration (ppm)	Removal Efficiency (%)
Degussa P25	231	6
Non-doped	210	17
Fe-doped	250	36

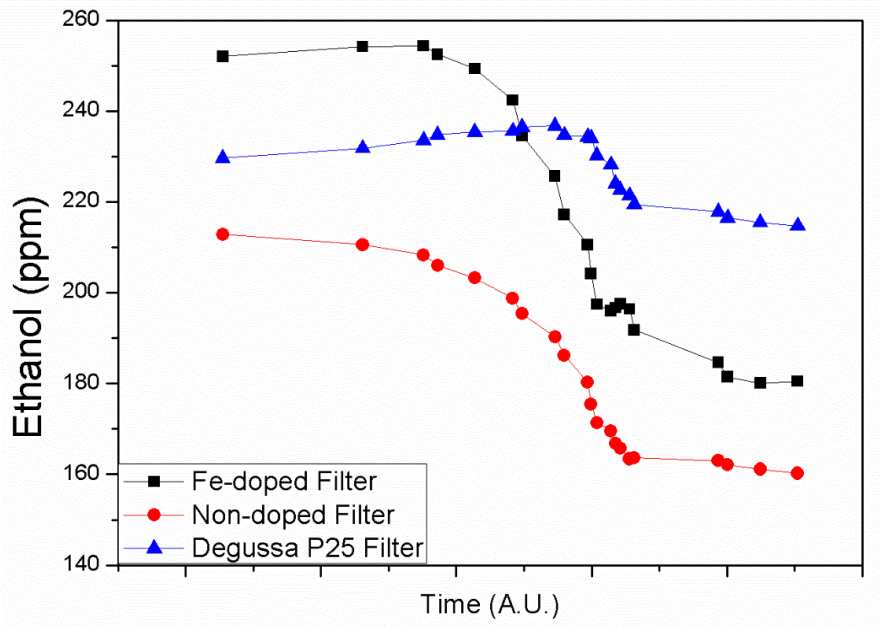


Figure 5.15: Comparison of catalyst against ethanol under same PCO conditions.

This study demonstrated that modification of the TiO_2 had positive effect on enhancing the performance of the filters. Fe-doped TiO_2 was six times more efficient compared to Degussa P25 against ethanol. Non-doped filter prepared with doped TiO_2 without any doping material addition showed an efficiency around 17% which is triple times of Degussa P25 deposited filter. These studies are the proof of the effect of catalyst on the filter.

It was also studied with different doping materials beyond the Fe doping for observing the efficiency of different catalysts and comparision of doping materials with each other. In this study, N-doped as nitrogen doping and co-doped which was a combination of Fe and N doping material were tested against ethanol as shown in **Table 5.10**. Distance was arranged as 15mm and 10 minutes of irradiation was applied

in the pressurized reactor. Performance results of the filters are showed in **Figure 5.16** with changing time.

Table 5.10: Effect of doped material on removal of ethanol.

Filter Type	Initial Concentration (ppm)	Efficiency (%)
Non-doped	210	17
Fe-doped	250	36
N-doped	200	12
Co-doped	180	11

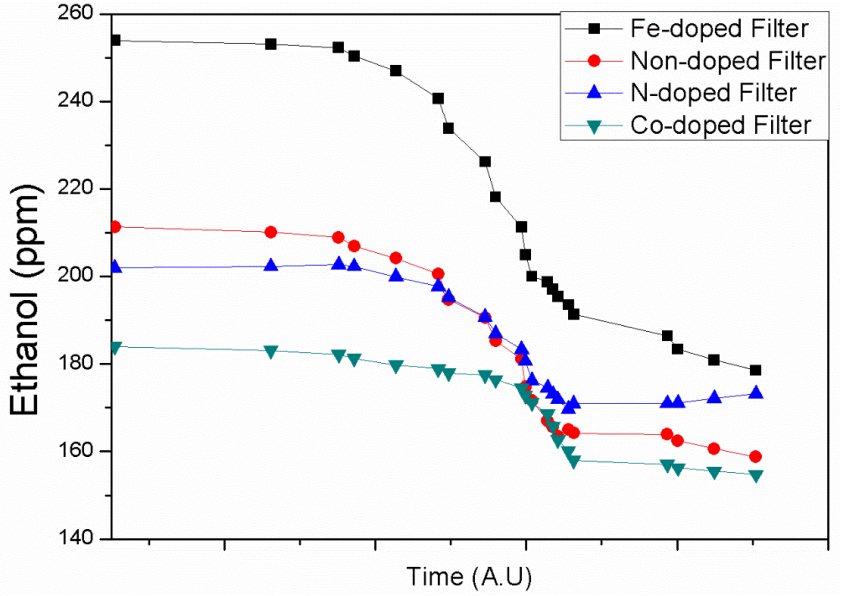


Figure 5.16: Effect of doping material on removal of ethanol.

Performance results of Non-doped, N-doped and co-doped were quite close to each other. Although the efficiencies of these filters were less than Fe-doped filter, they were higher than Degussa P25 deposited filters. Modificated TiO_2 resulted with high efficient filters and by changing the doping materials, performance of the filters were varied.

From previous studies, Fe-doped filter was observed as the highest efficient among the doped filters. Because of the effect of study parameters during PCO reactions, these parameters were changed for enhancing the activity of the filter. One of the most significant system parameter that influencing the filter efficiency is the applied light

intensity onto the filters. Thus, light intensity was varied by changing the current from the potentiometer without any change on distance or ambient conditions. Two different applied power values which one was 120 mW as lower and the other one was 360 mW as higher power compared to our standard 240 mW studies. **Table 5.11** and **Figure 5.17** explains the study properties.

Table 5.11: Effect of light intensity on removal of ethanol for Fe-doped filters.

Applied Power (mW)	Initial Concentration (ppm)	Efficiency (%)
120	200	30
240	250	36
360	200	23

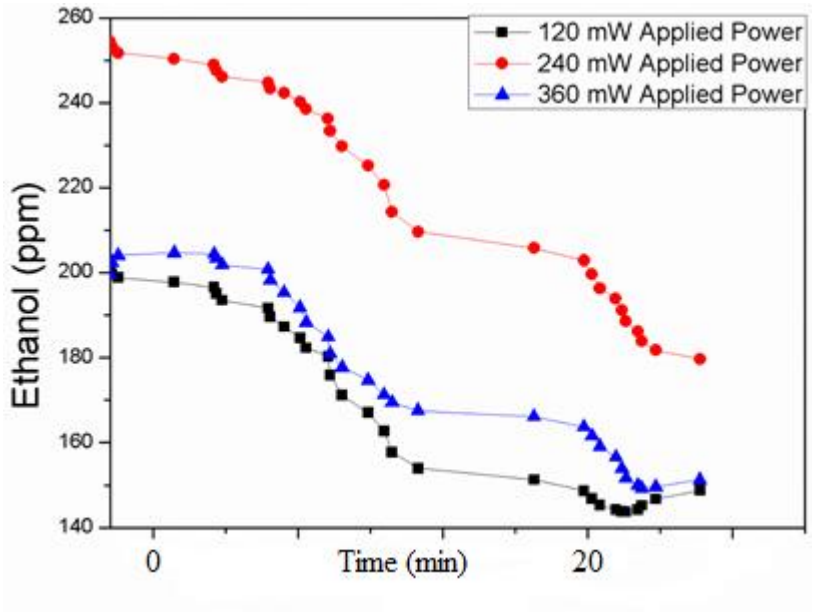


Figure 5. 17: Effect of light intensity on removal of ethanol for Fe-doped filters.

According to this study, 240 mW has the highest efficiency value comparing to lower and higher one. Although, the best efficiency was expected from highest applied light intensity, it had the lowest due to the elevated temperatures as a result of heating of LEDs in the reactor.

5.4.3.2 Toluene removal studies

In this section, similar tests performed against ethanol were repeated for toluene as well because of the important effects of toluene sourced from engine and jet fuels on cabin crew and passengers in aircrafts cabins.

Filters with different amounts of TiO_2 loadings were tested by varying distances between 5 mm and 15 mm for obtaining the optimum TiO_2 loading and distance parameters. Toluene removal efficiencies and studies were demonstrated depending on filter type in table and graph form in **Table 5.12** and **Figure 5.18**. UV-LEDs illuminated e-20, e-40, e-60, e-180 and sandwich filters from 15 mm away.

Table 5.12: Different filters for removal of toluene with 15mm distance.

Filter Type	Initial Concentration (ppm)	Efficiency (%)
e-20	170	-
e-40	170	9
e-60	233	28
e-180	233	18
Sandwich	200	23

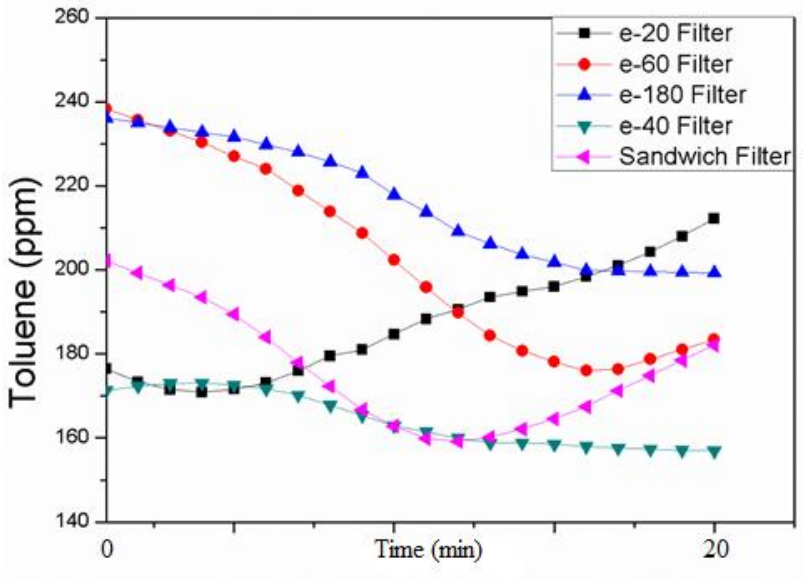


Figure 5. 18: Different filters for removal of toluene with 15mm distance.

Because of the more complicated chemistry, the reactions observed from toluene was different compared to ethanol degradation studies. E-20 filter was not effective against toluene, in fact higher amount of toluene was observed as final concentration compared to initial concentration after PCO reaction for 10 minutes. However, efficiencies around 10% – 30% were acquired from e-40, e-60, e-180 and sandwich filters. Even though total catalyst loading on the surface of the filters were the same for sandwich and e-20, the efficiency values were quiet different, sandwich also had the same amount of TiO_2 loading in the filter with e-40, 23% degradation of ethanol was observed for sandwich filter while 9% was monitored for e-40. E-60 filter had the highest removal rate by 28%.

In this test, filters were studied for 10 minutes with 5 mm away from the light sources for comparision of distance effect on removal efficiency of toluene for the same filters with previous study as can be seen on **Table 5.13** and **Figure 5.19**.

Table 5.13: Different filters for removal of toluene with 5mm distance.

Filter Type	Initial Concentration (ppm)	Efficiency (%)
e-20	230	14
e-40	234	23
e-60	234	23
e-180	195	25
Sandwich	170	17

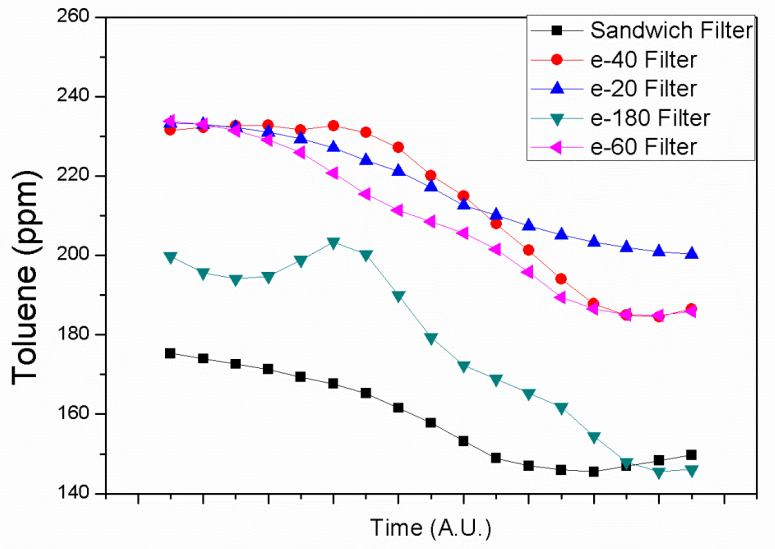


Figure 5.19: Different filters for removal of toluene with 5mm distance.

As can be seen in **Table 5.13** and **Figure 5.19** filters demonstrated different removal rates of toluene which were higher compared to 15 mm studies. Toluene was degraded with the same rates which were around 25% for e-40, e-60 and e-180 filters. Degradation rate of toluene for e-40 increased dramatically for 5 mm studies compared to 15 mm, on the other hand e-60, e-180 and sandwich filters had almost same removal rate of toluene. According to graph highest efficiency value was around %25 which was obtained from e-180 filter. e-40 and e-60 showed the same performance against toluene at same initial concentration. In despite of total amount of TiO_2 in sandwich filter was equal to e-40 filter, degradation rate of toluene for sandwich filter was less than it due to the total TiO_2 loading on the upper surface of the filter which could be lighted directly was half of the e-40 filter.

6. CONCLUSIONS AND RECOMMEDIATONS

Passenger products, diffusion from meal and beverage services, bio-effluents, combustion by-products are the primary reasons of formation of Volatile Organic Compounds (VOCs) in aircraft cabin environments. VOC containing air reduces flight comfort and it can be harmful for passengers health. Headaches, dizziness, nausea, nose and throat irritation, loss of coordination, damaged to liver, kidney, central nervous system, and cancer can be caused by the high concentration of VOCs. Hence, cabin air filtration is one of the most important system which filtering contaminated air and supporting clean air into the aircraft cabin. Especially, advanced filters were improved for removing of ethanol, benzene and toluene which are found as varying concetrations of pollutants in the aircraft cabin environemnt. Current technologies are not sufficient for removing all VOCs from the cabin, and there are still some diffuculties for maintanence process and economical sustainability problems. PCO is a promising technology for overcoming from this challenging situations of current technologies.

Aim of this study was designing, developing and testing of a high efficient nano fibrous filters for removal of some target VOCs under illumination of UV light by using PCO method. The fabrication and tests of the filters were continued as optimizing the system. Nanofibrous filters were manufactured by combination of electrospinning and electrospraying for production of NFs and depositing of catalysts. As a novel study, light source was changed to LED which is a novel technology for healthier and sustainable applications.

The experiments demonstrated us that, the nanofibrous filters had different efficiencies against choosen VOCs under illumination of traditional fluorescent UV-lamp and UV-LEDs. Efficiencies of the filters were changed by varying the testing parameters and filter properties such as illumination time, light intensity, TiO_2 loading, doping material. By changing the applied power, ligh intensity value was increased which improved the performance of the filters. However, light intensity value after a point

decreases the efficiency because of elevated temperatures in the reactor. Although, TiO_2 loading was one of the most important parameter for enhancing the filter against VOCs, it must be avoided from agglomeration of the NPs which decreases the total active surface area. Modification of the filter was made by doping of the filter with different materials such as Fe, N, CO as combination of Fe and N and non-modified but self produced TiO_2. Fe doping was most effective doping material enhancing the filter properties, but it still need to be optimized.

For improving efficiency, adding adsorbents such as carbon into filter media can be a good perspective. Carbon adsorbents will behave like a contaminant catcher, catalyst can destroy the contaminant while one adsorber holds the contaminant. It can be predicted that this method can increase the performance of the filter. Further studies will concentrate on addition of carbon nano-materials to filtration systems.

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APPENDIX A

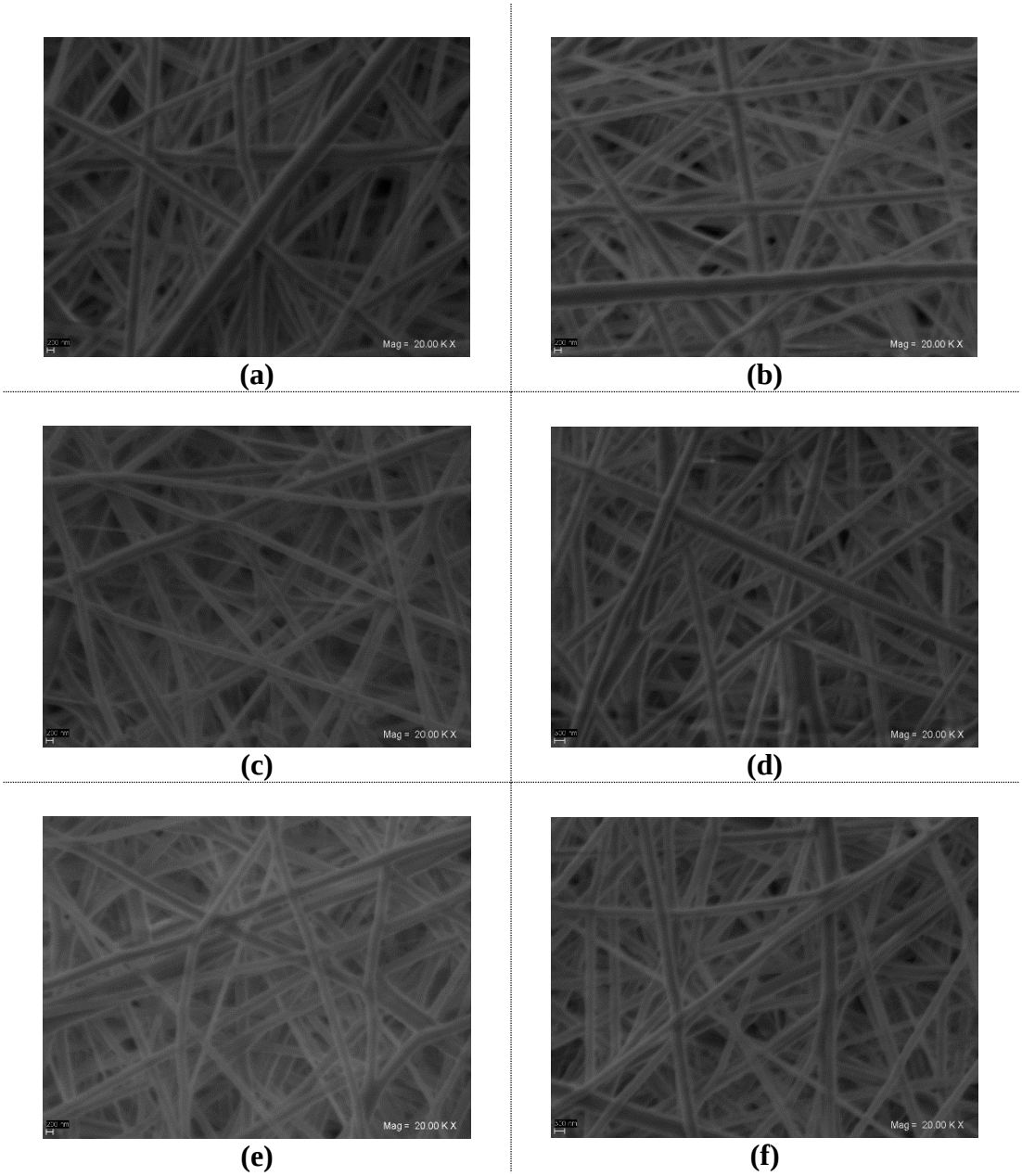

Figure A. 1 : Optimization Studies: (a) 20kV - 0,7mL/h. (b) 20kV - 1mL/h. (c) 25kV - 0,7mL/h. (d) 25kV - 1mL/h. (e) 30kV - 0,7mL/h. (f) 30kV - 1mL/h.

CURRICULUM VITAE

Name Surname:	**Arda Küçüksarı**
Place and Date of Birth:	**Antalya / 20.02.1988**
Address:	**Abbasağa Mah. Bostanüstü Dere Sok. Efe Apt. No:38 Beşiktaş/İstanbul**
E-Mail:	**ardakucuksari@gmail.com**
B.Sc.:	**Metallurgical & Material Engineering Yıldız Technical Univeristy**

Professional Experience and Rewards: