İZMİR KATİP ÇELEBİ UNIVERSITY ★ GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCE

A DESIGN OF ETHYLENE REMOVAL NON-WOVEN TEXTILE BY USING NATURAL ZEOLITE AND POTASSIUM PERMANGANATE

M.Sc. THESIS

Ayşenur DURU

Department of Material Science and Engineering

Thesis Advisor: Prof. Dr. Salih OKUR

JUNE 2015

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<u>**İZMİR KATİP ÇELEBİ ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**</u>

DOĞAL ZEOLİTLER VE POTASYUM PERMANGANAT KULLANILARAK ETİLEN TUTUCU DOKUSUZ YÜZEY TEKSTİL ÜRÜNÜNÜN TASARLANMASI

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To my family,

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ABBREVIATIONS

ACC	: 1-Aminocyclopropane Carboxylicacid
AP	: Airpermeability
BET	: Branauer Emmett Teller
BK-NZM	: Binderand Potassium Permangante Coated Natural Zeolite Mineral
CAS	: Controlled Atmosphere Storage
Cd	: Cadmium
CPP	: Chlorime- Polyproplone
DEU	: Dokuz Eylul University
EVA	: Ethylene Vinyl Acetate
FFV	: Fresh Fruit and Vegetable
FT-IR	: Fouier Transform Infrared Spectroscopy
FV	: Fruit and Vegetables
HCl	: Hydro Chloric Acid
IEC	: Ion Exchanging Capacity
IKC	: İzmir Kâtip Çelebi University
IR	: Infrared Spectroscopy
$KMnO_4$	: Potasyum Permanganate
K-NZM-P	: Natural Zeolite Mineral Modified With Potasyum Permanganate Padded Nonwoven
K-NZM-p-pow	: Potassium Permanganate and Natural Zeolite Mineral Padded Powder
LPG	: Natural Gas
MACC	: Methionine 1-Aminocyclopropane Carboxylic Acid
MAP	: Modified Atmosphere Packeting
MET	: Methionine
NZM	: Natural Zeolite Mineral
NZM-C	: Zeolite Mineral Coated Nonwoven
NZM-P	: Natural Zeolite Mineral Padded Nonwoven
NZM-pow	: Natural Zeolite Mineral Powder
NZM-p-pow	: Natural Zeolite Mineral Padded Powder
NZM-c-pow	: Natural Zeolite Mineral Coated Powder
PBU	: Primary Building Unit
PE	: Polyethylene
PET	: Polyethylene Terephthalate
SAM	: S-adenosylmethionine
SEM	: Scanning Electrone Microscopy
WVP	: Water Vapour Permeability
VOC	: Volatile Organic Compound
XRD	: X-Ray Diffraction
1-MCP	: 1- Methylcyclopropan

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A DESIGN OF ETHYLENE REMOVAL NON-WOVEN TEXTILE BY USING NATURAL ZEOLITE AND POTASSIUM PERMANGANATE

SUMMARY

Ethylene has a significant role in plants development and maturing, and is produced as gas hormone by plants themselves. In 1 μL L^{-1} concentrations, it has beneficial effects for fresh fruits and vegetables (FFV) but when this gas is accumulated around the FFV it causes aging and deterioration. During the storage, transport and marketing it affects the quality and freshness of FFV. There are technological solutions for eliminating the ethylene gas accumulating in storage atmosphere but these techniques are practical for rutine usage and have high cost.

Natural minerals have a very low cost, a great potential for practical use and are easily attainable to improve the storage conditions. Natural zeolites are one of the most promising materials that have desirable properties such as ion exchange, catalyzer, adsorption and molecular sieve. Due to their superior properties and advantages, they attain a great place in many areas. Zeolites have large surface area so they are used as bed materials for potassium permanganate used for ethylene decomposition.

Nowadays textile nonwoven surfaces have increasing attention in technical and industrial fields. They can be modified to meet any needs with their unlimited opportunities, in many fields where the performance and quality are required.

In this study, textile nonwovens were modified by using natural zeolites and potassium permanganate, which is used as ethylene removal textile. This combination can be used as a practical and disposable product. For evaluation and characterization of samples, particle size analysis, surface (BET) analysis, SEM, XRD, FT-IR, air permeability and water vapor permeability tests were conducted. Adsorption performance properties were tested via IR spectrum changes. Nonwoven textile provided extended surface area and performance, and eliminated the toxic effects of potassium permanganate that causes health problems. A new kind of product was obtained by using natural zeolites, which are found in abundant amounts in Turkey.

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DOĞAL ZEOLİTLER VE POTASYUM PERMANGANAT KULLANILARAK ETİLEN TUTUCU DOKUSUZ YÜZEY TEKSTİL ÜRÜNÜNÜN TASARLANMASI

ÖZET

Sebze ve meyvelerin kendiliğinden ürettikleri etilen gazı büyüme ve gelişmelerinde önemli bir rol oynar. 1 µL L^{-1} civarındaki konsantrasyonlarda üretildiğinde bitkiye faydası olduğu gibi fazlası bitkinin çabuk olgunlaşmasına ve akabinde hızla çürümesine sebep olur. Bu durum meyve ve sebzelerin depolanma, taşınma ve marketten tüketiciye ulaşacağı zamana kadar meyve ve sebzelerin istenilen kalite ve tazelikte olmalarında büyük bir problem teşkil etmektedir. Meyve ve sebzelerin saklama koşullarını iyileştirebilmek adına geliştirilen teknolojik yöntemler kesin etkili sonuçlar verse de kullanım açısından pratik olmadığı gibi maliyetleri oldukça yüksektir.

Saklama koşullarının kalitesini arttırmak için ortamdaki nemi, kötü koku oluşumuna sebep olan gazları ve ürünlerin çürümesine sebep olan etilen gibi gazların uzaklaştırılabilmesi için doğal minerallerin kullanılması pratik ve maliyeti düşük bir çözüm olarak karşımıza çıkmaktadır. Adsorpsiyon, katalizör, iyon değiştirebilme ve moleküler elek özellikleriyle kendilerine oldukça geniş kullanım alanları bulan doğal zeolitler bu türden kullanımlar için en uygun minerallerden biridir. Etilen absorpsiyonunda yaygın olarak kullanılan potasyum permanganat için de geniş yüzey alanı sağladığından uygun bir zemin malzemesidir.

Günümüzde tekstil malzemeleri özellikle non-woven (dokusuz) yüzey teknolojisinin gelişmesiyle birlikte kendilerine geniş kullanım alanları bulmuşlardır. Dokusuz yüzeyler ihtiyaca göre modifiye edilerek sınırsız alanda sınırsız kullanım olanakları sağlar. Performans, üretim ve kullanım kolaylığı bakımından da istek ve ihtiyaçlara cevap verebilmektedir.

Bu proje kapsamında tekstil dokusuz yüzeyleri etilen adsorpsiyonunda kullanılan doğal zeolitler ve absorpsiyonunda kullanılan potasyum permanganat ile kaplanarak modifiye edilmiştir. Elde edilen etilen tutucu tekstiller kullanımı pratik ve kolay olan tek kullanımlık ürünler halinde üretilmiştir. Yüzey alanı geniş olduğundan zeolit için uygun bir tekstil tabanı oluşturmuştur. Elde edilen elyafların etilen adsorpsiyon performanslarının incelenmesinde IR spektrumlarının miktara bağlı değişimlerinden faydalanılmıştır. Performans özelliklerinin ve karakterizasyon çalışmalarında parçacık boyutu analizi, yüzey alanı (BET) analizi, SEM, FT-IR, XRD, hava geçirgenliği testi, su buharı geçirgenliği testi yöntemlerine başvurulmuştur. Ülkemizin kaynakları bakımından oldukça zengin olan doğal zeolitlerin değerlendirilebileceği alternatif bir ürün elde edilmiş olacaktır.

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1. INTRODUCTION

Ethylene gas, which has quite simple structure, has a non-negligible importance for vital activities of plants. From the seeding to growing, fruiting and senescence, it is included in the life of the plants. The first study about ethylene in plants is conducted by Anton Nlcxcy 100 years ago. During the following years, researches on ethylene acting as plant hormone has been sustained and especially in recent years, it attracts attentions. Ethylene is indeed produced by plants itself and involved to the metabolism by self-triggered mechanisms. It promotes plant’s growing, developing and ripening phenomena. Even at low concentrations such as 1 μL L^{-1} concentration, it becomes very effective (Suslow, 1997).

Effects of ethylene not only continue during the plant’s life in earth, but also it maintains its existence after harvesting of fruits and vegetables. In some cases, synthesis of ethylene after harvesting has beneficial outcomes. Harvesting before ripening and crudely storage of fruits is one of the most used methods to provide enhance of crops endurance. Raw crops are exposed to ethylene gas and rapidly ripen before marketing. However, ethylene can cause detrimental results as well. After harvesting, all crops spend a storage or transportation time. Lately harvested crops or different concentration sensitivities result in vast amount of waste. Ethylene concentration in storage spaces directly effects fruits ripening. It is very crucial to prevent accumulation of ethylene in a closed place. Ethylene production amount differs according to each fruit. While some of them are stopped to produce ethylene after harvest, some others continue to produce. Sensitivity to ethylene also specific for all fruits and vegetables. Ignoring these occasions and storage of all kind of crops together without classifying, leads to early ripening of crops that are more sensitive to ethylene exposure. Storage time and shelf life of fresh fruits and vegetables is associated with controlling of ethylene concentration in storage spaces (Erdoğan, Sakızcı, & Yörükoğulları, 2008; Saltveit, 1999).

Ethylene is actually subject of biochemistry and biosynthesis research fields because of its hormonal function in plant’s biology. However, its detrimental effects on over-ripening of FFV leads to search for alternative solutions to prevent the damages in widespread area-s, especially industrial fields (Ayoub, Driver, & Taub, 2004). One of the solutions utilized to remove excessive amount of ethylene in storage spaces is modified atmosphere pocketing (MAP). However, this method is required advanced technologic devices that are only affordable by developed companies for advanced storage spaces. It has not only high cost outlay, but also it is very complicated for ordinary usages (Alver, 2013).

There are, of course, practical productions based on principles adsorption and decomposition of ethylene. Potassium permanganate is very effective substance that easily reacts with ethylene. Pocketing of this substance in small sachets is one of most used practical solutions. On the other hand, potassium permanganate has toxic effects on FFV. It is required to be avoid from their directly contacts with crops. Another hazardous effect of potassium permanganate is its outcomes of reaction with ethylene. Because of their reactions, carbon dioxide and water are produced and accumulate in excessive amounts that influence adversely the quality of storage conditions. That is why this product is not a sufficient solution by itself (Alver, 2013).

Natural zeolite minerals are one of the most promising materials in ethylene adsorption and existed in abundant amounts throughout the world. Easy mining process and low-cost production advantages provides the zeolites to be reputable alternative to active carbons, synthetic adsorbents or other minerals (Alver, 2013; Erdoğan et al., 2008; Rushdi I. Yousef, El-Eswed, & Al-Muhtaseb, 2011). A mineralogist named Freiherr Axel Fredrick Cronstedt first recognized zeolites in 1756. 40 of 600 zeolite types are natural zeolites. The most knowns are Analcime, Natrolite, Clinoptilolite, Chabazite, Philipsite, Heulandite, Stilbite, and Mordenite (Bilgin & Koç, 2013; Suslow, 1997). In Turkey, quite rich zeolites reserves are existed especially in Gordes and Bigadic. They have a remarkable market share in many field thank to characteristic properties such as adsorption, catalyst, ion exchanging and molecular sieve (Bilgin & Koç, 2013; Erdoğan et al., 2008). Especially they have valuable contributions to adsorption technologies in removing of trace amount impurities in gas mixtures or separation of gas/solid mixtures and gas analyse (Auerbach, Carrado, & Dutta, 2003).

Structurally made from alumina silicamolecules are in lattice form including water molecules and cations. Regular and homogenous lattice structure gives rise to formation of pores through which fluid substances are penetrate easily. Regular porous structure underlies the molecular sieve property and provides physical adsorption. Cleaning of radioactive wastes, purification of liquids and gasses, separation of gasses, odor control, and additive material for agricultural usages are some examples of adsorption applications (Bilgin & Koç, 2013; Suslow, 1997). Zeolites are able to be applied on papers as adsorber, ion exchanger and also particle filter (Crowley, 1966) or used as zeolite powder/pellet bed in air conditioning systems for sorption activities beside the heating and cooling (Restuccia, Freni, & Maggio, 2002).

Adsorption researches on natural and synthetic zeolites are conducted in worldwide. However, literature bases are very limited. There are industrial products in the market for usage FFV storage in the forms of film, paper or pellets in sachet. According to Suslow's studies, these products have low adsorption performance and need to be improved (Suslow, 1997).

Erdogan (2013) have completed a study on ethylene adsorption of native zeolites mined from Gördes and Bigadic. In this study, zeolites have been treated with cations (K+, Na+ ve Ca_2+) and observed the adsorption behaviors at 227K and 293K. Another treatment has been application of hydro chloricacid (HCl) to see whether it effects adsorptionperformance. Results have showed that acid treatment have enhanced the pore efficiency by augmenting pores and widening the pore sizes. Wider surface area have positively affected the adsorption performance of zeolites (Erdoğan et al., 2008).

Montmorillonite type of natural zeolites are modified to prolonged the shelf life of FF. In his study in 2011, Costa improved the mineral with silver ions by exchanging of Na^+ cations. Silver ions gained the antimicrobial properties to natural mineral. As a result of the study, it is observed that minerals were provides prolonged shelf life with the color, odor and taste quality(Costa, Conte, Buonocore, & Del Nobile, 2011).The similar study has been conducted by Can et al. in 2013. They have investigated the antibacterial characteristics of silver loaded natural zeolites. Modified zeolites have greate potential for antibacterial applications (Can, Korlu, & Ateş, 2013).

Technical textiles can be define as a textile improved with special treatment to gain high performance, versatility, practical usage, strength, functionality etc. without any esthetic concerns. Some of the prominent treatments are water repellency, inflammability, antibacterial and adsorption improvements. Technical textiles can be produced by either conventional methods (spinning, weaving, and knitting) or nonwoven production methods recently in demand. Nonwoven textile products gain an important place in constantly evolving industrial field. They can be produced to meet any kind desired properties (Horrocks & Anand, 2000).

In industrial field, nonwovens are mostly used as filter media for separation of solid, liquid or gas mixture, purification processes, air quality controls, etc. Among the lately conducted studies, adsorption performances also play a part. Lim (2006)has studied coating of polypropylene nonwoven with zeolite treated with ion exchanging and TiO_2which is a greate agent for indoor air quality (Dong, Bai, Liu, & Zhu, 2007). They have used acryl, ethylene vinyl acetate (EVA), chlorine-polypropylene (CPP) as binders. Coated material is examined for air quality performance and deodorization by Gastec method (Lim et al., 2006).

Another study in which textile and zeolite meet is conducted by Grancaric and others (2009). They have used cotton/polyester fabric by coating with zeolite particles to improve an UVR protective and antibacterial product. Zeolite here provides wide surface area for application of Azalin and FWA which were utilized for synergistic protection. It has been observed that activated zeolites have been presented as greate immune stimulator agent which also heals the wound.This study have succeed by obtaining an antibacterial and UVR protector textile product (AM Grancaric & Tarbuk, 2009; Ana Grancaric, Tarbuk, & Kovacek, 2009)

In 2011, Tiber have investigated a mineral modified textile product. Pertlite powders have been applied onto the 100% cotton fabric by coating method. It has been observed that the mineral modified textile not only has the ability of UV protection, flame retardancy and water repellency, but also is greate in removal of Cr ion and dyes from wastewater. Antibacterial properties are also in improvable stage (Tiber, 2011).

In this study textile, nonwovens were modified by using natural zeolites and potassium permanganate to be used as ethylene removal textile that can be used as practical and disposable product. Nonwoven provided extend surface area as well as the performance and eliminated the toxic effects of potassium permanganate that causes health problems. A new kind of product was obtained by using natural zeolites which our country has great reserve.

1.1. Ethylene

Ethylene is simplest alkene and in the gas form under normal conditions. It is mostly known as plant hormone produced by plants itself so that promotes the plants' growing, developing and ripening at 1µl/l concentrations. During the developmental process, all plants produce ethylene. However, after harvest ethylene synthesis activity changes depending on the plants’ climacteric or non-climacteric character. Climacteric fruits maintain to produce ethylene after harvest while non-climacteric fruits cease (Abeles, Morgan, & Saltveit Jr, 2012; Söylemezoğlu, 1998).

All fruits and vegetables (FVs) have different reactions to ethylene level in the atmosphere. Depending on the sensitivity some of the fruits can be effected in very low levels while some others are effected very little or do not show any reaction even in very high rates. Even ethylene is a very significant factor in plants’ life; it can cause some negative results when it comes to postharvest processes. For example, both apple and tomato are climacteric fruits but ethylene sensitivities are 10-100 l/kg and 1-10 l/kg respectively. In case of random storage of the FVs results in deterioration of more sensitive one (Abeles et al., 2012).

Transportation, storage and selling processes require long terms. During these processes, sustaining freshness as well as the quality of the foods became a critic concern. It possessed to search for solutions of senescence problems stem from ethylene (Söylemezoğlu, 1998).

1.1.1. Physical and chemical properties

As a simplest alkene, ethylene is of double bonded two-carbon compound. Its pure form is colorless, flammable gas with ether like odor. Molecular weight of ethylene is 28.5 g/mol and the relative density is 0.978. Melting, freezing and boiling points are 181^{o}C, 169.5^{o}C, 103.7^{o}C, respectively.

Ethylene consists of two carbon and four hydrogen atoms in the unsaturated form of hydrocarbon, also known as the smallest member of alkenes with formulation of C_2H_4 or $H_2C=CH_2$, and structural formula is given in Figure 1.1.

As shown in the Figure 1.1 ethylene is of planary molecular structure and the angles of the bounds are 1200. Bounds existed five sigma between carbon and hydrogen atoms. Second bound between two carbon atoms is pi bound. Due to the double bound, ethylene can reacts with halogens, sulfuric acid and the other double bounded chemicals and dissolves in water, alcohol, benzene, acetone, ether etc. In case of exposure to ozone, oxygen or potassium permanganate, ethylene easily oxidize.

Ethylene can also polymerize and engenders polyethylene (PE) which is well known as PE plastics widely used in industrial packeting (Abeles et al., 2012).

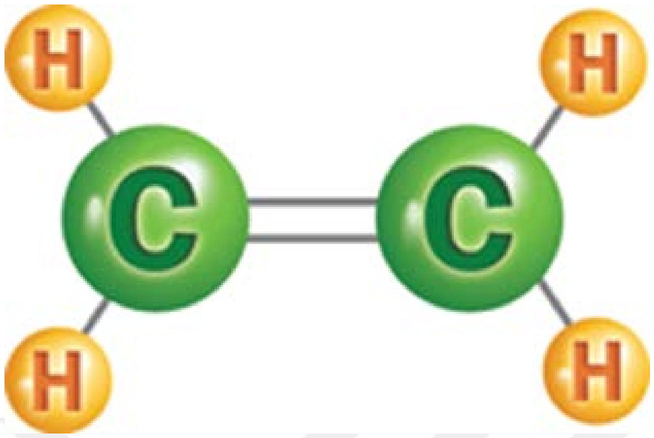


Figure 1.1: Molecular structure of ethylene

1.1.2. Biosynthesis of ethylene

There are so many ways to obtain ethylene by chemical reactions. Exposure to any oxidation reaction, radiation, heat or light can be caused to compose or decompose of organic compounds to ethylene. For example, decomposition of ethane by the heat is one of the most used ethylene production method.

Naturally production of ethylene based on physiological changes in plants. Plants synthesis ethylene as a natural hormone to promote vital activity such as growing, developing and ripening. Ethylene synthesis in plants is best stated by the Yang Cycle named from Shang Fa Yang who has made great contributions to studies on ethylene. Ethylene synthesys by Yang Cycle is given in Figure 1.2. According to this cycle the production pathway starts with the methionine (MET) is a kind of amino acid. Adenine addition to MET converts it to S-adenosyl methionine (SAM). The most important stage comes with the synthesis of 1-aminocyclopropane carboxylic acid (ACC). ACC enzymes get involved in cycle by the stimulation of intrinsic (developing) or extrinsic (wounding) influences. The amino butyrate compound of SAM is separated and the production of ACC is completed. The rest of SAM continue to its cycling to Methionine. On the other side of process, ACC is oxidized to ethylene. For oxidation reaction, more oxygen and less carbon dioxide is needed. In case of excessive amount of ACC is existed in the environment, it is expected to see increasing of ripening activity due to the excessive ethylene exposure (Abeles et al., 2012).

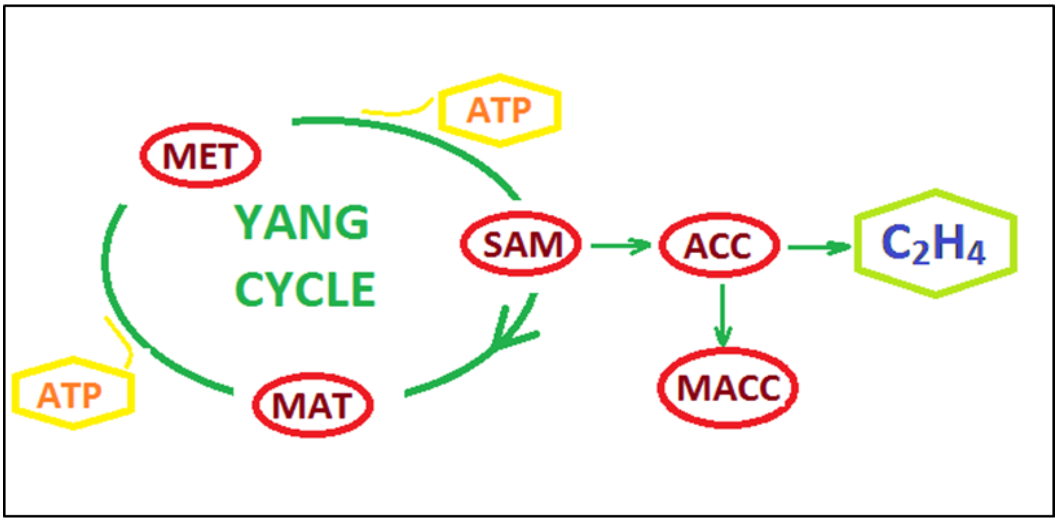


Figure 1.2: Ethylene synthesis by Yang Cycle

Ethylene synthesis is self-stimulated since the amount of synthesized ethylene interferes the production of ACC enzymes. Growth regulators or side reaction MACC production from ACC reduces and keeps under control the amount of ACC. Lowering the oxygen level also reduces the oxidation as well as the ethylene level (Abeles et al., 2012).

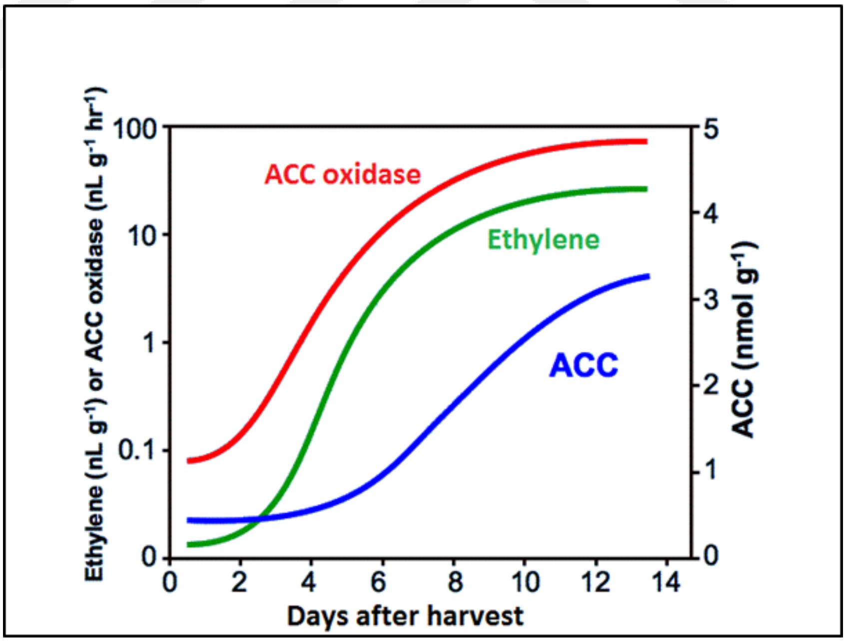


Figure 1.3: Ethylene synthesis and ACC correlation

1.1.3. Hormonal tasks of ethylene

Ethylene is one of the five hormones required to regulate plants developmental activities. It is efficient from seed germination to senescence. It has stimulative and inhibitive tasks some of them listed below;

- Germination of seed,
- Sprouting and root elongation,
- Flowering,
- Respiration,
- Synthesis of pigment,
- Ripening,
- Chlorophyll destruction,
- Abscission,
- Senescence (Abeles et al., 2012).

1.1.4. Effects of ethylene on fresh fruits and vegetables

During the development period, almost all plants produce ethylene even in low concentrations. By the ripening process, ethylene production differs according to plants' climacteric situation. Plants are categorized in two group as their respiration behavior named climacteric or non-climacteric (Söylemezoğlu, 1998; Tigchelaar & McGlasson, 1978).

Climacteric; in some vegetables and fruits (VF), respiration shows increase in the first stages of ripening. As the respiration increase, their conformation changes. This situation is named as "climacteric" and first observed by Kidd and West in 1924. They have investigated apples' respiration and ripening behaviors after harvest (Kidd & West, 1925).

Non-climacteric; in 1954 Biale and Young found out some other VFs such as citrus fruit do not respire during the ripening process. Even after harvest these VFs do not produce ethylene. Some examples of climacteric and Non-climacteric FVs are given in Table 1.1 (Biale, Young, & Olmstead, 1954).

The main issue based on the respiration difference between climacteric and non-climacteric VFs is ripening conditions as well as the ethylene production. Climacteric VFs produce more ethylene as they have ripen. Down from the germination plant employs the ethylene for developmental procedure.

Table 1.1: Climacteric and Non-climacteric fruits and vegetables (Söylemezoğlu, 1998)

Climacteric	**Non-Climacteric**
Apple (Malus sylvestris)	Berry (Prunus avium)
Apricot (Prenus armeniace)	Cherry (Prunus cerasus)
Avocado (Persea americana)	Cucumber (cucumis sativus)
Banana (Musa sp)	Grape (Vitis vinifera)
Cherimoya (Annona cherimolia)	Lemon (Citrus limonia)
Kiwi (Actinidia cherinensis)	Ananas (Ananas comosus)
Fig (Ficus carica)	Mandarin (Citrus reticulata)
Mango (Mangifera indica)	Strawberry (Fragaria)
Passion Fruit (Passiflora edulis)	Orange (Citrus sinensis)
Peach (Prunus persica)	Bilbery (Vaccinium corymbosum)
Pear (Pyrus communis)	
Plum (Prunus sp)	
Tomato (Lycopersican esculentum)	
Watermelon (Citrullus ranatus)	

After the development is completed, intrinsic ethylene starts to accumulate until it reaches to threshold value and subsequently triggers ripening, accelerates the respiration (Karaçalı, 1990).

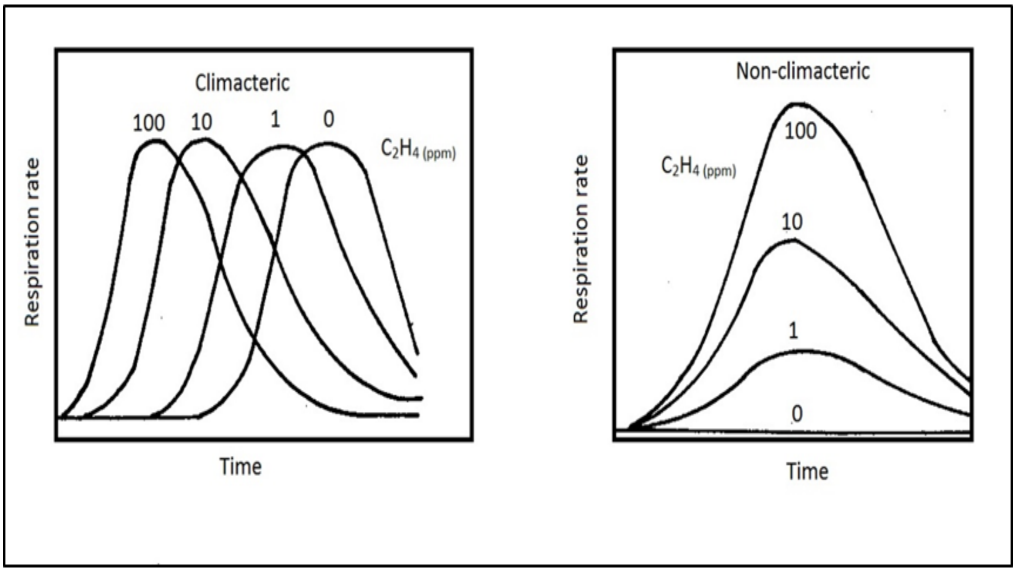


Figure 1.4: Respiration rates in climacteric and non-climacteric fruits and vegetables (Söylemezoğlu, 1998)

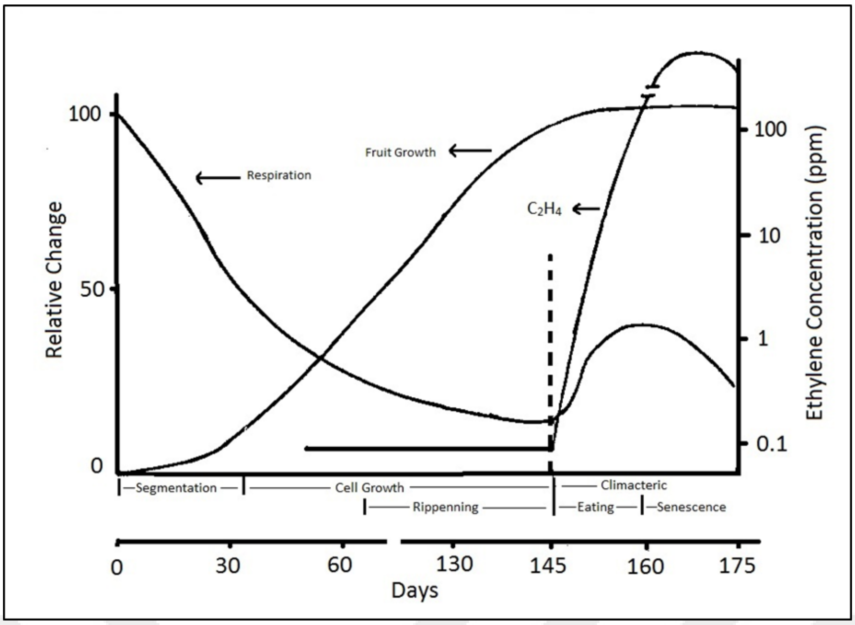


Figure 1.5: Respiration, ethylene and fruit growth relations in climacteric fruits (Söylemezoğlu, 1998)

The threshold value is specific for each climacteric VFs. According to sensitivity duration and the quantity of the ethylene production is depend on this value. For instance, even they both are climacteric fruits; apple is durable at 100 ppm ethylene in a storage room while endurance limit of a kiwi fruit can only reach up 0.01 ppm. In case of the fruits had extreme sensitivity differences have been kept in the same storage, it is expected to encounter deterioration of the fruit which is more sensitive to ethylene. Excessive amounts of ethylene always effects the quality of fruit (Saltveit, 1999).

Table 1.2: Ethylene production in some crops (Reid, 1985)

l/kg	Crops
0.01-0.1	Berry, citrus, grape, strawberry
0.1-1.0	Cucumber, okra, ananas, huckleberry,
1.0-10	Banana, fig, mango, tomato
10-100	Apple, avocado, cantaloupe, nectarine, papaya, peach, pear, plum
>100	Cherimoya, passion Fruit.

Although ethylene has detrimental effects on VFs, it has commercial value in fresh fruit and vegetable (FFV) industry. Early harvested crops can stand during the storage and transportation without deteriorations. Before the marketing section, in the storage room, they are exposed to ethylene gas diluted with the air in the optimum combination of carbondioxide (CO_2), oxygen (O_2), temperature and the humidity. If the process is applied precisely and controlled carefully, it is possible to obtain the best-qualified VFs (Saltveit, 1999).

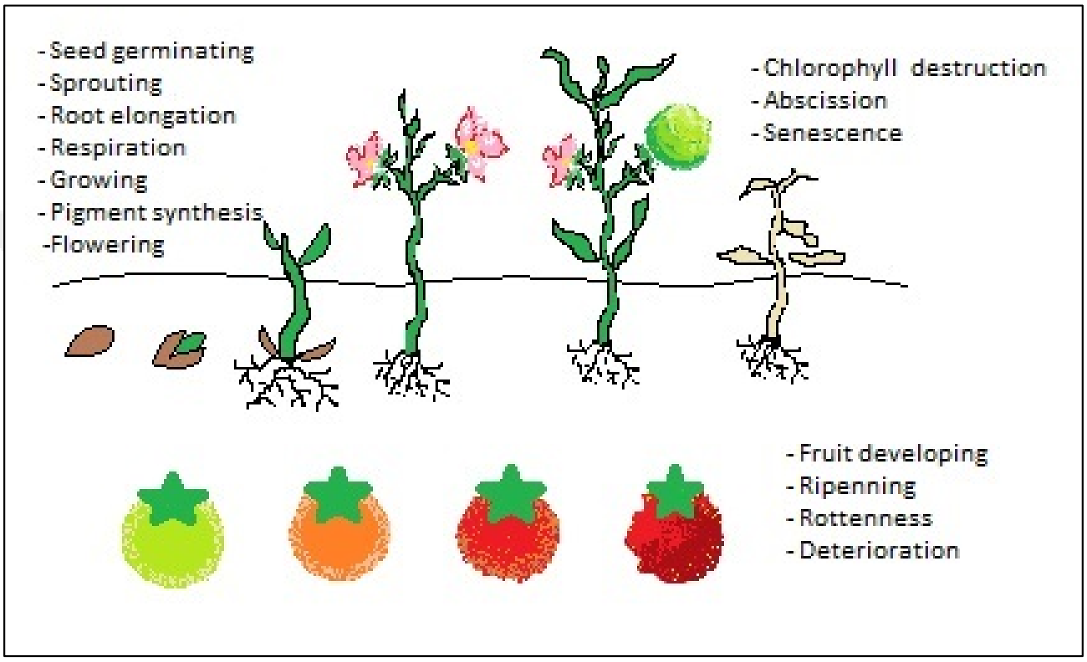


Figure 1.6: Ethylene effects on plant developing and fruit ripening

1.1.5. Ethylene removal techniques

Fresh fruits and vegetables (FFV) prolong their freshness for a while even after harvest. In the storage duration, they consume all nutritive elements until the quality indications are exhausted. This situation brings up some cautions to take.

1.1.5.1. Controlled atmosphere storage

After harvesting FFVs continue to respire, consequently CO_2 and H_2O occur. Amount of the oxygen in the environment and the temperature are both effective in respiration. Although reducing the oxygen ratio in the storage rooms is a solution to decrease the respiration, it is inadequate by oneself. Cooling of storage rooms is also effective. Nevertheless, under a certain degree, FFVs encounter some physiological degradations. Controlled Atmosphere storage (CAS) is a method combined temperature and gas ratio in optimum degrees. Lowering of O_2 and highering of CO_2 levels in freezer decelarate respirations. Another function of this technology is that ethylene levels can be decrease.

However, this method is quite complex as well as costs much and only can be applied technical infrastructured storage rooms. Concerned companies employ this technique for commercial purposes (Thompson, 2010).

1.1.5.2. Modified atmospherepocketing

Consumers prefers the fresh foods because they do not contain chemical ingredients and easy to prepare. Modified atmosphere packeting (MAP) of fresh foods prolonges the shelf life of products as well as provides the qualified packetint, transfering and storage for expensive foods. MAP is briefly the packeting of foods with a certain group of gaseses but air. Eliminating of O_2 and filling CO_2 and N_2 instead provides and artificial athmosphere which inhibites the developing of some microorganisms, bacteries and mold.

Advantages of MAP;

- Extends the shelf-life to 50-400%
- Prevents significant wastes
- Retrenches the transportation costs
- Provides hihg qualified products
- Provides oportunity of packetting of sliced foods.
- Isolated packetting
- Less usage of ingredients
- Odorless and practical packetting

Desadvantages of MAP;

- Extra costing issues
- Temperature coltrol needed
- Different formulationf for all kind of foods
- Spesific qualification for technical needs

- Providing safety of packets
- The more volume exceeds, the more gas is used (Kılınç & Çaklı, 2004; Pocas, 2001).

1.1.5.3. Using 1-Methilcyclopropen

1-Methylcyclopropen (1-MCP) is gas under normal circumstance with the moleculer weight of 54 and the molecular formula is C_4H_6. It is 10 times reactive than ethylene. So when it applied to FVs it easyly attaches to reactive groups which ethylene reacts. Generally, it inhibits rippenning and senescence, and retards ethylene production, color changes and softenning. It minimalizes ethylene’s effects but cannot stop the intrinsic production of ethylene (Kasım & Kasım, 2007).

1.1.5.4. Ethylene scavengers

Previously mentioned techniques are expensive to casual usage. It is posibble to obtain cheaper and more practical production as well. Ethylene is a very active gas so the many options are available to remove it by the adsorption, absorption or chemical reactivity phenomena.

Potassium permangnate ($KMnO_4$) is mostly used ethylene removal by chemical reaction. It is commercially obtainable in very small sized packets called sachets. Its colur is purple and as the reaction happens, colour changes to brown to indicate how long it is cable to reacts with ethylene. Because $KMnO_4$ is a toxic chemical and the purple color is contaminative, it is not directly contacted to FV. It packed in sachets (Brody, Strupinsky, & Kline, 2001; Ozdemir & Floros, 2004).

Figure 1.7: Ethylene sachets samples

Activated carbon products are also great alternatives for ethylene removing. Their PdCl modified types are successful in accumulation preventing and breakdown of ethylene. Due to the its porous structure, activeted carbon is used to adsorbing gasses, odours, vapor, VOC from air or composit gasses as well as filtering of liquids. They are existed in sachets for commercially to be used as air purifications. Some metal catalyzed active carbon products are also avaible and popular in the Far East (Vermeiren, Devlieghere, Van Beest, De Kruijf, & Debevere, 1999).

Palladium promoted materials also has the commercial potential to as ethylen scavengers. They have greate adsorption capacity even more than potassium permanganate with the 4162 Lg-1 under normal conditions (Terry, Ilkenhans, Poulston, Rowsell, & Smith, 2007).

Because of adsorption properties of pourus structured eart materials such as silica, alumina, zeolite etc. they are alternative productions for ethylene removing. They are of high surface area which can be also modified with $KMnO_4$. This provides $KMnO_4$ to extend trough the surface of pores. This improved product both adsorbs and chemically reacts and decompose the ethylene. These products are also commercially avaible as pact in sachets sized ranges from 5g to 30g. Some of supplier companies are Ethylene Control Inc. (USA), Air Repair® from Delta Track Inc.(Pocas, 2001).

1.1.6. Ethylene oxidation reaction with potassium permanganate

Oxidation is a kind of redox reaction. During the reaction, electron exchanges occur between oxidant and reductant. Permanganates are great oxidant agents because of the Mn(VI) includings which makes the substance vesatile. They have a significant place in green chemistry due to the eco-friendly speciality (Dash, Patel, & Mishra, 2009).

Potassium permanganate is a great oxidant agent for oxidation reactions of organic compaunds (Mortazavi, Ziaie, & Khayamian, 2008; Shaabani, Bazgir, Teimouri, & Lee, 2002; Wills & Warton, 2004). In an oxidisable medium, potassium permanganete reacts with substant and decomposes to manganese dioxide (Carr, 2012).

The Firt study about the potassium permangante is a greate oxidant for ethylene conducted by Forsyth in 1967, while the researches on prolonging of apples shelf life. Following researches were on postharvest life of climacteric and non-climateric fruits and their durability. Even in low concentrations, ethylene response the potassium permanganete. However, a large area and low amount of ethylene circumstance reduces the posibility of encountering these two compounds. This is why potassium permangante is required to load on large surfaces (Wills & Warton, 2004). Generally, solid substances such as perlite, silica gel, zeolite, alumina, activated carbon, vermiculite and celite are greate bases for potassium permanganate (Jadhav, Wadgaonkar, Joshi, & Salunkhe, 1999; Vermeiren et al., 1999; Wills & Warton, 2004). Potassium permanganate can be recycled if it loads onto copper. However it is very difficult to yield back it from mineral solids (Jadhav et al., 1999).

Under normal cicumstances, potassium permangante is violet purple colour. After oxidation reaction its color turns to brown. This is also a indicator for reaction rate. As a result of ethylene and potassium permangante, acetat and ethanol occur. Finalreaction comes into action after a range of reations. Reaction needs humidity to be started (Vermeiren et al., 1999).

$$3C_2H_4 + 2KMnO_4 + H_2O \rightarrow 2MnO_2 + 3CH_3CHO + KOH \quad \textbf{(1.1)}$$

$$3CH_3CHO + 2KMnO_4 + H_2O \rightarrow 3CH_3COOH + 2MnO_2 + 2KOH \quad \textbf{(1.2)}$$

$$3CH_3COOH + 8KMnO_4 \rightarrow 6CO_2 + 8MnO_2 + 8KOH + 2H_2O \quad \textbf{(1.3)}$$

Combination of equation 1 and 3 results in ;

$$3CH_2CH_2 + 12KMnO_4 \rightarrow 12MnO_2 + 12KOH + 6CO_2 \quad \textbf{(1.4)}$$

Instead of equation (1.3), reaction can continue as;

$$CH_3COOH + KOH \rightarrow KCOCH_3 + H_2O \quad \textbf{(1.5)}$$

Combining of equations (1.1), (1.2), (1.5) give the following equation.

$$3CH_2CH_2 + 4KMnO_4 \rightarrow 3KCOCH_3 + 4MnO_4 + KO + H_2O \quad \textbf{(1.6)}$$

Outcomes of these reaction chain are CO_2, KOH, H_2O, MnO_2 and $KCOCH_3$.

1.2. Zeolite

Zeolites are hydrated alumina-silicate minerals in the group of alkali and alkali earth. They have been formed million years ago by changing of volcanic ashes in the aqueous medium. Their crystal lattice structure is tetrahedral composition of SiO4 and AlO4 molecules with the formulation of $M_xD_y[Al_x+2ySi_{n-(x-2y)}O_{2n}].mH_2O$ ($M=Na^{+1}$, K^{+1}; $D=Mg^{+2}$, Ca^{+2}, Si^{+2}, Ba^{+2}) (Köktürk, 1995).

Fredrick Crostedt, Swedish mineralogist, first recognized zeolites in 1756(Köktürk, 1995). Due to his observation about the mineral behaved like boiled water when it is heated, Crostedt coined the name “zeolite” by gathering the words “zeo” and “lithos”, respectively means “to boil” and “stone”. For 200 years, there was not any significant research carried out except Damours discovery on reversibly dehydration of zeolite (1840). By the technology and some analyses techniques developed (X-ray, IR adsorption, NMR, ESR), mystery of the zeolite started to reveal and it called scientists attention. In 1925, Wiegel and Steinhoff carried out an experimental research that they found out “molecular sieve” property of zeolite. According to the results, zeolite could adsorb some molecules (water, formic acid methyl and ethyl alcohol) which are small enough to pass through the zeolites pores while the others stayed out (benzene, acetone, and ether). McBain (1932) who also contributed to molecular sieve researches first used statement of “molecular sieve” by using Chabazite. In 1858, Eichhorn discovered the ion exchange capability of natural zeolites. Following researches also proved that zeolite had catalytic properties. These versatile properties provide opportunity to be used in wide range usage area. Today it is possible to see natural and synthetic zeolites in industrial fields, environmental pollution control and agriculture and stockbreeding fields where the adsorption, ion exchange and catalytic properties are needed (Auerbach et al., 2003).

As the industrial and commercial importance of zeolite rose, researchers veered to obtain zeolites that are more efficient and in the mid-1930s, they came up with the idea of synthetic zeolite. In 1948, the most successful synthetic zeolite, Linda A was produced. Although synthetics have better performance, cost issues gave rise to search for natural zeolite reserves. Today the richest zeolite reserves of the world is located in USA, Japane, and Italy. Turkey harbors the 40 % of whole world reserves, mostly in Manisa-Gordes and Balıkesir-Bigadic, totally 50 billion tons of zeolite (Erdoğan et al., 2008).

1.2.1. Structural properties of zeolites

All the special properties of zelites based on the combination of its molecular ordering and chemical composition. As being an ordinary silicate, zeolite is in tetrahedral position in which there is always a Si^{+4} or Al^{+3} atoms in the center of primary building unit and O^{-2} atoms are bounded as shown in Figure 1.8. 3-dimentional combination of PBUs generates crystal lattice (Barrer, 1978).

Inter linkage of the micro pourus structures is provided by the windows. Hence 2 or 3-D infinite tunnels or gaps are come into view.

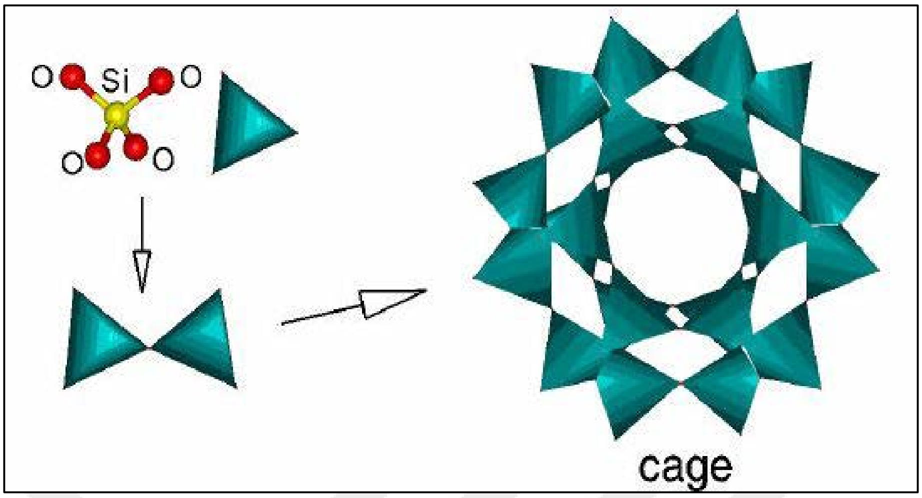


Figure 1.8: Molecular and crystal structure of zeolite (Barrer, 1978)

These gaps are 20 % - 50 % of whole volume. Zeolites molecular sieve property stems from the gaps, liquid or gas molecules can be easily adsorbed in. Size of the pores depend on crystal structure and relocatable ions. These sizes change between 3^0A and 10^0A (Tsitsishvili, 1992).

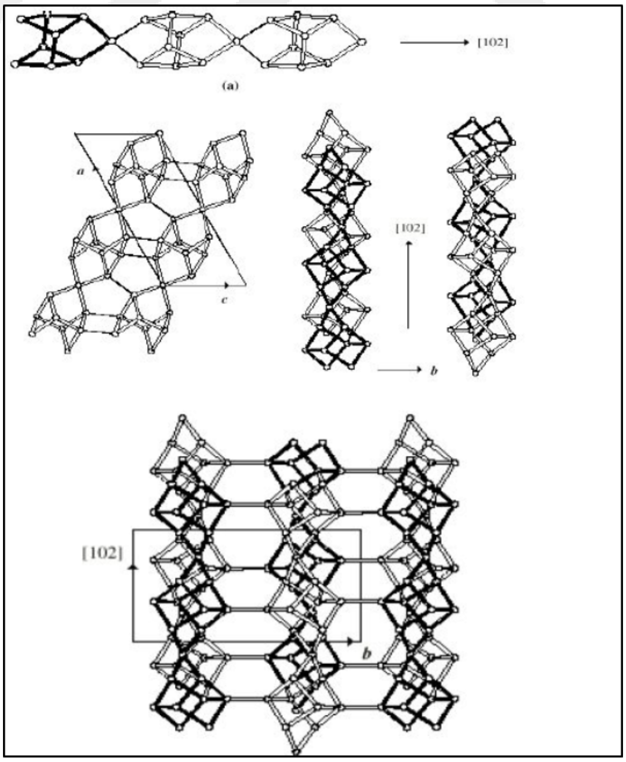


Figure 1.9: Construction of zeolite lattice (Barrer, 1978)

1.2.2. Classification of zeolites

1.2.2.1. Natural zeolites

Natural zeolites have high adsorption capacity even in low pressures or high temperatures. This situation stem from stability of crystal structure. As the Si / O ratio rise, resistance to changing against to temperature will also rise, so the adsorption capacity.Water belong to structure starts to evaporate in 150 0C and higher temperature (700) causes evaporation in composition. Pourus structure is the main idea of the zeolite that 50% of volume is gap and inner surface is 90 % of total surface area (1000 m^2/g). Pore sizes change between 3A and 10A according to type of zeolite. It is possible to make the pores more homogen by treated with acid (Sağdıç, Kandemir, Karalı, & Dimoglo, 2007).

Number of the type of zeolite ever recorded is over 40. Most featured of them are analcime, natrolite, clinoptilolite, chabazite, philipsite, heulandite, stilbite, mordenite (Köktürk, 1995). Table 1.3 includes some characteristic features of them.

Table 1.3: Characteristics of natural zeolite minerals (Polat, Karaca, Demir, & Naci-Onus, 2004)

Zeolite	Gap Volume	Temp. stability	Ion Exc. Capacity meq/g	Density	Si/Al ratio	Pore size
Analcime	18	High	4,54	2.24-2.29	1,63	2.6
Natrolite	23	Low	5.26	1,76	1,44-1,58	2.6x3.9
Clinoptilolite	34	High	2.16	2.16	4.25-5.25	3.9x5.4
Chabazite	47	High	3.84	2.05-2.10	1,6-3	3.7x4.2
Phillipsite	31	Middle	3.31	2.15-2.20	1,7-2,4	4.2x4.4
Heulandite	39	Low	2.91	2.18-2.20	-	4.0x5.5
Mordenite	28	High	2.29	2.12-2.15	4,17-5	2.9x5.7
Stilbite	39	Low	-	2.10-2.20	-	4.1x6.2

Natural zeolite formation is based on accumulation of volcanic tuffs in salt water, fresh water lakes, shallow or deep-sea regions and reacts with water. It is also occurs as a result of low heat embedded metamorphism of Al-Si sedimentary. Hydrothermal or hot mineral water affection on Al-Si materials causes formation of natural zeolite minerals (Gülen, Zorbay, & Arslan, 2012).

Table 1.4: Formation of zeolites (Bilgin & Koç, 2013)

Type of Formation	Temperature	Type of zeolite
Deep sea sediments	4-50	Phillipsite, Analcime, Clinoptilolite
Degradation		Phillipsite, Clinoptilolite, Chabazite, Mordenite, Erionite,
Alkali and salt water lake	20-50	Gismodin fojasite, Gonaidite, Natrolite, Analcime
Infiltrated well water (basic)		Heulandite
Infiltrated well water (acidic)		Phillipsite, Mordenite, Chabazite, Erionite, Tomsolit, Moselite
Shallow embedded diyagenise (low heated hydrothermal)	25-100	Skolesite, Heulandit, Stilbite
Sea embedded diagenesis (middle heated hydrothermal)	100	Lamonite, Analcime
Low metamorphism	200	Warakite, Yugovaralite, Analcime, Primer Magmatic
Primer magmatic		Analcime

1.2.2.2. Synthetic zeolites

Increasing industrial demand and not being met by natural zeolite gave rise to work on synthetic zeolite. Hence, as a result of intense study, first successful synthetic zeolite Linda A was produced in 1948, by Union Carbide Corporation. Linda A (Zeolite A) distinguishes its 1:1:1 ratio of Si:Al:Na structural property. Besides of 47% of gap volume, it has better ion exchange capacity, electronically charged pores and hydration capability (Omisanya, Folayan, Aku, & Adefila, 2012). The framework of Zeolite A consists of cubic formation of eight tetrahedra and octahedron of twenty four tetrahedra (12 SiO_4 and 12 AlO_4) or ß-cage (Sherman, 1999).

Faujasite-type zeolites (Zeolite X and Y) is the composition of (Na_2, Ca, Mg) $_{29}[Al_{58}Si_{134}O_{384}]240H_2O$. PBU including six cavities each of them is 13 0A. Total volume of unit cell rice up 12.7 nm^3. Si/Al ratios, which specify the Zeolite X and the ZeoliteY are respectively 1-1.5, and 1.5-3.

Synthetic zeolites are usually synthesized by mixing alumina and silicate solution in alkali hydroxide or organic bases then crystallizes. Crystallization process occurs in a closed hydrothermal system. During the process, temperature rises constantly and pressure changes naturally (Georgiev, Bogdanov, Angelova, Markovska, & Hristov, 2009; Omisanya et al., 2012). There are some parameters to affect the reaction;

- Si/Al, OH- and inorganic cation ratio,
- Reactants
- Temperature
- pH
- Continuous of process

When it comes to compare synthetics and naturals, synthetics are always costs much more than naturals but the performance of them is better and synthetic zeolite family is more crowded than natural zeolites with over 150 type (Köktürk, 1995). Nevertheless, natural zeolites have growing potential in industrial fields due to its rich reserves around the world and modification capability (Munson, 1973).

1.2.2.3. Clinoptilolite

Clinoptilolite owns its Greek name from the meaning of “oblique feather stone” It is the most common and commercially available mineral occurred volcanic rocks (Polat et al., 2004). It is member of heulandite type of zeolite and has similar structure with heulandite. Molecular formula is:

$$AD\ [Al\ (A+2D)\ nSi–(a+2D)\ nO_2]\ mH_2O$$

A is stated as Li, Na or K and D is Mg, Ca, Sr or Ba. Number of oxygen atoms are usually n=36 and number of water molecules are m=24. Molecular structure is of monoclinic C-centered. Wide porous structure is suitable for cation moving. However, channel blockage can be shown in case of variation in size, location or number of cations. Cation composition and Al/Si is a characteristic property for each type of zeolite.

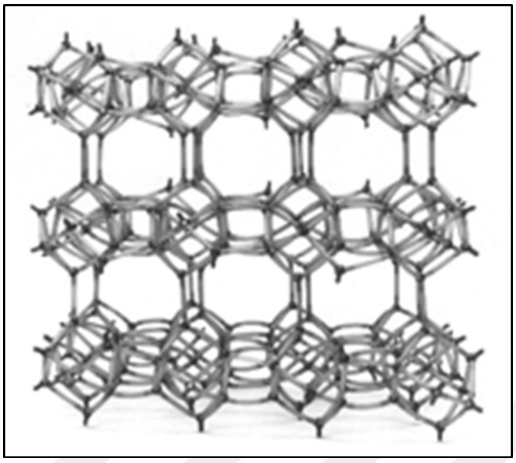


Figure 1.10: Framework structure of structure of (Zeoponix, 2015)

Framework structure of Clinoptilolite is given in Figure 1.10. 10 member ring channels and 8 member ring channels are parallel and linked by 8 member channels. This configuration arise the 2-D channel system (Ackley, Giese, & Yang, 1992).

Table 1.5: Structural properties of Clinoptilolite

Secondary Building Unite	Unite 4-4-1
Framework density	1.71 g/cm^3
Largest molecule adsorbed	O_2
Density	2.16g/cm^3
Void volume	0.34 cc/cm^3
Dehydrated effect of dehydration	Stable in air up to 700C
Kinetic diameter, g, A	3.5
Si/Al	4.25-5.25

1.2.3. General properties and application fields of zeolites

1.2.3.1. Adsorption properties and applications

Adsorption can be define as adherence of fluid substances on surface by the mean of physical gravitational forces. An unsolvable solid leaved to gas or liquid environment starts to adsorb fluid from there until it reaches to maximum concentration. This phenomenon can be occur as reversible. Solid phase is named as adsorbent while fluid is named as adsorban (Bilgin & Koç, 2013).

Adsorbents are mostly used for purifications of waste water. Heavy metals or other contaminants can be filtered from water by this way. During the action atoms, molecules or ions adhere to the surface of adsorbent. Utilizing the right adsorbent is the critic subject as the interaction between adsorban and adsorbent designate the efficiency of adsorption. Different chemical composition of adsorbent is required to sustain adsorban diversity.

- Expectations from adsorbents can be listed below;
- Non-poisonous
- Non-hazardous for environment
- Inexpensive and obtainable
- Required to be in accurate composition to react with adsorban
- Unsolvable
- Recyclable
- Scientifically acceptable
- Wide surface area

Zeolites are very suitable adsorbents due to their porous structure. This structure provides wide surface area to zeolite. Furthermore, water in original composition can be evaporate at 350-400^{o}C, hence it is possible to enhance the surface area. They can adsorb any molecule smaller than their pore sizes. They can adsorb gas at amount of 30% of their own weight. Acids to exchange cation (H+) and chemically modify can treat them. Acid treatments give opportunity for interactions with extra kind of chemicals and extra widened surface area (Bilgin & Koç, 2013).

When it comes to adsorption, mostly known material is activated carbon due to its high porous structure. However, activated carbons have difficulties in production and cost high prices. This problem leads to search for natural alternatives. Naturally occurred adsorbents are abundantly existed and quite easy to obtain and process in very low prices (Ackley, Rege, & Saxena, 2003).

Natural zeolites are one of the most common natural adsorbents and already used for adsorption applications. Some of applications are listed below;

Ethylene adsorbents; ethylene, naturally produced gas hormone by the plants, are able to cause damages in fresh fruits and vegetables in case of accumulation in excessive amounts. Zeolites are being used for adsorption of ethylene from atmosphere during the storage of crops after harvest.

Adsorption heat pumps; during the refrigerating, adsorban in the evaporator adsorbs the heat from environment and starts to evaporate. Vapor is adsorbed by the dried adsorbent. Zeolites are mostly used adsorbents in refrigerating systems.

Wastewater purification; cadmium (Cd) and lead (Pb) are the metals encountered in wastewater. For the adsorption of these metals from water, zeolites are one of the most common materials used in industry. At elevated temperatures and effective coordination fields, zeolites shows better performance in adsorption of metal ions.

Adsorption of VOC and vapor; zeolites are used to observe diffusion adsorption behaviors of VOC and vapor by porous materials. Adsorption of water-soluble substances such as methanol and Asheton and water-insoluble substances such as benzene and toluene is observed under gradually temperature rise conditions (Gülen et al., 2012).

1.2.3.2. Molecular sieve properties and applications

Molecule sieve is defined as selective adsorption of substances depending on physical properties of cation and electrical charge dispersion in adsorbent. Uniform porous structure adsorbs molecules that are small enough to pass through the pores and bigger molecules stay out. This provides filtration separation of composed substances (Breck, 1984).

Zeolite also a porous structured mineral that have molecular sieve property. When it is compared to activated carbon or silica gel, it has large scale of pore size alternatives accordingly more advantages for applications required pore size variation.

Molecular sieve property effects from heat and dehydration of zeolite. Rising temperature causes destruction of crystal structure of zeolite. Oxygen ratio rises in the structure as the temperature rise and pore size becomes larger as the structure changes. Dehydration, on the other hand, causes relocation of cations and this situation give rise to changes in electrical charge dispersion. Dehydrated zeolites selectively adsorbs molecules such as H_2O, CO_2, and H_2S.

Table 1.6: Application field of natural zeolite minerals according to pore size

Application Field	Mineral Purity	Pore Size	
Manure additive in Agriculture	70-90 % Clinoptilolite	1-3 1-4 0,5-1,5	0,8-2,8 0,8-3,8 0,8-2
Animal feed additive	Minimum % 85 Clinoptilolit	<1, < 0,8, < 0,5, < 0,1	
Domestic water purification	Minimum % 85 Clinoptilolit	0,5-1,5 0,8-2	
Pool water purification	Minimum % 85 Clinoptilolit	0,5-1,5 1-4	1-3 2-5
Removing of ammoia based odours	% 75-85 Clinoptilolit	2,8-4,76	3-5
		1-4	
Other applications	% 60-99 Clinoptilolit	9-15	

Molecular sieve applications of zeolite utilized for purifications and bulk separations. Some of the applications are drying, natural gas (LPG) included cracked-gas facilities, insulative glass cooler, CO_2 removing, natural gas separation facilities, sulphuric compounds removing, cleaning of natural gas and liquid petrol, preventing pollution, Hg, NO_3, SO_4, removing etc (Bilgin & Koç, 2013).

1.2.3.3. Ion Exchange properties and applications

Ion exchangers are insoluble solid substances including weakly bounded anion or cation. Ions can easily replace in electrolyte solution. For example; positive (+) ion in liquid solution can replace with the (+) ions of solid in the liquid or negative (-) ion solution exchanges its ions with solids (-) ions. This process continues until the system is neutralized. Total exchanged valence amount required to be equal (Bilgin & Koç, 2013).

Zeolite has ion exchanging property by means of weakly bounded cations in their structure. +1 valence atom in zeolite replace with +1 valence atom in solution. If the zeolite has +2 valence, then it replace with two +1 valence atoms in solution. When exchange is finished, mass loss can be observed in the solution (Bilgin & Koç, 2013).

Ion exchanging capacity is stated as IEC. It is also considered total mole exchange amount in a gram or 100 gram. IEC values of zeolite are shown in Table 1.7.

Table 1.7: Ion exchanging capacity of zeolite (Bilgin & Koç, 2013)

	Ion Exchanging Capacity of Zeolite (meq/gr)										
Ion type	1.50	2.00	2.25	2.50	2.75	3.00	3.25	3.25	3.50	3.75	4.00
	Amount of loaded ion according to ion exchange capacity of zeolite (g ion/g zeolite)										
Na^{+}	0.034	0.040	0.046	0.052	0.057	0.063	0.069	0.075	0.080	0.086	0.092
K^{+}	0.057	0.068	0.078	0.088	0.098	0.108	0.117	0.127	0.136	0.147	0.156
Mg^{+2}	0.018	0.021	0.024	0.027	0.030	0.033	0.036	0.040	0.043	0.046	0.049
Ca^{+2}	0.030	0.035	0.040	0.045	0.050	0.055	0.060	0.065	0.070	0.075	0.080
NH_4^{+}	0.028	0.033	0.037	0.042	0.047	0.051	0.056	0.061	0.065	0.070	0.075
Cs^{+4}	0.049	0.058	0.066	0.074	0.082	0.091	0.099	0.107	0.115	0.123	0.132
Cu^{+2}	0.048	0.056	0.064	0.071	0.079	0.087	0.095	0.103	0.111	0.119	0.127
Pb^{+2}	0.155	0.181	0.207	0.233	0.259	0.285	0.311	0.337	0.363	0.389	0.414

Ion exchanging property stems from Al amount in the structure is more than Si amount. Lack of +3 value is required to take alkali or earth alkali from outside. Weakly bounded cations can easily exchange in cation reach solution(Colella, 1996).

Ion exchange property of zeolite is used to produce water hardness improver detergents, adherence of isotopes in wastewater of nuclear reactors, purification of waste water in urban and rural regions and environmental applications. Especially removing of NH_4^{+} ions has been positive outcomes. NH_4^{+} ions have very hazardous effects on marine creatures. They leads accumulation of algs and destroys the ecology. Zeolites mined from Bigadiç İn Turkey is very useful alternative for this applications (Erdoğan, 2005).

1.2.3.4. Catalytic applications

Zeolite mineral differs from other catalyzers because its repetitive tetrahedral structure made from Al and Si. They can be used in their original or modified form according to requirements to enhance the performance. Catalytic property stems from the cations located in the center of molecule. It especially arise from ion exchanging, activeness, selectiveness, and stability properties of zeolite. It can preserve the catalytic property for a long time thanks to its durability to temperature and pressure conditions and positive regenerative characteristics (Bilgin & Koç, 2013).

Table 1.8: Catalytic applications of zeolite (Bilgin & Koç, 2013)

Hydro carbon conversion	Selective formation Dehidratasyon
Alkylation	Fuel obtaining from methanol
Cracking	Izomerization
Hydro Cracking	Inorganic
Organik Kataliz	H_2S Oxidation
Hidrogenation ve Dehydrogenation	NO_2 reduction
Hydro alkylation	CO Oxidation
Methanation	H_2O - O_2 + H_2 conversion

1.2.3.5. Other application field of zeolites

Besides the well-known applications, zeolite has many other applications such as energy sector; cleaning of; construction, health, chemistry. It is used as additive material for paper-mache and concreate grout. In health sector, it is employed for toothpaste and medicine production. It is also used instead of phosphate in detergent sector (Bilgin & Koç, 2013).

In energy sector, zeolites are used for cleaning of nitrous oxide and hydrocarbons in gasification of coal, removing of carbon dioxide in natural gas purification, also used as heat changer in solar energy and catalyzer in process of petrol production (Gülen et al., 2012).

Zeolite has great interest in agricultural usage for long decades. Zeolite tuffs are used to keep under control and remove bad odors of fertilizers. It is also used as carrier for fertilizers or pesticide and preparing the earth. ph Balance is provided by natural zeolites in acidic volcanic earth. Zeolites are also good additives for animal feed in stock farming (Gülen et al., 2012; Polat et al., 2004).

1.3. Technical Textiles

Technical textiles are the products that have very crucial place and market share in industrial sector. In century we are going through, its application fields develop rapidly as the technology improve. On the other hand, technical textile is a new name of an old term. Many textile products have been used for technical concerns besides clothing or domestic purposes, since centuries ago. For example, there are many proofs that shows woven products for road building and fishing nets had been used as geotextile ın Roman times (Horrocks & Anand, 2000).

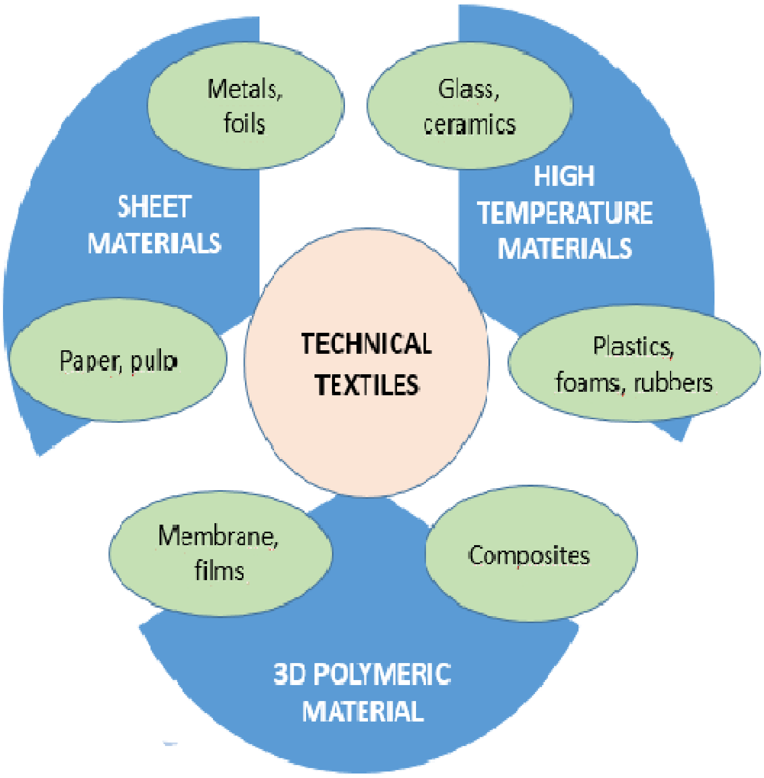


Figure 1.11: Applications of technical textiles (Horrocks & Anand, 2000)

In general, scope, technical textiles have many applications in wide area that is givin in Figure 1.11. These applications are needed to be classied in certain titles that are given in Table 1.9.

Table 1.9: Classification of technical textiles by applications (Horrocks & Anand, 2000)

Fields	**Scopes**	**Examples**
Agrotech	Agriculture, horticulture, aquaculture, forestry	Nets, ropes, lines, nonwovens for reclamation, protection, covering containment application, etc.
Buildtech	Construction and building	Tents, marquees, awnings, etc.
Clothtech	Cloths and footwear with enhanced comfort properties	Yarns, fibers, fabrics for producing of interlinings, waddings, interlinings, sewing threats, etc.
Geotech	Civil, geotextile	Erosion production textile, toxic waste filtration geo-membranes, etc.
Hometech	Household textiles, furnitures and floorcoverings	Carpets, curtains, slipcover, mops, etc.
Indutech	Conveying, filtering, cleaning etc.	Filters, conveyer or abrasive belts, seals, gasket etc.
Medtech	Medical and hygienic products	Diapers, wipes, gowns, drapes, dressings, pads, etc.
Mobitech	Automobiles, railways, aerospace and railway	Air bags, safety belts, tyre, military aircraft components etc.
Oukotech	Environmental productions	Filtration or adsorption media, oil spill products, etc.
Packtech	Pocketing	Bags, sacks, etc.
Protech	Protection products	Ballistic vests, life jackets, protective clothing for firefighters or soldiers, etc.
Sporttech	Leisure and spot	Racquet frames, fishing rods, balloon fabric, parachute, paraglider, etc.

Technique textiles exists everywhere in any form in the daily life. Raw material of textiles and production processes are as various as the application fields. Both natural fibers (cotton, wool, jute, sisal, flax) and man-made fibers (viscose, polyester, polyamide, glass) have significant place in technical textile area. Before the synthetic fiber are found out and developed, natural fibers used for technical needs. However, they got an importance in some field where their specific properties are needed, they become insufficient for high performance and low cost needs that leads to look for new alternatives - manmade fibers (Can, 2008).

First commercially produced manmade fiber is viscose rayon. From clothing to footwears, conveyor bands and belts, many textiles are produced from viscose due to its high performance. However, it has very bad wet tensile strength. That is why it is mostly used for papermaking, disposable products or cleaning.

The needs that even viscose failed to meet, filled by polyamide and polyester the new type of synthetic fiber. Their abrasive resistance, thermoplastic, thermoset, tensile strength and moisture resistance properties are regarded as almost perfect. That is why they are known as the most produced and used material for technical textiles. Their clothing comfort performance are weak so, they are blended to natural fibers to enhance the endurance.

Polyolefins are one of the foremost synthetic fibers. Low density, abrasive resistance, and moisture resistance properties are ideal for technical textiles. Thanks to the low thermal resistance, they are preferred to produce nonwovens by melt-blow method in a very low costs. As they are hydrophobic materials, they are used in places where the water resistance is needed.

Glass fibers are, though, just included to technical textile world, they rapidly gain an importance. Isolation, heat resistance, water repellency and many other properties are the proofs that they are needed in technical textile. Inflexibility is very small problem besides its high quality performances. The most known application of fiber glasses is its hollow fiber form o used for fiber internet web.

When it comes to production processes, the most known processes are conventional methods (knitting, weaving, and spinning). However, as the technology improves, interest to the synthetic fibers is rose up and new production methods have been born such as dry laid and wet laid web formation and electrospinning. The most valuable outcome of these production techniques is stated as nonwovens (Horrocks & Anand, 2000).

1.3.1. Filtration textiles

Filtration is defined as a separation process of compounds in a solution, mixture or suspension. Filtration products are permeable to one or more compound in solution and non-permeable to remaining. Filtration aims the purification of filtrated substances. Textile materials are used for filtration, especially solid-gas and solid-liquid phasesTextile filters can be design to meet needs in any form of woven, nonwoven or combinations produced from desired raw material. Finishing process are also applied to improve filter properties. Due to the three dimensional and complicated fibrous structures, textile materials are very suitable for filtration processes. Their dust collection efficiency effects the filtration at 25-99 % ratio. Some examples of filters are shown in Figure 1.12.

Figure 1.12: Examples of filtration textiles (Vaibhavlaxmispinningmills, 2015)

In industrial field, filters has very significant importance due to purification of materials provides energy conservation, enhances the productivity and efficiency, recycles the valuable materials, removes the impurities and improves the environmental aspects. Many textile filters are available in types of air purifiers, personal protective materials, oil and fuel filter, waste water and chemical filters etc. (Adanur, 1995; Aslan & Kaplan, 2010; Hardman, 2000).

1.3.1.1. Principles of filtration

Basic principles of filtration is cleaning of impurities in a fluid media. This process occurs by the fluid motion towards the filtration surface. During this transition, solid particles attach to the surface. It is prevented from passing to the other side. The cleaned fluidcontinues across to other side of surface. The structure of the filter material is critical to this phenomenon. Filter thickness, fiber structure and finesse of the filterdetermines the porosity of the filter. Wherein the porosity, known as the volume of fluid or air in the total volume of the filter material. Large amount of the volume of a filter is composed of pores. Fluid permeability depends on the size of these pores. At the same time, the width may also determine the size of the particle filter. Filtration it is related to other factors affecting the fluid. The density of the fluid speed and impurities can influence the yield of filtration (Adanur, 1995).

Filtration mechanism in four cases;

Surface transition; such a filtration prevents the passing of larger particles by remaining them in the filter surface via the pores of filter the pores.

Depth migration; this type of filtration is seen in the filters that have pore (commonly seen in nonwoven). Where the pores are thinner, particles are collected on the inner surface and trapped in these parts.

Depth filtration; This filtration method is mostly effective in fluid filtration. The particle sizesarethinner thanpores sizes of filters. Filtration process is conducted by theinertial stop, separated by one of diffusion or electrostatic attraction force.

*Cake (surface) filtration;*In this method, particles are accumulated on or in the the surface and prevented from passing to the other side. Porosity is gradually decreases from which the filtration satars. The particles are accumulated on the surface. This mesthod is generally used for bag filters and it is ideal solution for effaceable products (Aslan & Kaplan, 2010).

Particle filtration in the five cases.

1. Interception; passing the particles from the fiber surface, if the distance between the fibers is retained by the fibers is smaller than the diameter. It is released from the airflow and trapped in the filter.

Particles that are affected by this transition from a particle size of greater distances.

2. Inertial deposition; large particles without changing the way they move in the same direction as the fluid. They collide with the fiber they encounter along the way and stopped by them.
3. Random diffusion; fine particles zigzag moves in the right way instead of fluid. This event is meant to Brownian vibration. This would be more likely to hold on to progress through the vibration of the fiber particles. Temperature andfilter thickness affects the diffusion brpwni in the opposite direction.
4. Electrostatic deposition; the filter particles can only be attached by mechanical means and remain in the fibers it is difficult to achieve. This electrostatic charge is loaded with the filter installed opposite to particulate materials. Filtration is seen as the first stage in the filtration efficiency of the load positive effect. Eventually, the load amount is gradually reduced and efficiency is reduced. However, thanks to the creation of particles deposited on the surface of the cake the cake in time,productivity is increased again (Adanur, 1995; Aslan & Kaplan, 2010).
5. Gravitional forces; It shows sinking particulate weight in accordance with the effect of gravity. And halt the supplied multiplying the fiber during the fall (Adanur, 1995). Figure 1.13 indicates filtration mechanisms.

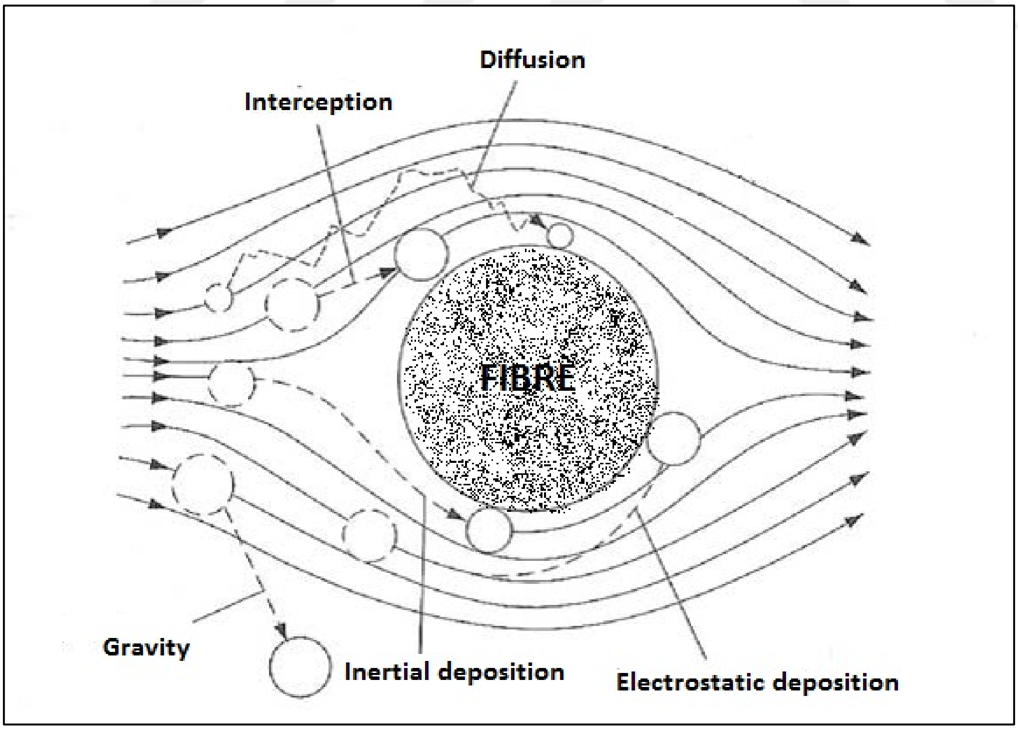


Figure 1.13: Filtration mechanisms (Adanur, 1995)

1.3.1.2. Filtration methods

Adsorbance; impurities are not always composed of solid particles. Filters are used in the liquid with the adsorbent material in the separation of the dissolved impurities giving rise to substances in the liquid. The majority of these filters are activated carbon material having a high porosity. Furthermore, for drinking water purification usege, the hydrocarbon structure supportedadsorbents filter can be made. Among other adsorbents, aluminum, zeolite and ion exchange resins are available soda cooked are placed. Such filters are preferred in the ventilation system and air conditioning for elimination of bad odors (Aslan & Kaplan, 2010).Activated carbons are also used in form of textile filters for indoor air quality as well as used in protective clothing and households (Von Blucher, 1987).

Absorbance; absorbent surfaces, which are porous structures act as sponge, cleans the surfaces by absorbing pollutants. The most known of these materials are nonwoven fibers. They are usually placed in the interface and used to facilitate liquid flow. For example; in diaper or sanitary napkins, they are placed in the interface and allow liquid absorption surface. However, these substances usually do the parsing process, they are not included in the filter categories. In case of they show selectivity, they can be used as filterin different application areas in. For example, polyolefins are hydrophobic materials, but they are good for oil adsorption material.They are used in cleaning oil spills in the water as well.Raw material withthe high absorbency are not prefered for this purpose. For example, resistance of cellulose is reduced when it adsorbed excessive amount of fluid and broken down. Therefore, synthetic products are preferred.

Elektrofiltration; the basic principles of electrofiltration is that the filter charged the oposite charge to particles. Electrostaticly charged filter pulls the particles throogh itself and collects them on the surface. Similarly, positively charged filters are used to remove ions dissolved in the liquid. The latest studies are based on the optimum electro charging of filters, effects of different solvents to charging and reasons of the alteration of electrical charging.

Anti-microbial; these kind of filtrations are produced via subjecting to chemical finishing to gain some properties such as growth inhibition of yeast, fungi and micro –organisms.

Compost structures; Filters formed by the combination of webs in different structures are the most common kind of filters. In this way it is possible to produce enhanced performance and strength filter materials (Aslan & Kaplan, 2010).

1.3.1.3. Filtrations materials

Feature structure of the fibers and fabrics is one of the most important factor in filtration. The fibers fineness of the filters effect the the pore size and strength. The more thin fibers are thin, the more the particle capturing capacity is high. The cross section of the fibers also affects the filtration efficiency. Imperfections in the cross section of natural fibers increases the surface area as well as the friction properties.

The most widely used natural fiber in filter production is the cellulose fiber. Some of these cellulose fibers are cotton linters, flax, abaca fiber, esparto fibers used in industrial filters, coffee filters, and vacuum bags. Apart from this, the wool fibers are preferred for dust collection filtration and gas mask due to its static properties.

Among the synthetic fibers, most preferred type one is polyester fiber (PET) due to the strength and chemical resistance properties and economical advantages. Filament form of punched nonwovens are prefered in air filtration and stapels are used by blending with cellulose fibers for liquid filtration. Polyamide can be used in air and liquid filters.The polyaramide fibers are used for high temperature filtration process requiring the. By providing moisture adsorption capacity in addition to heat, it prevents against static electricity and are highly resistant to chemicals.

1.3.2. Nonwoven materials

1.3.2.1. Definition of nonwoven

Nonwovens can be defied as randomly location of natural or synthetic fibers and on a plane and fixing of the web by extra processes such as chemical, thermal or mechanical. The first known nonwoven are woolen felts produces from animal hair by combination of thermal and mechanical processes under humidity atmosphere conditions. However, developing technology gives new perspectives to nonwoven production. New generation nonwovens are able to produce from the composition of staple or filament fibers with plastic films, metal foils, foam layers or other textile waste fiber and to held in stabile form different kind of fixing methods are applied (Russell, 2006).

1.3.2.2. Production process

Classification of nonwovens based on type their production methods. Because the nonwoven materials are existed in various kinds, production methods also become various. However, based on the main principles these methods are divided in three groups, dry laid, wet laid and polymer laid formations and electrospinning method.

1.3.2.2.1. Dry-laid web formation

Dry-laid webs can be formed by two different methods; carded-laid formation and aerodynamic (air flow).

Carding is a mechanical process that the staple fiber are taken from bales and then opening and blending process is applied to obtain homogenous web. Opened fibers are transported via pipes which air flows though. Blending and carding are accurately provided during the transportation. Well carded webs are laid on a conveyor band. If it is desired, webs can be laid in layers by motion of conveyers. Finally the web is send to finishing process to become completely nonwoven web.

In aerodynamic process, very short cut fibers are moved by air flows to a perforated drum and collected on the drum by layers. The drum is supported by air holes which suck the fibers onto drum. Fibers on the drums are located very randomly and voluminous. This is why air-laid webs are softer and sparser than mechanically carded webs. The web is transferred to conveyor band to pass other processes.

Dry-laid webs can be oriented in parallel, cross or mixed forms. Parallel oriented fiber webs are not durable enough when they are compared to cross and mixed forms. In these forms fiber are held each other very well in many positions. As a result of random positions cross linked fiber webs have better strength in both vertical and horizontal directions (Hutten, 2007; Russell, 2006).

1.3.2.2.2. Wet laid web formation

In wet-laid web formation, first very dilute water/fiber suspension is prepared in tanks. Fibers are randomly dispersed in water. Pipes or chambers are used for transportation. During this process fibers are floated in water to neatly reposition. They are transferred to a multi porous conveyor and filtered from the water. Wet web is pressed via two cylinders to remove the water as possible. After the cylinders, temporary binder is applied on the surface to keep the web in stable form until the permanent bonding.

Before the finishing process web is required to dry to remove whole water in it. Finally the web is prepared for fixing and finishing processes.

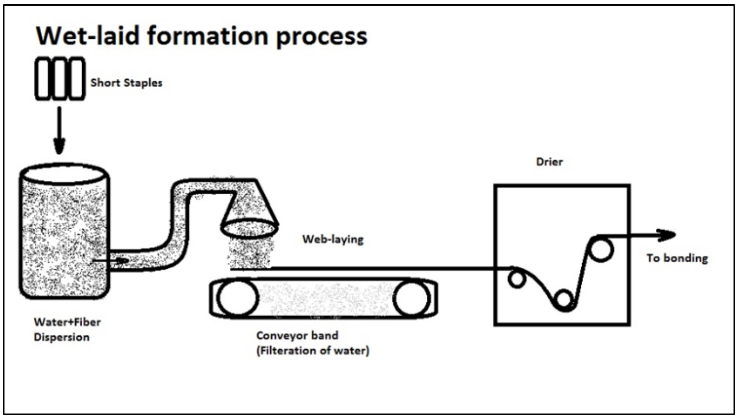


Figure 1.14: Wet-laid formation process (Russell, 2006)

In wet-laid web, Orientation is quite perfect. Fibers are located in many positions which is gained to web very elastic structure and strength in both vertically and horizontally. Via this method, it is possible to utilize countless type of fibers and their combination. Especially, it is very suitable method for staples which are too short to be used for spinning and yarn production. Both man-made and natural fibers have a valuable place in this sector.

1.3.2.2.3. Polymer- laid web formation

There are two production methods for polymer-laid webs. Both are based on the same principle. Polymer is prepared in a tank in liquid form, then pulverize via a multi porous dose. Pores can be design in desired size or forms. Polymer liquid comes out of the dose as an infinite filament that are laid to a conveyor band. It is possible to obtain parallel laid web or cross laid webs can be obtained by changing of conveyors moving directions at a regular intervals.

Nonwovens that are produced according to this process have the most strength structure. One other advantage of the process is that extrusion, bounding and fixing process are all come true in one unite which makes production more technologic and more practical as well as less complicated and less expensive.

The polymer liquid is prepared by melting or solving with a convenient solvent. Relying on the preparation type of polymer liquid, two type of production method come to the fore; melt-blown and flash spinning.

In melt blown methods, thermoplastic polymers are heated to very high temperatures to obtain low viscosity melt. Melted polymer is extruded from dose to a cool air shower. Rapid cooling fixes the melted shape to filaments which are collected on a conveyor band in the web form and brought to bounding and fixing processes via a thermal bounding process or a binder application.

What is different from melt blown, flash spinning do not include high temperature melting process. Instead, polymer is solved in an appropriate solvent and a low viscosity solution is prepared. Then solution is sprayed with a low pressure to a chamber to meet another chemical to remove solvent. What is only left, filament form of polymer that is laid no a conveyor to be brought next section. Fiber webs are fixed together and nonwoven surface is prepared for finishing process (Horrocks & Anand, 2000; Russell, 2006).

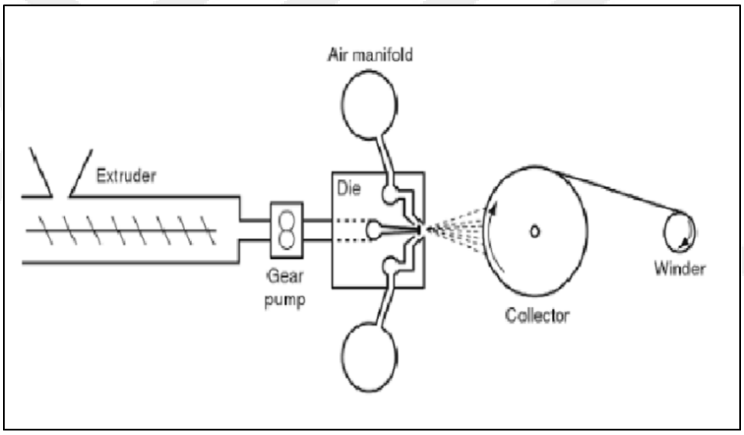


Figure 1.15: Schematic display of polymer-laid formation method (Russell, 2006)

1.3.2.2.4. Electrospinning method

Electrospinning method is first invented by Formhals in 1934. This method is based on the electrostatic forces to spin fiber. The spinning mechanism is settled on linear plane. Polymer solution is moved from one end to another by a potential tension. An electrode connected with the energy source is inserted to polymer chamber while another one is a linked to a grounded conductive plate. When the electrical current come into action it attracts the polymer. The liquid is moved with the current to the plate in form of fine strings. Polymer is in liquid phase while it is in the chamber. When it meets to air, turns to solid, means fiber. Because the polymer is flows by the current it is forced to move fast. Velocity caused the fiber to be sized in nano scale.

Fibers collected onto the plate are construct a nonwoven surface in thickness of micron or nano (Özdoğan, Demir, & Seventekin, 2006).

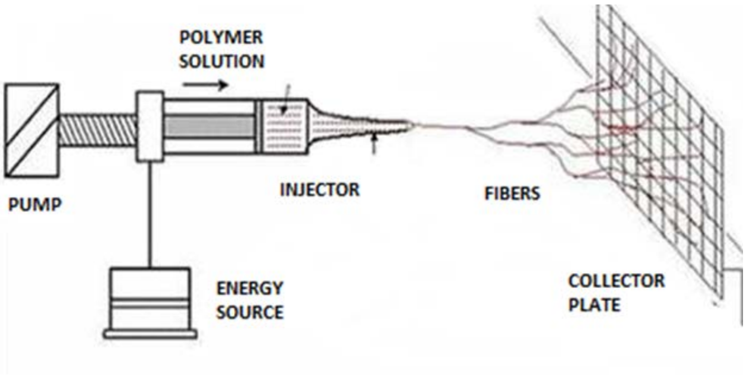


Figure 1.16: Electrospinning Method (Özdoğan et al., 2006)

- Structural properties are depends on some parameters given below;
- Concentration of polymer
- Polymer viscosity
- Distance between collector plate and injector
- Potential energy at the extrem point
- Flow rate

Fibers produced by this method are very thin, webs as well. Their mechanical duration is too weak to prefer for any application. This is why they are mostly used as coating material to specialize the other products. Base material provides mechanical strength and nanofiber enhance the performance quality.

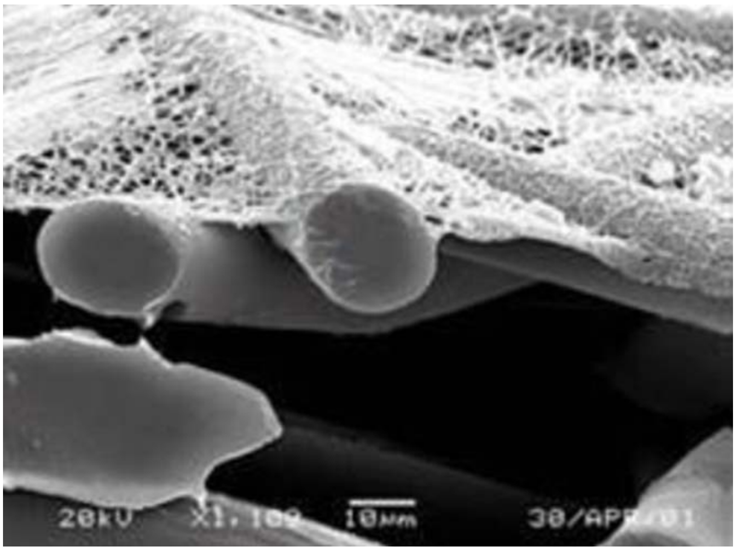


Figure 1.17: Electrospun bound nanofiber onto base textile (Özdoğan et al., 2006)

Base textiles can be chosen from any textiles made from naturel or synthetic fibers. These kind of combined products are very useful for filtration applications.

Electrospinning is also one step process like meltblown and spunbond in nonwoven production. Without any additive process requirement, a nonwoven surface can be coated onto any woven, knitted or nonwoven textiles of cellulosic, polyester, polyamide or glass fibers (Özdoğan et al., 2006).

1.3.2.3. Bonding types of nonwovens

There are three types of bounding method which are ordered below;

- Mechanical bonding
- Chemical bonding
- Thermal bonding

1.3.2.3.1. Mechanical bonding

The principle of the mechanical bonding is fixing the web by physically connecting of fibers. Friction between the fibers prevents and limits their motion in the web. The more fibers connects the each other, the more friction occurs and fibers stayed stable. There two methods for mechanical bonding.

1.3.2.3.2. Punching method

In this method very special needles are used. Needle tip is in thorny form which provides holding and moving of the fibers. Nonwovens are punched in frequent intervals. During the needles' motion fiber are stocked around the thorns and moves with them. Fibers replace, link and hold to each other without any permission to scattering which means they got felt. This method gives opportunity to make layers at desired numbers and punch them together. It is almost appropriate for any kind of fibers as well.

1.3.2.3.3. Water jet fixing

This method is utilized for carded-laid, air-laid or wet laid webs' fixing. Very high-pressure water is injected to webs in frequent intervals. Water pressure at 300-bar act as needle and provides the tangling of fibers around each other which makes the web more strength. The thickness of nonwoven and fixing degree is arranged by water pressure.

1.3.2.3.4. Thermal bonding

This method is useful only for thermoplastic fiber. To link the fibers each other, temperature intervention is applied. Fibers that are soften and little melted by the effect of temperature and they stick to each other at the contact points. The more contact points are existed, the more connection and strength fixing is occurred.

In this methods, not only the fibers are bond on their own, but also binder can be used to provide more strength structure or for fixing of non-thermoplastic fibers. Adding thermoplastics to blend is also a solution for thermoplastic bounding. Blended fiber acts as binder in this situation.

For thermal bonding, various manners are used;

- *Hot calendaring*; calendars are provide heat for melting and pressure for connecting and sticking. Thermoplastic binder or fibers easily melts and linked to each other. This method effects the thickness. Maximum middle thickness nonwoven is produced.
- *Hot air*; fiber web is exposure to hot air. Thermoplastic binders or fibers melt and stick to each other at touching points. With this method, it is possible to obtain more voluminous nonwoven.
- *Ultaschall;* A patterned cylinder is used in this method. Pattern parts are heated and fiber is only stiched at heated point and bond.

1.3.2.3.5. Chemical bonding

In this method, main point is using chemical binders. Any type of chemical binders (powder, foam or liquid) are available in market. These binders are made from copolymers mostly knowns are acrylic, vinilacetate/etiol and stryrol-butadien binders. Binders can be solve in water and solution is prepared in desired concentrations. Application methods can be preferred as printing, spraying or impregnating (Horrocks & Anand, 2000; Russell, 2006).

1.4. Adsorption

When an activated solid is left to the gas or vopur environment, it is observed that the volume of the gas decrease at constant pressure or pressure decreases and volume stays constan. As a result of these observations, it is observed that a portion of the gas or vapor is retained by the solid. The gas or vapor molecules can enter the interior of the rigid or cling floor surface. This event can be happen in two ways. The first one is called as absorption and the second is adsorption. If both event occurs at the same time, event is mentioned sorption. Gas or vapor adhere the through the clean solid surface layer by layer. In this phenomenon, solid fluid substances are named as “adsorbent” and “adsorban”, respectively. Adsorption is just accumulation of fluids on the solid surface and a special situation of absortion. It is crucial to separate both situation from each other. Adsorption is effected by temperature and gas pressure (Ruthven, 1984).

Adsorbents are porous materials which means solid have gabs inside in the form of micro sized hollows, channels or cracks. According to pore sizes, they are named as micropore (smaller than 2nm), macropore (between 2-50nm), mezopore (larger than 50nm). Total pore volume in a gram solide is defined as spesific pore volume and the sureface area is specific surface area. As the pores get smaller then the number of them increases as well as surface area (Davidson, 2000).

Adsorption process required to occurre following three conditions;

1. Dissolved substance is required to be attached to the surface of the material and must pass through the solvent liquid film surrounding the adsorbent. This transition is named as film diffusion.
2. The substances collected on the surface of the adsorbent, required to complete a process called the particle so that fluid enters to interior part of solid.
3. By the first two part is accurately done, physical forces bounds the fluid and solid substance to eache other.

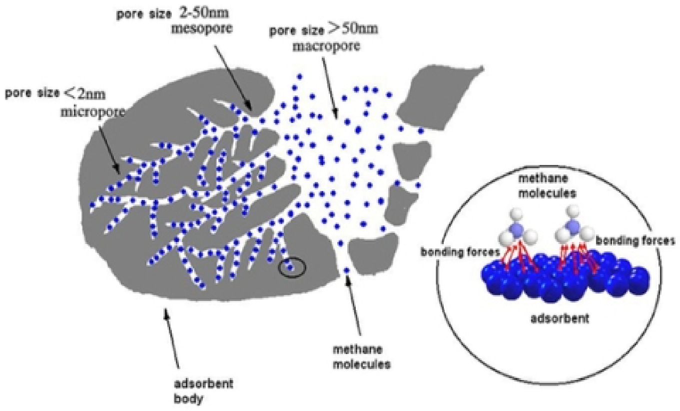


Figure 1.18: Fluid adsorption of a porous solid material

1.4.1. Types of adsorption

All adsorption phenomena that occur on solid surfaces can be divided into two main groups: physical adsorption and chemical adsorption.

1.4.1.1. Physical adsorption (Physisorption)

Forces provide linkage between adsorbent and adsorban. This is why physical adsorption is also called as “Van der Waals adsorption”. These forces are weak but effective at long distance. For this reason, stucture of the molecules or ions and their mobility on the surface do not change. Adsorption balance is reversible and require less energy. The energy released during the process is 2-5 kcal / mol. Activation energy is not available here. However, electrostatic forces mediate. In this type of adsorption, adsorbed layer may be thicker than one molecule. In case of the temperature rises or threshold heat of absorban is exceeed, adsorption amount rapidly decreases. Physical adsorbtion is reversible. That is why adsorban abandon the surface as the concentration decrease (Ruthven, 1984).

1.4.1.2. Chemical adsorption (Chemisorption)

In chemical adsorption, chemical bonding between adsorbent and adsorban substance by occur usually covalent bounds. Chemical adsorption is specific, carried out by more powerful forces that in the physical adsorption. The reaction is irreversible. Released activation energy during the process of 10-50 kcal / mol. Hence, chemical adsorption occurs faster at higher temperatures. Adsorption creates single layer on the surface. It stops by the time reactive ends are used up.

Chemisorption contains chemical interactions that are results of the electron transfer stem from adsorbent adsorban substance. Chemisorption also called activated adsorption. Physical adsorption are occurred at temperature -20 kJ / mol, while chemisorption is occurred at -200 kJ / mol. Physical adsorption of the adsorbed molecules must overcome the potential barrier to move in a particular adsorbent surface (Ruthven, 1984).

1.4.2. Adsorption isotherms

Adsorption in gas phase only depends on the pressure in case the temperature and subtants are constant. This situation is expressed by the adsorption curves called

“Adsorption izoterms”. An adsorption prosses best recognized via izoterms. It enlights the adsorban’s tendency to adsorbent. Adsorption izoterm is the caracteristic curve of adsorban amount at unit mass of adsorbent at a constant temperature and pressure (Rushdi I Yousef, El-Eswed, & Ala’a, 2011).

1.4.2.1. Feundlich Adsorption isotherms

In 1907 Freundlich expreed the adsorption as;

$$\frac{x}{m} = kPn \tag{1.7}$$

It introduced the empirical correlations where the x is the amount of adsorbed gas mass, P is partial pressure of the adsorbed gas, k and n are the constants of the adsorban and adsortion at a given temperature. Although there is a theoretical meaning of this constant relationship, it is corresponded to experimental results.

Logarithm of the equation;

$$log\,\frac{x}{m} = log\,k + n\,log\,P \tag{1.8}$$

If the $\log P$ is placed to horizontal axis and $\log \frac{x}{m}$ is placed to verticular axis, a straight line is obtained. Constant volues, n and k, can be determined (Rushdi I Yousef et al., 2011).

1.4.2.2. Langmuir Adsorption isotherms

In 1915, Langmuir teorised an isotherm equation suitable for all pressure ranges. Equation is improved kinetics by Langmuir, thermodynamics by Volmer, statistics by Fowler. It is possible to calculate the physical adsorption heat, surface area and porous density. Heat of adsorption is low. The heat emitted during operation are located in close to the heat value of the gas concentration.

In chemical adsorption, molecules are hold by valence forces on the surface. These forces are higher than the physical adsorption forces. Many adsorption isotherms were derived for both adsorptions. Langmuir derived his famous izoterm from thetheori that chemical adsorption on surface is a single molecular layer, by considering the dynamic equilibrium on surface is known to equation with his own name.

During the adsorption, initial concentration of adsorban rises. When it reaches the maximum adsorbance value, whole area of the adsorbent become covered by the layer of adsorban. Adsorbed molecules does not replace and maintain immobility. Adsorption enerjy stays stabile as well. Equition of Langmuir adsorption isotherm is best explain the relation of adsorban and adsorbent;

$$\frac{x}{M} = \frac{b\left(\frac{x}{M}\right)' Ce}{1+b\ Ce} \tag{1.9}$$

x: total amount of adsorbed substant
M: total amount of adsorbent (solid)
b: Adsorption constant
Ce: molar concentration of adsorban at equilibrium (Langmuir, 1918).

1.4.2.3. Brunauer – Emmett – Teller (BET) adsorption isotherms

BET adsorption isotherm is based on the considering of adsorption layer by layer. It is assumed that adsorption maintains even the whole surface is covered by adsorban. Upcoming adsorption substance accumulates on first layer. Each layer is adsorbed according to Langmuir isotherm (Brunauer, Emmett, & Teller, 1938).

$$\frac{x}{M} = \frac{b\ Ce\left(\frac{x}{M}\right)'}{(Cs-Ce)(1+b-1)(\frac{Ce}{CS})} \tag{1.10}$$

X: total amount of adsorbed substant
M: total amount of adsorbent (solid)
b: Adsorption constant
Ce: molar concentration of adsorban at equilibrium
Cs: Maximum adsorbed substance concentration

1.5. Infrared Spectroscopy

Infrared (vibration) spectroscopy is based on a material's adsorbing capacity of infrared lights. Homo-nuclear (N_2, O_2, Cl_2) molecules adsorb infrared lights and respond as infrared spectrum. While the wavelength of infrared lights are among the 1000-300000 nm, mostly used wavelengths are among the 2500-25000nm. This range is stated as infrared spectral region. In the ınfrared spectroscopy, the number of the waves, not the wavelength, expresses lights. The number of the waves is cm^{-1}. According to expression previously mentioned (2500-25000nm) wavelengths are shown as 4000 cm^{-1} and 400 cm^{-1}. If the wavelengths are less than 400 cm^{-1}, it means these waves are in the level of rotation energy and the molecules in the air can easily adsorb them.

Infrared spectroscopy is generally used for structural determination with electronic or NMR spectroscopies. Each material has a special infrared spectrum and it is more complicated the ultraviolet spectrum. This situation results from infrared light has the same energy level with molecule and molecule has many oscillation centers. During the vibration, distance between the atoms consistently extends and shrinks which creates an electrical field. If both electrical field vibration and the infrared light vibration fits together, the molecule adsorbs the light. The electrical charge dispersion of the molecule became asymmetric and its dipole momentum increases. Dipole momentum of some other molecules such as N_2, O_2, and Cl_2 does not change so they cannot adsorbs the infrared light (Sağdıç et al., 2007).

2. MATERIAL AND METHOD

2.1. Materials

In this study, poylyethyleneterephthalate was used as textile base, natural zeolite mineral was used as modifier, potassium permanganate was used as zeolite modifier material, acrylic binder was used for padding application and auxiliary materials given in Table 2.1 below were used for coating process.

Table 2.1: Materials used in study

Materials	Properties	Supplier
100% Polyethylene terephthalate (PET)	40 % 6 x 55 PET 40 % 15 x 64 PET 20 % 4 x 51 Melt Punch + Thermal (180^{o}C) Fixing	Salteks Tekstil San. ve Tic. A.Ş, Istanbul-Turkey
Natural Zeolite Mineral	40 µ - Clinoptilolite type	Rota Mining, Istanbul-Turkey
Potassium Permanganate	-	Kimetsan, Ankara-Turkey
Acrylic Binder	-	OrganikKimya A.Ş, Istanbul-Turkey
EC4811 EC2811	PU coating polymer	Rudof-Duraner A.Ş, Bursa-Turkey.
DA3000 DA3100	Defoming agent	
FX8011	Cross linker	
TH 815 TH 5020	Thickener agents	

2.1.1. Preparation and modification of natural zeolite mineral

Clinoptilolite type of natural zeolite minerals were purchased from Rota Minning Co. Ltd. as powder form sized over 40µ. They were milled to 20µ via bead milling machine, Retsch PM100, in 1000rpm for 20min. They were washed with 1M HCl for better performance (Erdoğan et al., 2008). Natural mineral zeolite powder is named as NZM-pow.

Plenty of powder was used for modification with potassium permanganate, KMnO4 purchased from Kimetsan Co. Ltd. Saturated $KMnO_4$ solution was prepared, mixed with powder and K-NZM paste was prepared. It is measured that the mixture has 7.68 pH value. Optimization of pH value is not considered in this study. Mixture was dried by oven at 100°C for 24h, and then milled again. Obtained powder named as K-NZM-pow.

To observe affects $KMnO_2$ binder to zeolite and for practical analyze, binder added solution was prepared according to same recipe will be applied to nonwoven samples and applied on NZM powder, dried at 100°C for 24h, milled at the end. Binder added natural mineral zeolite was names as BK-NZM-pow.

2.2.Method

2.2.1. Preparation of nonwoven textile samples

For zeolite application on non-woven textile two application methods were used; padding and coating methods. Three type of textile were obtained; natural zeolite mineral padded nonwoven textile named as NZM-p, natural zeolite mineral modified with potassium permanganate ($KMnO_4$) padded nonwoven textile named as K-NZM-p and natural zeolite mineral coated nonwoven textile named as NZM-c.

2.2.1.1.Padding method

Padding solutions were prepared as 300 ml in 50 g/lt ratio zeolite inclusion.Samples were cut in 30 x 15 cm sizes. The pick up ratio is 100%. Solution recipe is given below;

- 15 gr NZM / 15 gr $KMnO_4$ modified NZM
- 15 ml acrylic binder
- 270 ml distilled water
- AF = 100 %

Solutions were mixed for 5 min by using magnetic stirrer. Samples were immersed to the solution, then been treated by foulard, Rapid Labortex Co. Ltd. They were dried and fixed at 130°C for 7 min in laboratory type drying machine, Rapid Labortex Co. Ltd.

2.2.1.2. Coating method

Coating paste was prepared as 150 gr with 20 % zeolite inclusion (w:w). Sample were cut as 25 x 40 cm in sizes. Recipe of coating paste is given below. The coating polymers and auxiliary chemicals were supplied from Rudof-Duraner A.S/ Bursa-Turkey. All the coatings were done by using a laboratory type coating machine ATAÇ CO. LTD. in Dokuz Eylul University Finishing Laboratory.

-	24 gr EC4811	PU coating polymer
-	82.2 gr EC2811	
-	0.6 gr DA3000	Defoming agent
-	0.6 gr DA3100	
-	10.62 gr FX8011	Cross linker
-	0.6 gr TH 815	Thickener agents
-	0.2 gr TH 5020	
-	30 gr NZM	

Sample was dried at 100°C for 2 min in a laboratory type drying machine Rapid Labortex Co. Ltd. This procedure was applied for three times to same sample. In final step sample was fixed at 170°C for 2 min for cross-linking.

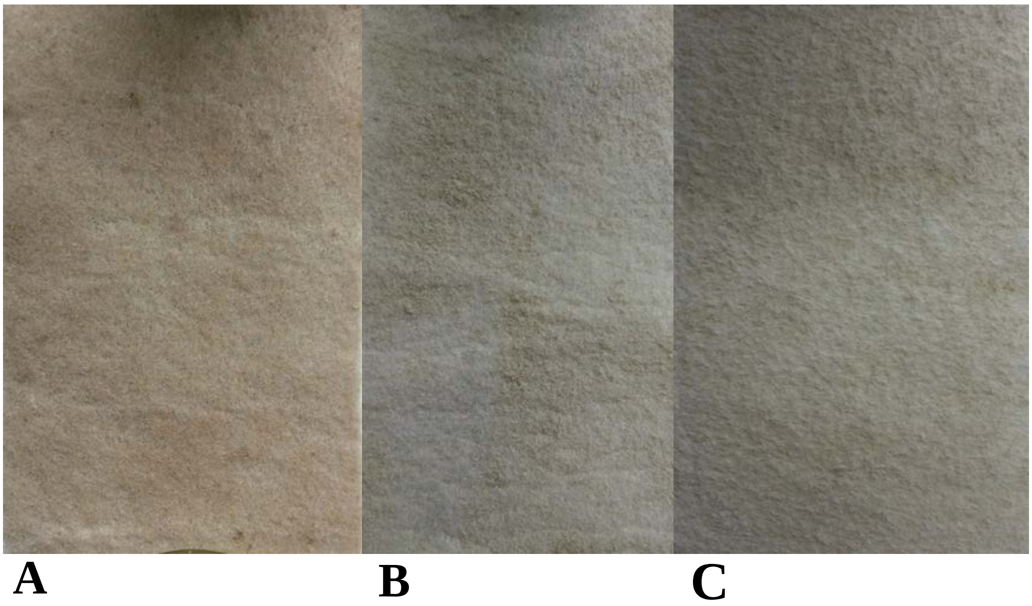


Figure 2.1: Treated nonwoven samples.A is NZM-p nonwoven; B is K-NZM-padded nonwoven; C is NZM-c nonwoven

Table 2.2: Mass unit of treated and untreated

Sample name	Untreated nonwoven	Coated nonwoven
NZM-p	175 gr / m^2	329.7 gr/m^2
K-NZM-p	175 gr / m^2	248.8 gr/m^2
NZM-c	175 gr / m^2	362.163 gr/m^2

2.2.2. Characterization Methods

For characterizing performance evaluating, particle size analysing, BET analyse, XRD, FT-IR, SEM, air permeance and water vapour testings were utilized.

Experimental process and tests have been carried out in Izmir Katip Celebi University, Material Science and Engineering laboratories and Dokuz Eylül Unıversity, Textile Engineering laboratories.

2.2.2.1. Particle size and surface area (Brunauer-Emmett-Teller) analyses

Three type of powder samples (NMZ, K-NZM, BK-NZM) were analyzed by particle size analyzer Malvern-Mastersizer Hydro200S. To determine the surface area of the particles, The Brunauer-Emmett-Teller (BET) method was applied by Quantachrome NOVA Tensiometer.

2.2.2.2. SEM (Scanning Electron Microscope) analysis

SEM analyse is employed to evaluate the general image of nonwoven samples after treatments and NZM powder distrubution on samples' surface. Modified type of NZM powders are also prepared to observe affects of binder and potassium permangante.

2.2.2.3. FT-IR (Fourier Transform Infrared Spectroscopy)

Obtained nonwoven samples are analised by Thermo Scientific iD5 ATR FT-IR Spectometer device to evaluate the results of padding and coating process in chemical compositions.

2.2.2.4. XRD (X – Ray Diffraction)

To observe the effects of padding and coating prosess to zeolites crystalline structure, XRD analyse are conducted via Bruker D2 Phaser device. Any changings in crystal structure of natural zeolites causes the differens in porous structure as well as the adsorption property.

2.2.2.5. Adsorption analyses

IR spectrum have been utilized to determine ethylene adsorption capacity of the samples. An experimental setup has been installed to measure ethylene concentration in a closed area.

First a system based on IR spectrum was installed to determine ethylene adsorption capacity of prepared samples. Measurements were performed via FT-IR Thermo Scientific Nicolet iS5- iD1 Transmission device by which solid, liquid or gas phase substances are enabled to test. Device has a glass chamber for gasses. This part was enhanced by adding an extra glass chamber (jar) for samples. The chamber provided a limited environment to control concentrations with its 100ml volume. Because the FT-IR chamber was stable for each measurement, it was ignored.

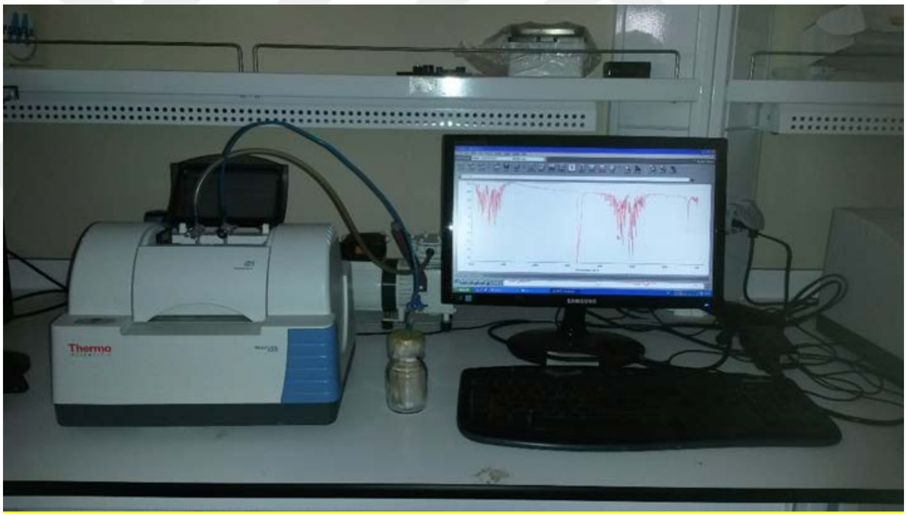


Figure 2.2: Experimental setup

In next step, pure ethylene gas IR spectrum was determined and the constant wavelengths were confirmed without considering concentration. In the same way chamber was vacuumed and IR spectrum of the environment sterilized from gas was observed to compare the gas and vacuum factor.

As it seems in Figure 2.3, graph A is belong to ethylene IR spectrum and graph B is belong to stable atmosphere without any specific gas including ethylene. Although ethylene has very simple structure, it includes very strong bound in its molecule. Because of H-C-H out of plane wagging, very strong bands are observed at 900 cm^{-}

^{1}(11 µm). Weak adsorptions are seen at 1400cm^{-1} (7.1µm) from H-C-H scissoring and 3.100 cm^{-1} (3.2 µm). Double bond in the ethylene does not adsorb the IR lights. As a result it is not possible to obtain IR peak for C=C bond in C2H4. Double bonds vibrate symmetrically and they are IR inactive. As the concentration rised, peak hight also rised.

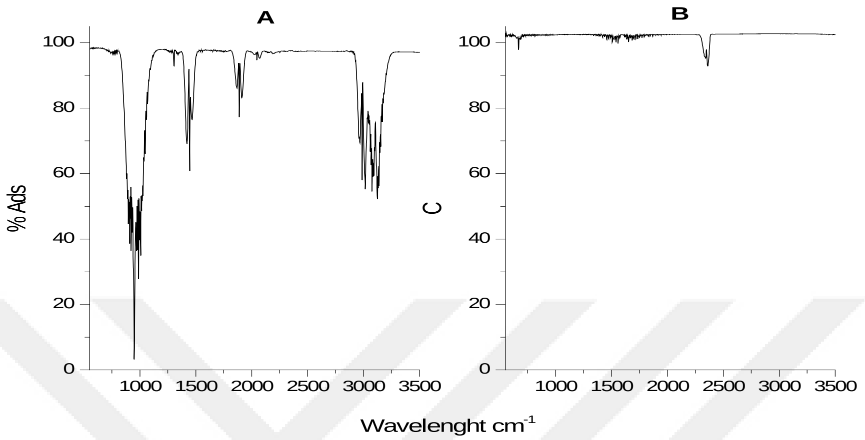


Figure 2.3: IR spectrum for ethylene (A) and none ethylene (B) conditions

Third step was creating a standard scale for increasing concentration values. For each concentration value, FT-IR gave a spectrum for ethylene in a constant infrared adsorption value. This situation can also be observed in visual of spectrum. To observe the ethylene adsorption of samples, it is considered the behavior of the peaks at 950 cm-1 wavelenght. The reference peak of ethylene changes, as the concentration changes. Amount of the gas is linear to absorbing of infrared lights.

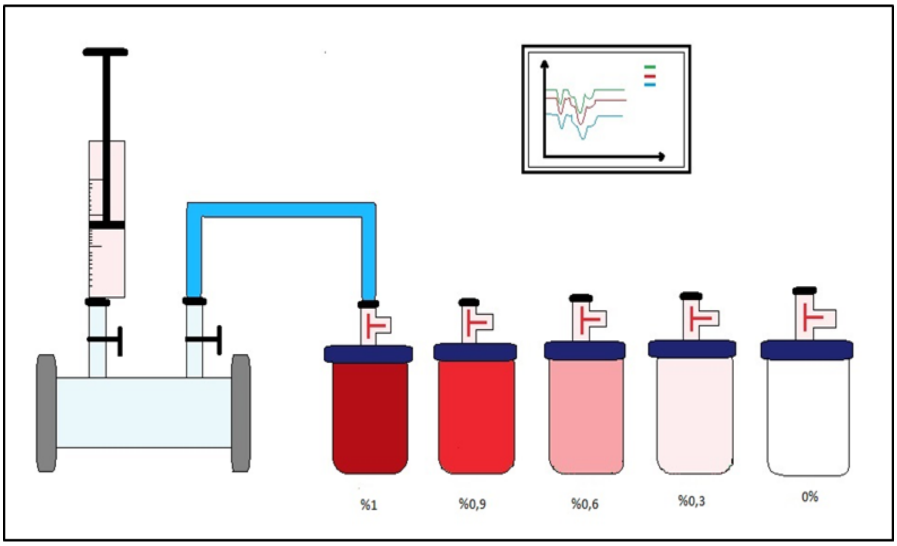


Figure 2.4: FT-IR responses change according to concentration

For the sample adsorption measurements, small pieces were cut from the samples and they were inserted to jars. For the minimum level of ethylene concentration 0.1 ml ethylene gas injected to jars. Samples were kept in gas for 24h to adsorb the ethylene. FT-IR spectrum was measured of the jar. This process was repeated with increasing concentrations until the ethylene peak was observed. Finding the ethylene peak shows that the sample approached the saturation level in ethylene adsorption.

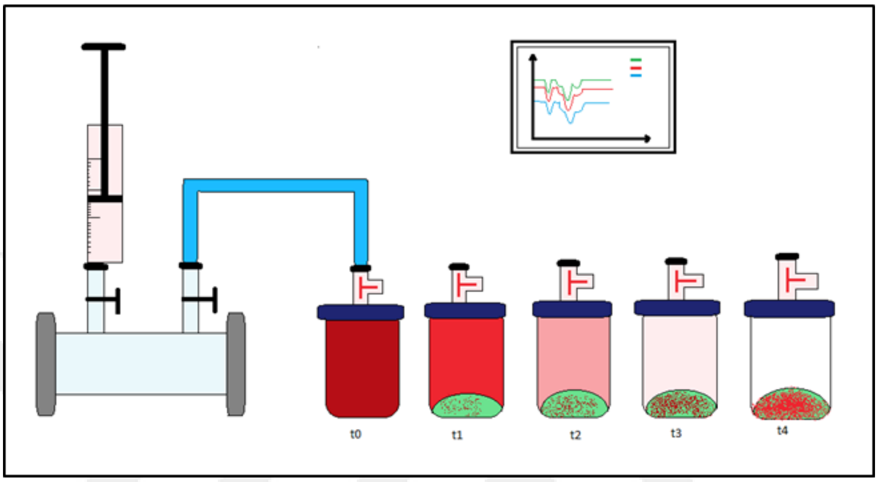


Figure 2.5: Ethylene adsorption testing of sample

2.2.2.6. Air permeability

Air permeance (AP)analyse of nonwoven textile samples were carried out at Dokuz Eylül University , Physical Testing Laboratory, aacording to TS 391 EN ISO 9237 standarts via Textest air permability tester device. Testing area of the sample was mesured 20cm^2 and applied pressure was 200 Pa. Tests were conducted in the air conditions at 20 ±2°C temperature and 65±5% relative humidity.

2.2.2.7. Watervapor permeability

Water vapour permeability (WVP) analyse were carried out at Dokuz Eylül University, Chemical Testing Laboratory, according to TS 391 EN ISO 9237 standarts.

Principle of the test is based on the measuring of water vapour passes through the fabric under normal circumstance. Fabric was cut to fit device’s conteriners. Conteiners filld with 46 ml dilute water. Fabrics were fixed to top of conteiners and settled to device. After an hour, conteiners are weighed and put back to device. The second weigheing is carried out.

To calculate the water vapour permeability, equition is used below;

$$WVP = \frac{24M}{At} \tag{2.1}$$

WVP: water vapour permeance

M: Weight loss

t: time difference between weigheings (required to be at least five hours)

A: area of the conteriners (fabrics; A=0,0054113 m^2)

3. RESULTS AND DISCUSSION

3.1. Particle size and surface area (Brunauer-Emmett-Teller)analyses results

For observation of additive materials' affects to surface area and particle size BET and particle size analyse methods were utilized. Comparison of NZM, K-NMZ, BK-NZM powders were given in Table 3.1.

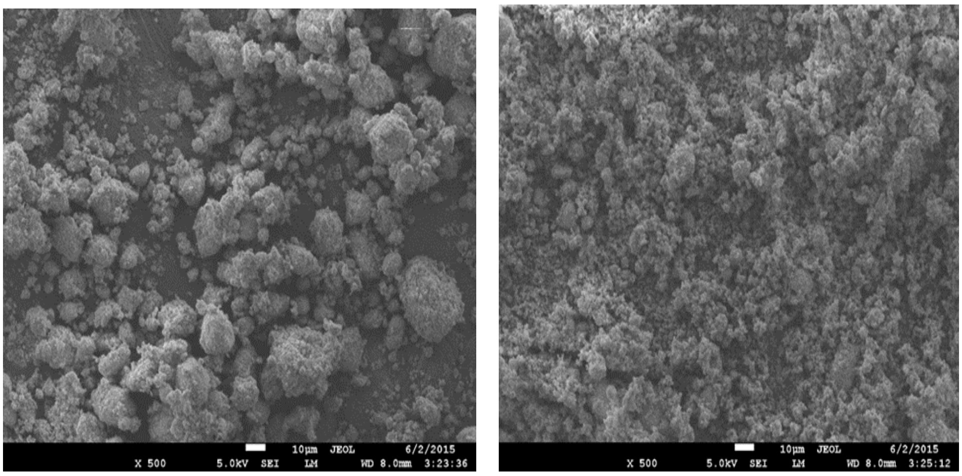
Table 3.1: Surface area and particle size distribution analyse

	NZM-pow	**K-NZM-pow**	**BK-NZM-pow**
Surface Area	36.327 m²/g	28.136 m²/g	23.995 m²/g
Particle Size Distribution	69 % ≤ 20 µ 31 % > 20 µ	72 % ≤ 20 µ 28 % > 20 µ	71 % ≤ 20 µ 29 % > 20 µ

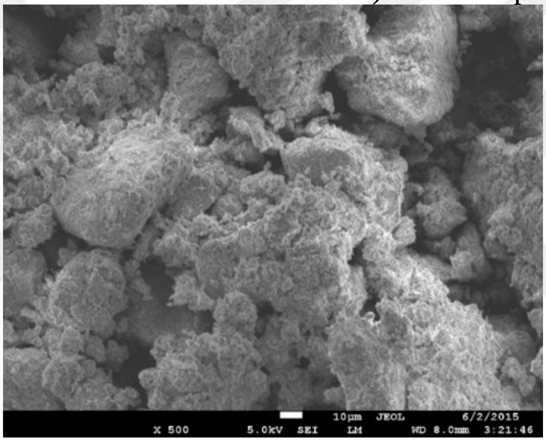
As it seems in Table 3.1, NZM-pow have the largest surface area with 36.327 m²/g. Applying potassium permanganate causes decrease the surface area to 28.136 m²/g. Addition of binder to solution also causes the decrease to 23.995 m²/g surface area. Changings in the surface area results from the blocking of zeolite pores or agglomerating of particles. However, it is obvious in the Table 3.1, after milling process, particle size disturbution of powder were shifted to be smaller than origanal sizes. While the natural zeolite powders are mostly compose of 20 µ sizes at 69 % ratio, potassium permangante added powders are at 72 % and binder added powders are at 71 % ratio.

3.2. SEM (Scanning Electron Microscopy)

Figure 3.1 inhibits the SEM images of modified natural zeolite powder at 500X magnification. The First image (a) belongs to natural zeolite powders. Although they are mostly in 20 µ sizes, they seem to be larger because they have agglomerated. The second image belongs to zeolite powder modified with $KMnO_4$. Addition of $KMnO_4$ prevents the agglomeration. K-NZM-pow samples are in 20 µ sizes, too. The Last image belongs to zeolite powder that is threated with binder and $KMnO_4$. Binder addition causes gathering of small particles. That is why BK-NZM-pow samples are in very large sizes.



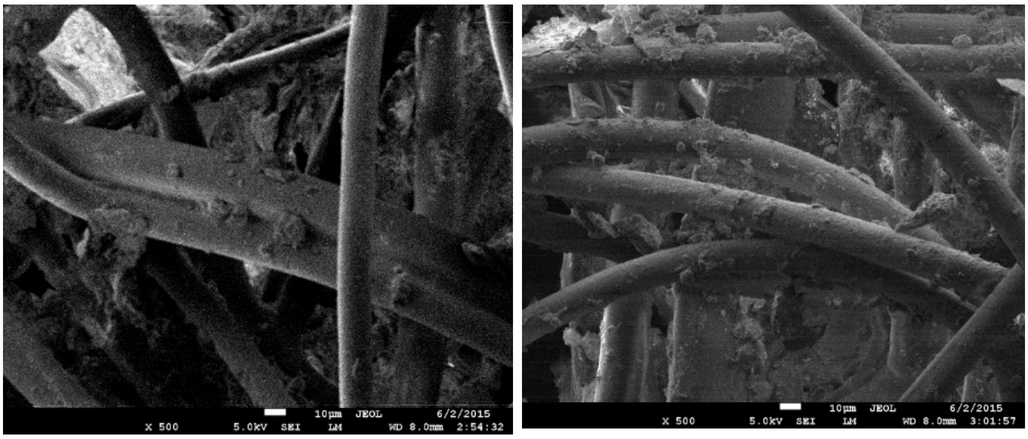
a) NZM-pow b) K-NZM-pow



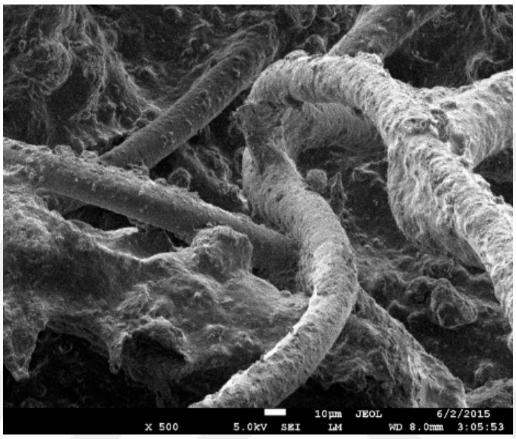
c) BK-NZM-pow

Figure 3.1: SEM images of powder samples

Figure 3.2 inhibits the SEM images of nonwoven PET modified with natural zeolite powder and $KMnO_4$/natural zeolite powder at 500X magnification. The First image (a) belongs to NZM-pow padded PET. Because of the agglomeration of NZM-pow via the binder, zeolite powders are in large sizes and dispersed heterogeneously The second image belongs to K-NZM-pow padded PET. Although $KMnO_4$ addition prevents the agglomeration in large scales, K-NZM-pow are dispersed heterogeneously. On the other hand, contrary to NZM-p sample, K-NZM-p sample has better powder dispersion on the surface. The Last image belongs to NZM-pow coated PET. It is obvious that the zeolite powders are well located through the nonwoven. However, coating substances causes the elimination of zeolite by covering them too.



a) NZM-pow padded PET b) K-NZM-pow padded PET



c) NZM-pow coated PET

Figure 3.2: SEM images of nonwoven samples

3.3. FT-IR (Fourier Transform Infrared Spectroscopy)

FT-IR spectrums of samples are given in Figure 3.3. Respectively NZM-pow, NZM-p-pow, K-NZM-p-pow and NMZ-c pow samples were characterized. Characteristic peaks of natural zeolite mineral state at 1021 cm^{-1}C–N stretching, 600-785cm^{-1}C–H bending, 1634cm^{-1}N-H bending and 3432cm^{-1}O–H stretching vibrations. Addition of binder at minimum scales leads to occur 851 cm^{-1},1152 cm^{-1}, 1380 cm^{-1}, 1450 cm^{-1}, 1730 cm^{-1}, 2977cm^{-1} vibrations. However, addition of $KMnO_4$ does not cause any visual effects on FT-IR spectrum. Amount of $KMnO_4$ is too little to be reflected to spectrum.

The last spectrum belongs to NZM-c sample which includes auxiliary materials for caoting process. It is obvious in the spectrum that extra chemicals causes critical affects on zeolite performance as they are in excessive amounts and almost dominant to zeolite.

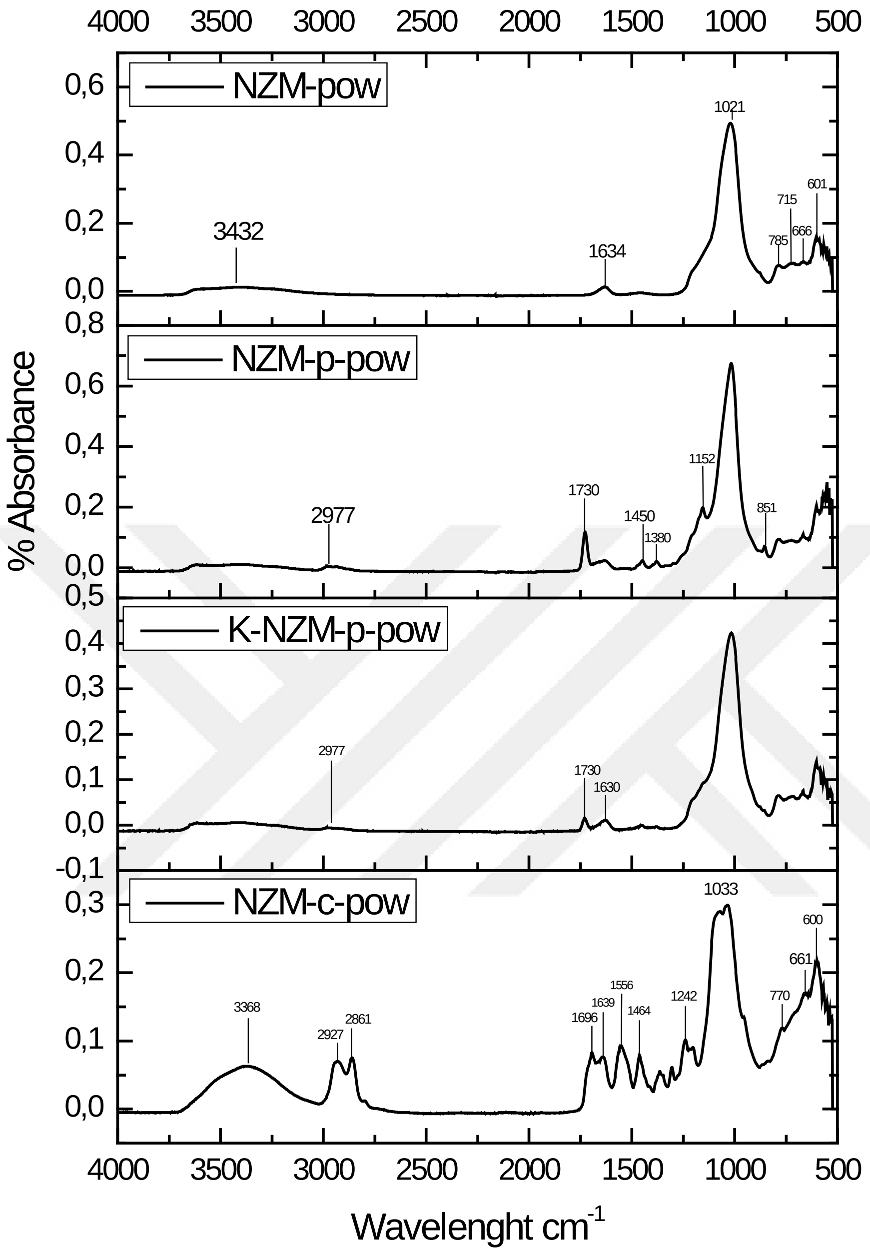


Figure 3.3: FT-IR spectrums of powder samples

3.4. XRD (X-Ray Diffraction)

To observe the effects of padding and coating prosess to zeolites crystalline structure, XRD analyse were utilized. Any changings in crystal structure of natural zeolites causes the differens in porous structure as well as the adsorption property. For XRD analyse, zeolite powders required to be independent from PET nonwoven textile. That is why NZM-p powder, K-NZM-p powder and NZM-c powder are filtered from the solutions of nonwoven application process and dried at the same conditions with nonwovens to be comparable with their original forms. These powders are named as NZM-p-pow for zeolites filtered from padded process, k-NZM-p-pow for zeolites modified with $KMnO_4$ filtered from padded process and NZM-c-pow for zeolites filtered from coating process. Powders are analysied by XRD device and compared with natural zeolite mineral powder (NZM-pow).

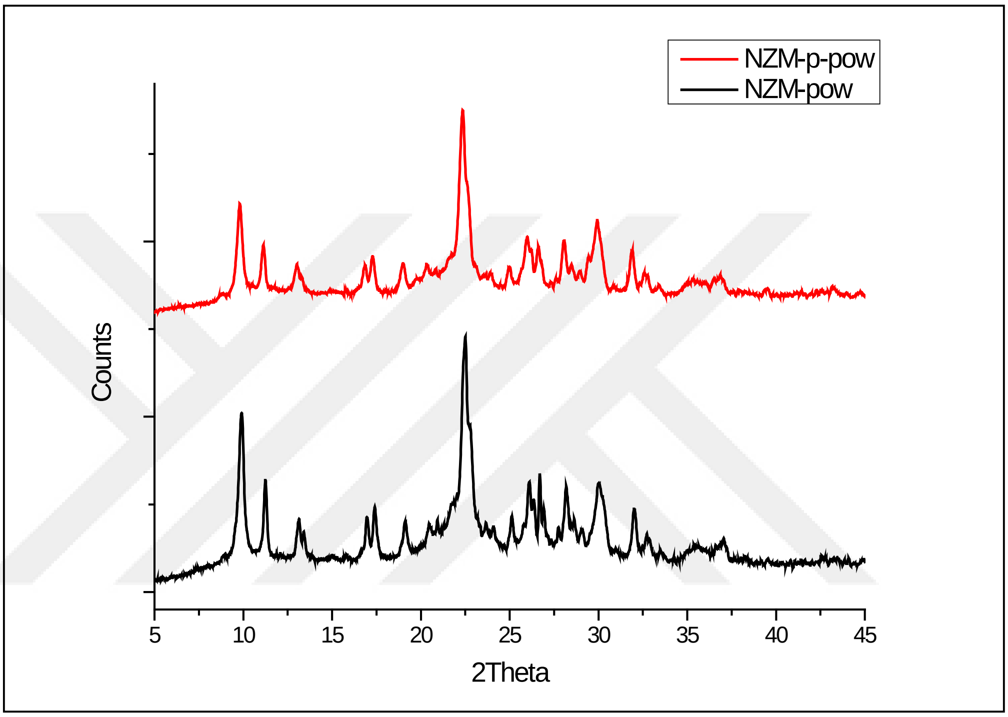


Figure 3.4: XRD analyse for NZM-p powder filterated from the padding solution

XRD Spectrums are stated in Figure 3.4 belongs to natural zeolite powder and its version treated with binder for textile application. It is much more obvious in Graph B that indicates there is a less amount difference between powders. NZM-p-pow includes polymeric binder which causes the powder seems less crystalline. However, crystalline structure of zeolite powder does not effected from binder adding. XRD spectrum of K-NZM-powder and NZM powder are compared in Figure 3.5. Both spectrums are mach perfectly. That is, on the contrary of first sample XRD results, neighter $KMnO_4$ or additive substance do not effects the crystal structure of Clinoptilolite. $KMnO_4$ vitiates the binder's effects that causes amorphism. Figure 3.6 indicates the XRD result of NZM-c sample coating paste. It is infered from the graph that crystalline structure of zeolite is not reflected on XRD spectrums. The zeolite amount in the paste is less than additive materials that includes mostly polymeric substance that eliminates the zeolite properties.

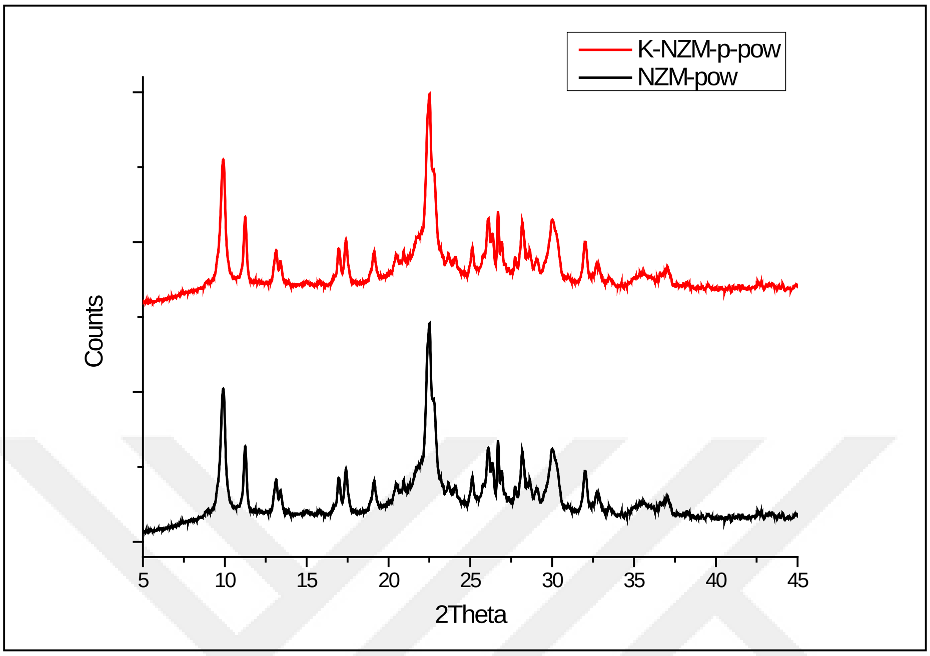


Figure 3.5: XRD analyse for K-NZM-p powder filterated from the padding solution

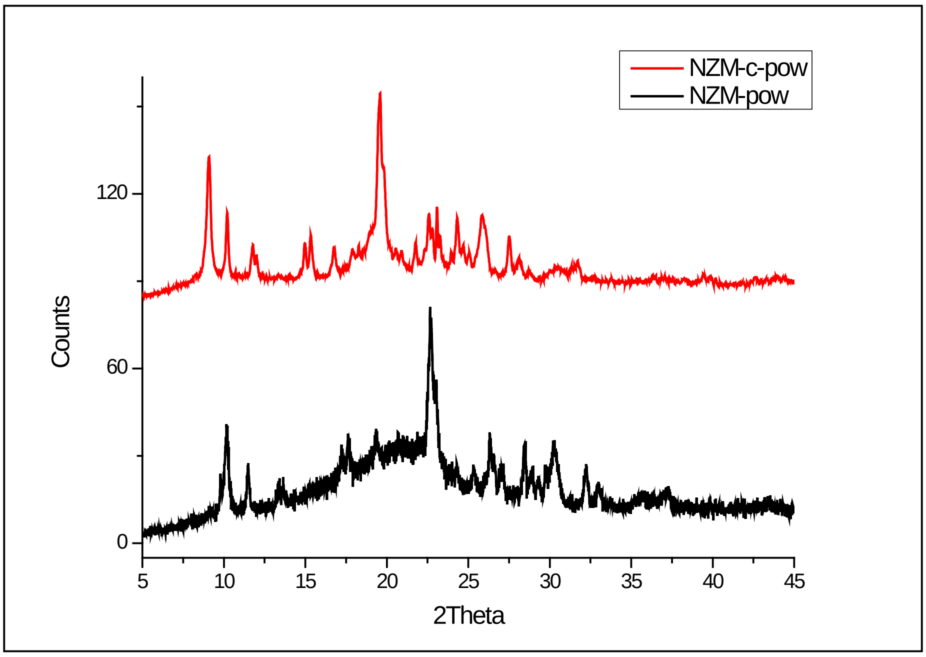


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Figure 3.6: XRD analyse for NZM-cpowder obtained from coating paste

3.5. Adsorption

Referans Measurements;

Concentration changes were provided by injecting of gas to jar (100ml volume) in 0,1ml increasing quantities. Injected gas values are started from zero and goes to 0.1ml, 0.2ml, 0.3ml, 0.4ml, 0.5ml, 0.6ml, 0.7ml, 0.8ml, 0.9 ml, 1ml, and concentrations are created as 0%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, respectively. IR adsorption percentages of concentration values are shown in Figure 3.7.

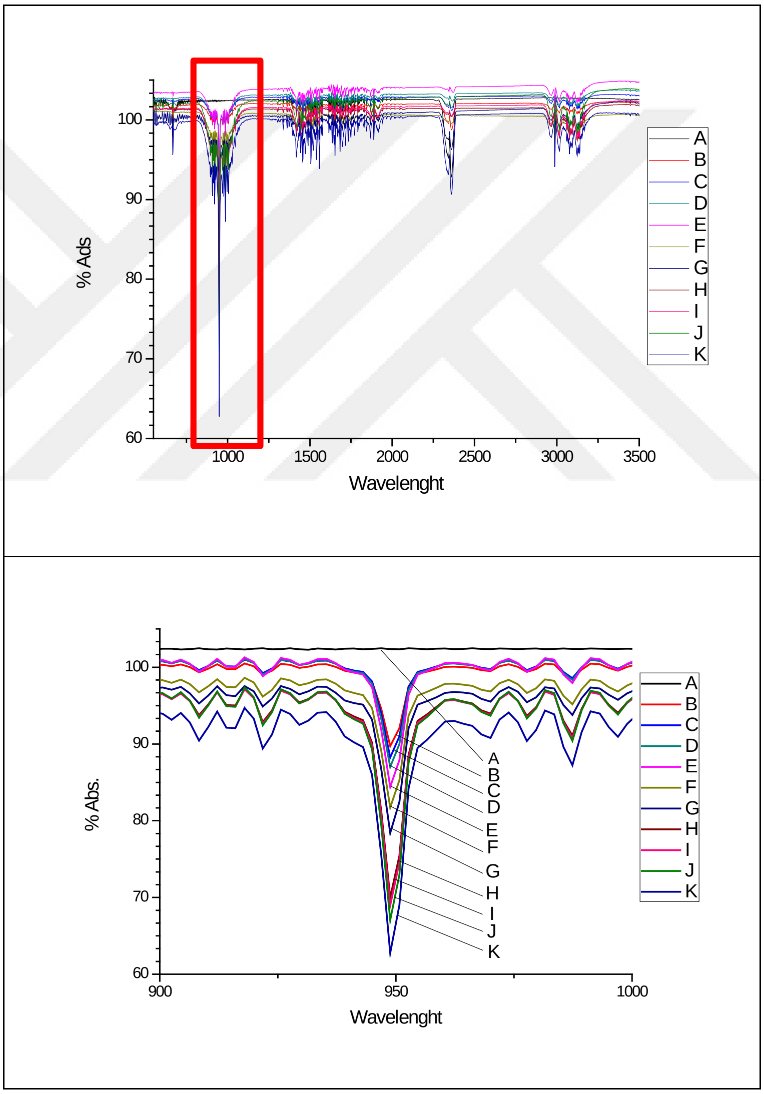

Figure 3.7: FT-IR Spectrum graphics for each concentration value

Table 3.2: IR adsorption values of concentrations

	A	B	C	D	E	F	G	H	I	J	K
Cnct.	0	%0.1	%0.2	%0.3	%0.4	%0.5	%0.6	%0.7	%0.8	%0.9	%1
IR ads.	0	8	10	11	12	15	18	19	26	28	31

IR spectrums of ethylene in different concentration were collected. Ethylene peaks at 950cm-1 wavelength were taken as reference. When the concentration is zero FT-IR do not show any response. 0.1 ml gas adding to chamber gave rise to ethylene peaks at 8% adsorption of IR light. Response of the 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1% concentration of ethylene were noted as 10, 11, 12, 15, 18, 19, 26, 28, 31 respectively.

Numerical values obtained from graphs showed that concentration increased as the IR light adsorption of ethylene increased. Graphical display of collected data is shown in Figure 3.8.

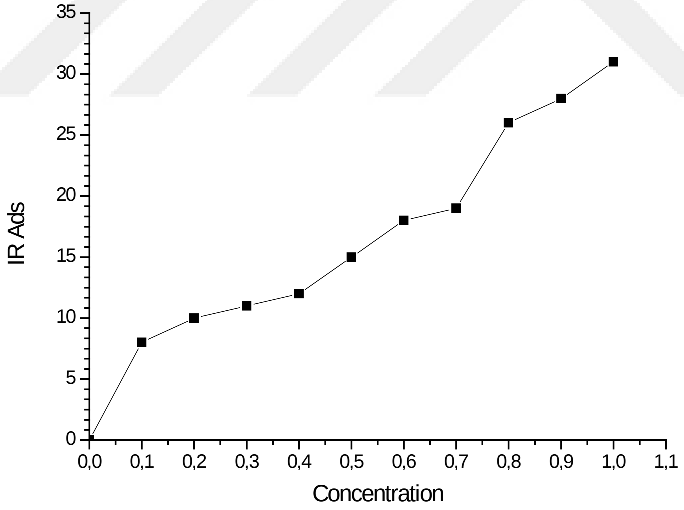

Figure 3.8: Concentration - IR adsorption graph at short scale

A wide range of concentration in jar is also measured to observe maximum ratio that brings the spectrum 100 % asorption as the meaning of saturation level in the jar, shown in Figure 3.9.

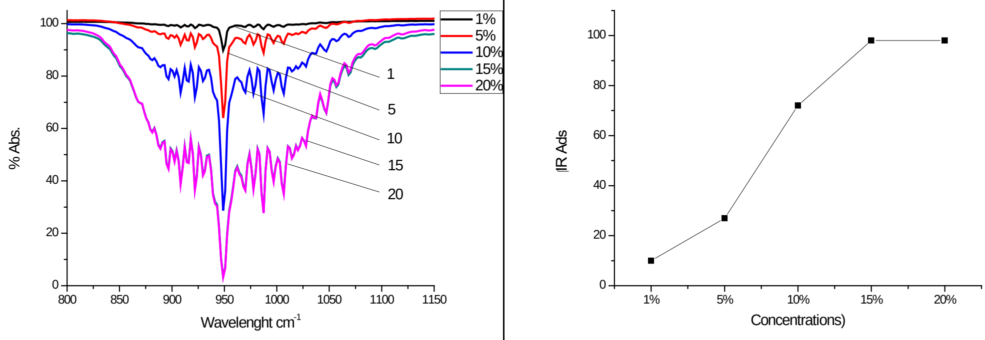

Figure 3.9: IR Adsorption-Concentration graph at wide scale

Ethylene adsorption of NZM-p sample;

Sample inserted the jar and isolated from air. 0.1 ml gas was added to jar and waited for 24h. IR spectrum was collected. There was no response for ethylene. This process repeated increasing concentrations from 0.1 to 0.9 ml injection. The latest spectrum gave a response for gas shown in Figure 3.10. According to reference measurements perceived concentration was under the 0.1% concentration value.

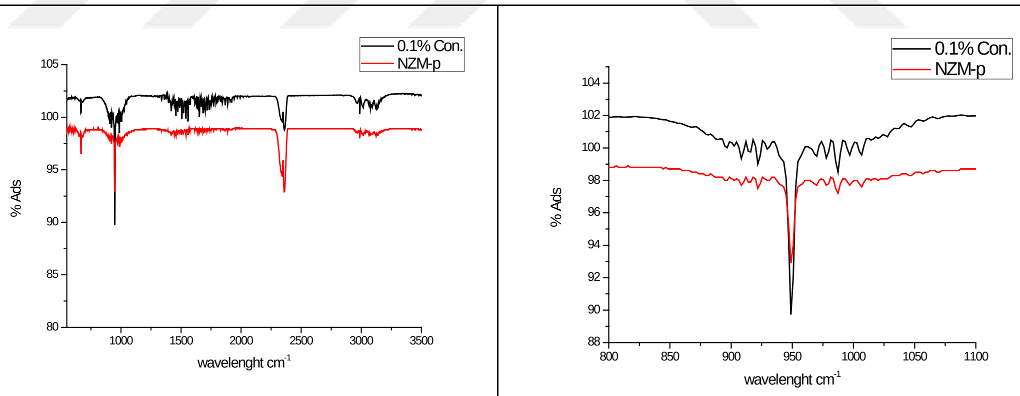

Figure 3.10: FT-IR ethylene response of NZM-p sample

According to obtained data from spectrum, sample left less concentration of gas than in 0.1% concentration level. Sample was assumed to adsorb almost all gas injected to the jar. To reach the maximum saturation level, it was continued to increase the ethylene amount in the jar at surplus amount.

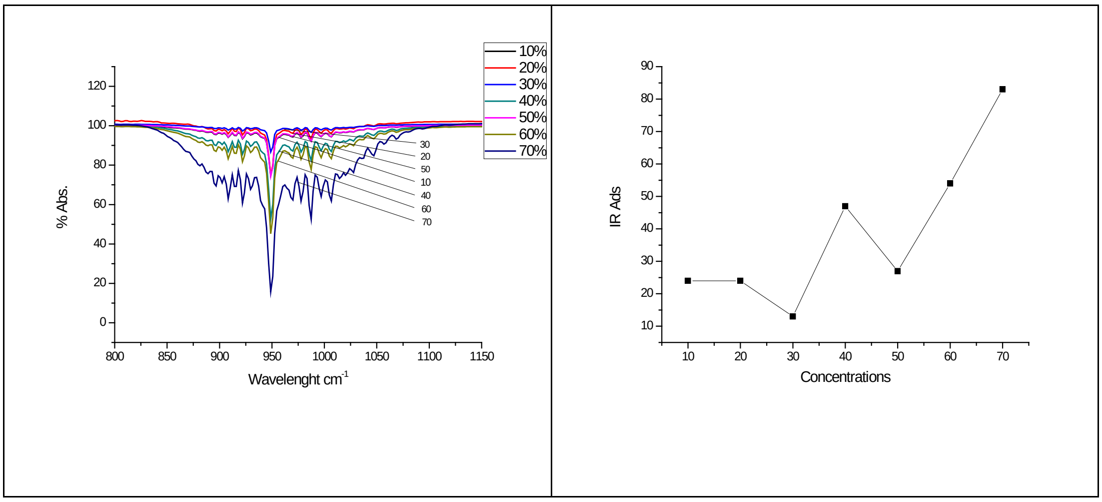

Figure 3.11: Maximum saturation level of NZM-p sample jar

Injection of extra gass was started at 10% concentration and continued to increes degrees until the jar gave 100% IR adsorption peaks. Figure 3.11, Graph A indicates the Ft-IR response according to added gases. When it is compared to referances at Figure 3.7, it is observed that FT-IR persived less amount of ethylene than it does in referances. It is clear in graph that same situation is observed for 20% concentration of gas. When concentration comes to 30 %, graph indicates decrease at that level. After that, it rise up at 40% and decrease back at 50% concentrations. However, following spectrums indicates that sample is about to reach concentration level. If it is compared to reference graph, it can be said that the samples interfere the concentration increasing. It pulls down the gas amount which means it adsorbs the gas from environment. FT-IR responces is edited to percentace adsorption values to plot the Graph B at figure.

Ethylene adsorption of K-NZM-p sample;

Sample was prepared for procedure. Starting from 0.1% concentration, ethylene injection was continued to the 1% concentration level. To determine the saturation level extra 2.5 ml gas added to jar. Total amount of injected gas is 7ml. The latest spectrum shows that perceived gas level is less than 0.1% concentration gas level. The saturation spectrum is shown in Figure 3.12.

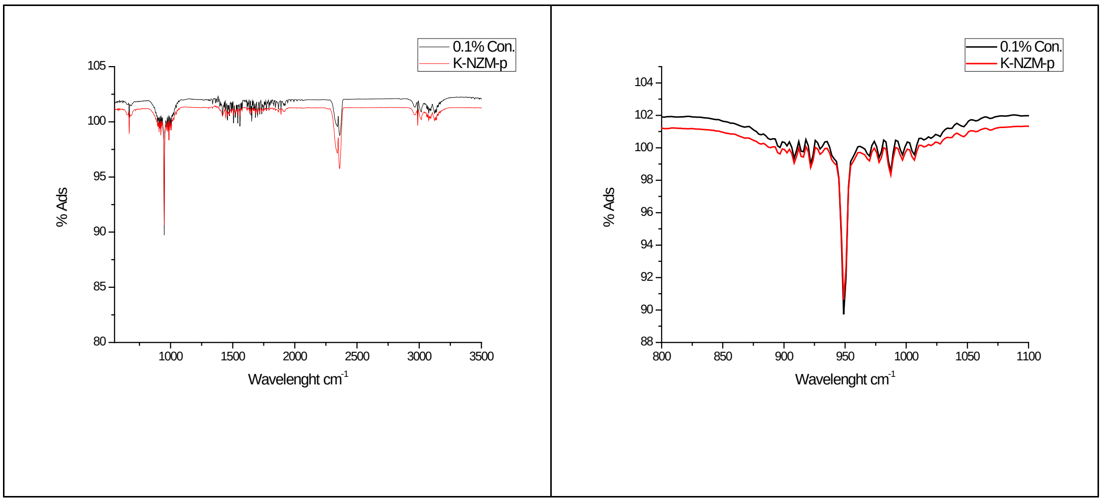

Figure 3.12:FT-IR ethylene response of K-NZM-p sample at saturation level

Adsorption analisys for K-NZM-p sample is starts from 10% and continues to 70% concentraions. Figure 3.13 Graph B shows that there is conctant decrease trough the 30%, the it starts to rise up and finally reachs the maximum saturation at 60%. Sample does not influence the gas level any more.

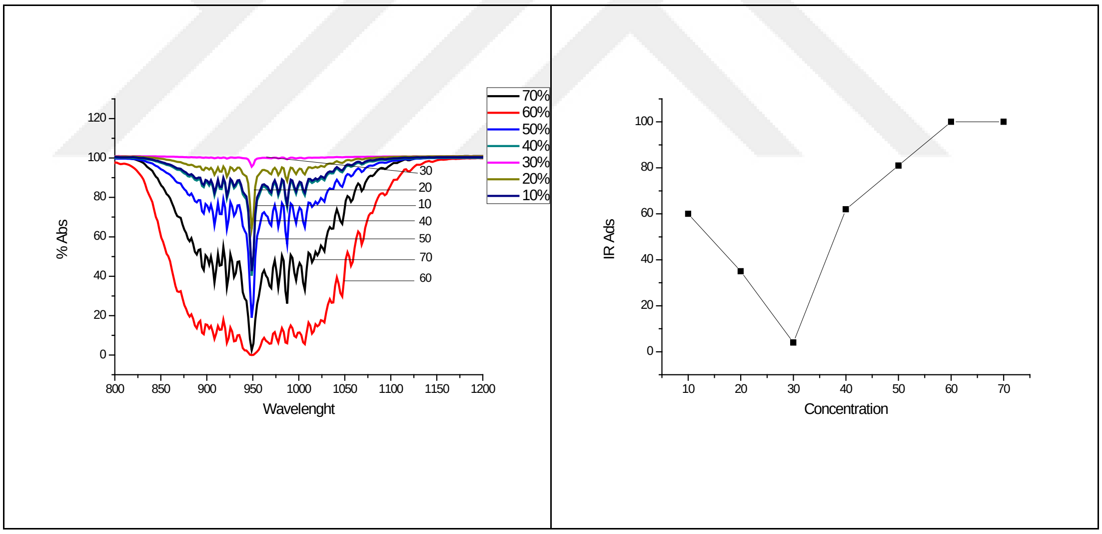

Figure 3.13: Maximum saturation level of K-NZM-p sample jar

Ethylene adsorption of NZM-c sample;

Same procedure for NZM-coated sample was carried out. Saturation level encountered after 0.6 ml gas injection. Ethylene spectrum is less than 0.1 % concentration level. Total injected ethylene gas and total adsorbed gas by sample is calculated as 2.1 ml.

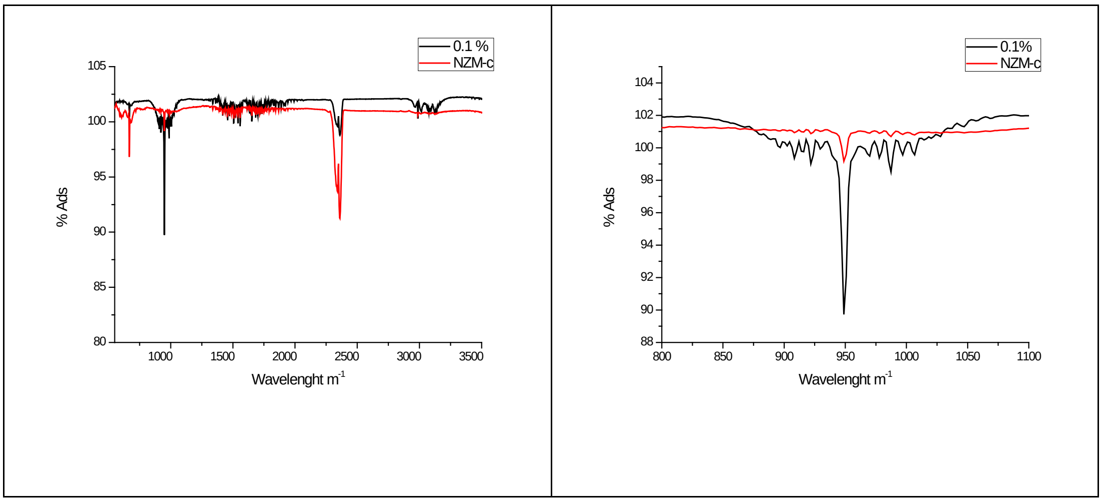

Figure 3.14: FT-IR ethylene response of NZM-c sample at saturation level

NZM-c sample is reaches the saturation levet at firt concentration level, 10%. Following measurements show that sample does not interefere the concentration changes. Sample has already complete its adsorption at first stage and reaches the maximum adsorption capacity that is given in Figure 3.15.

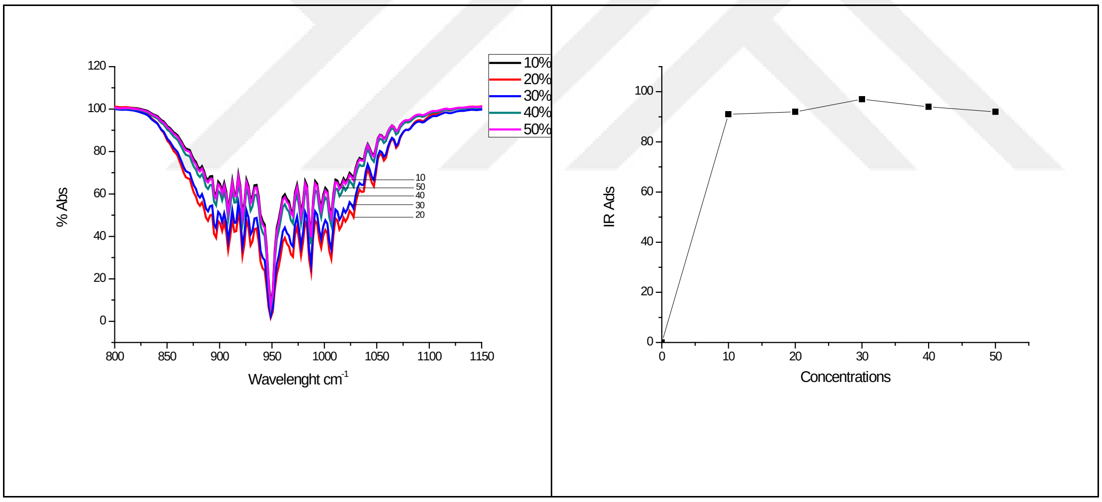

Figure 3.15: Maximum saturation level of NZM-c sample

3.6. Determination of air permeability

Air permeabilitytest were conducted to evaluate the samples air resistance as well as hiding power of materials to nonwoven.

Table 3.3: Determination of air permeance results

TEST 200 Pa (l/m^2/s)	**PET**	**NZM-p**	**K-NZM-p**	**NZM-c**
Test 1	3750	2810	2230	97,6
Test 2	3890	2650	2450	118
Test 3	3820	2640	2970	119
Test 4	3700	2670	2560	123
Test 5	3750	2960	2640	129
Test 6	3620	2590	2470	134
Test 7	3620	2620	2390	106
Test 8	3940	2840	2160	110
Test 9	4040	2620	2750	129
Test 10	3730	2590	2430	101
AVARAGE	**3786**	**2699**	**2505**	**116,66**

According to results of air permeabilty test, treated nonwovens are less permeable to air when untreated PET nonwoven is taken into consideration. Average air permeability value of PET nonwoven is 3786 l/m^2/s while NZM-p, K-NZM-p and NZM-c samples are 2699 l/m^2/s, 2505l/m^2/s and 116,66 l/m^2/s, respectively. Resistant to air results from the covering power of treatment materials. It is more obvious when padded samples are compared to coated sample. Coated sample has the less air permeability value.

3.7. Water Vapor Permeability

Water vopour permeability (WVP) test were conducted to evaluate the samples water vapour resistance. WVP tests are also significant for samples durability to humid athmosphere.

Table 3.4: Weighing results of WVP testing

Samples	**1. Measurement**		**2. Measurement**	
	1. hour	**5. hour**	**1. hour**	**5. hour**
Standart fabric	132,314	131,494		
PES	133,500	132,762		
NZM-c	134,916	134,569	135,805	135,401
K-NZM-P	132,390	131,614	134,337	133,530
NZM-p	133,461	132,684	132,799	132,041

After the tests procedure was conducted according to principles, results obtained from weighing (given in Table 3.4) were written to equation 2.1 obtained results are given in Table 3.5.

Table 3.5: Water vapour permeability of textile samples

Samples	First measurement	Second measurement	Average
Standart fabric	727.37		727.37 gr/m^{2}h
PES	654.63		654.63 gr/m^{2}h
NZM-p	689.224	672.371	680.798 gr/m^{2}h
K-NZM-p	688.337	715.835	702.086 gr/m^{2}h
NZM-c	307.8	358.361	333.805 gr/m^{2}h

As it shown in Table 3.5a standart fabric has water vopour permeability at 727.37 gr/m^{2}h. Untreated PET nonwoven's WVP is 654.63 gr/m^{2}h. After coating and padding process, it is obvious that nonwoven texile are effected differently. NZM-p sample has WVP values at 680.798 gr/m^{2}h while K-NZM-p saple has WVP-p values at 702.086 gr/m^{2}h; even they both have same application process at the same conditions. WVP of NZM-c sample is 333, 0805 gr/m^{2}h. When it comes to compare their WVP values, it is clearly obtained that; WVP of samples are K-NZM-p > NZM-p > NZM-c. This situation is explained by covering power of solution applied to PET nonwoven.

4. CONCLUSIONS AND RECOMMENDATIONS

Ethylene is one of the most important chemical used in industrial field, around the world. Some compounds such as ethanol, ethylene oxide, polyethylene polimer, they the raw materials for some products such as flexible bottles, films, panels and insulation materials, are derived from ethylene. Further, ethylene has a very important role in plant life as a development-triggering hormone. This property provides some benefits in fresh fruit and vegetable industry. Green vegetables get less harm during the transportation and storage. They have harvested before maturing and then exposed to ethylene to accelerate the ripening process. However, ethylene can cause damages in case of accumulation during the storage process. It is required to be removed from the storage environment.

In this study, we aimed to design and develope an ethylene removal nonwoven textile product by utilizing padding and coating methods. Three-different types of samples were designed and produced. The first sample was produced by padding technique, in which only zeolite particles were applied. In the second sample, the same method was used with zeolite particlesmodified with potassium permanganate after application onto zeolite due to its ability ofpermanent removel of ethylene by chemical reaction. In the last sample, only zeolite particles were applied with coating method, because potassium permanganate was very reactive to auxiliary chemicals inside the coating paste. Hence the functionality of potassium permanganate was diminished due to compositional change in the structure.

To observe the adsorption capability of samples, FT-IR spectrometer was used as a monitoring system. For this purpose, a 10 cm closed gas tube with ZnSe windows was used to measure ethylene gas concentration through collecting IR spectrums. The IR intensity in the gas spectrum for pure etyleneincreases linearly with increasing gas accumulation concetration inside the closed environment. Ethylene peaks were calibrated with respect to increase in the concentration. The FT-IR results show thatNZM-p and K-NZM-p samples were more sensitive to ethylene concentration compare to NZM-c samples. Since the surface of NZM-c samples was covered by coating paste, it is less sensitive to ethylene gas.

Initially ethylene concentration was always high, during the adsorption proceses due to its slow diffusion in to the pores of zeolite structure. According to Langmuir isotherm, adsorption occurs on the surface until the surface is saturated by the gas. Therefore, when the samples reached to the ethylene saturation level, the remaining gas simultaneously accumulated inside the gas measurement tube and finally intensity of IR absorption peaks reached to the 100% after awhile. The sensitivity against ethylene gas was decrease in the NZM-c samples since the zeolite particle surfaces was fully covered with the coating polymers. Thus, the sample did notadsorbe ethylene gas inside, so that the gas concentration remained highly at the same initial level and the IR absorption directly has showed 100%.

The adsorption results also show that adsorption of ethylene was not affected by the padding technique on the grounds thatthe acrylic binder did not cover pore structure of the zeolite particles. Opposite topadding technique, during the coating technique, the coating material has covered both nonwoven textile andthe pores of the bulk zeolite particles. Hence, the adsorption properties of the modified textile after coating techniques was decreased a lot.

This shows that the application methods was very important effect on adsorption process of the textile products. From the SEM images, it is seen that PET nonwoven did not be deformed during the padding process and acrylic binder did not cover the zeolite surface completely.

It is well known fact that humidity occurs due to the respiration of FFVs. It effects the atmosphere bad enough to cause deterioration in FFV. For this reason, air and water vapor permeability testswere conducted. Both tests show thatNZM-p and K-NZM-p samples have better responses which are close to standard specimen compare to NZM-c sample.

It is already known that ethylene is produced by the FFV and causes the over-ripening. Consequently, FFV becomes waste. In the light of this knowledge, NZM-p and K-NZM-p have good potential to be an industrial product for human consumption. Real ethylene gasses produced by FFV could be very promising to measure adsorption properties of the modified textile in future works.

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