DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

# DETERMINATION OF ODOR SOURCES IN DIFFERENT INDUSTRIAL SECTORS AND SELECTION OF APPROPRIATE CONTROL TECHNIQUES

by
Esat ŞAHİN

October, 2017
İZMİR

# DETERMINATION OF ODOR SOURCES IN DIFFERENT INDUSTRIAL SECTORS AND SELECTION OF APPROPRIATE CONTROL TECHNIQUES

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**Graduate School of Natural and Applied Sciences of Dokuz Eylül University**
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**by**
**Esat ŞAHİN**

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**İZMİR**

## M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"DETERMINATION OF ODOR SOURCES IN DIFFERENT INDUSTRIAL SECTORS AND SELECTION OF APPROPRIATE CONTROL TECHNIQUES"** completed by **ESAT ŞAHİN** under supervision of **PROF. DR. ABDURRAHMAN BAYRAM** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Prof. Dr. Abdurrahman BAYRAM

Supervisor

Prof. Dr. Mustafa ODABAŞI

(Jury Member)

Doç. Dr. Eftade GAGA

(Jury Member)

Prof.Dr. Emine İlknur CÖCEN

Director

Graduate School of Natural and Applied Sciences

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Esat ŞAHİN

# DETERMINATION OF ODOR SOURCES IN DIFFERENT INDUSTRIAL SECTORS AND SELECTION OF APPROPRIATE CONTROL TECHNIQUES

## ABSTRACT

Odor has become one of the important environmental issues in our day. Odor-causing emissions occur especially during production activities in various industries and this situation creates problems for both facilities and living quarters. In Turkey, The Regulation on Odorous Emission Controlling came in force as a result of increasing number of complaints about offensive odors. So, as a result of limit value exceedance of odor emissions derived from industrial activities, it became a necessity to make use of different methods for removing odors.

In the light of this information, within the scope of this thesis, samplings have been employed in different industries, such as oil production, rendering, livestock operation, yeast production, wastewater treatment, and brewery production, where complaints about offensive odors are very frequent. Samples were gathered from determined sources and they were measured in Air Polution Laboratory of Dokuz Eylül University by using dynamic olfactometric method. Then, a similar measurement was employed with the samples gathered from outlet points of odor control units.

As a result of aforementioned measurements for vegetable oil production, rendering, poultry operation, yeast production, wastewater treatment, and brewery production, concentration ranges are defined as Odor Unit per cubic meter respectively. Wet scrubbing for vegetable oil production rendering, wastewater treatment (lift stations), poultry operation and brewery production, bio-filtration for wastewater treatment and sludge disposal, and ozone oxidation for yeast production are identified as proper odor control methods.

As being a new environmental issue in our country, there are deficiencies in both sources and experiences about odor. It is expected that this thesis puts forward efficient and guiding results for both implementing and regulatory agencies. Thanks to these implications, it is aimed that odor-related issues can be solved faster and better.

**Keywords:** Odor, odor control, wet scrubbing, ozone oxidation, adsorption, biofiltration

**FARKLI SANAYİ SEKTÖRLERİNDEKİ KOKU KAYNAKLARININ BELİRLENMESİ, UYGUN GİDERİM YÖNTEMLERİNİN SEÇİLMESİ VE DEĞERLENDİRİLMESİ**

## ÖZ

Koku günümüzde en önemli çevre sorunlarından biri haline gelmiştir. Özellikle üretim faaliyetleri sırasında birçok endüstride kokuya neden olan emisyonlar oluşmakta ve ortaya çıkan koku tesis içinde ve çevresindeki yaşam alanlarında problem yaratmaktadır. Oluşan kokuların rahatsız edici boyutlarda olması ve şikayetlerin artması sonucunda "Koku Oluşturan Emisyonların Kontrolü Hakkında Yönetmelik" yürürlüğe girmiş ve sınır değerler belirlenmiştir. Bazı endüstriyel faaliyetlerden kaynaklanan koku emisyonlarının sınır değerleri aşması, oluşan kokunun çeşitli giderim yöntemleri kullanılarak giderilmesini gerekli hale getirmiştir.

Tez kapsamında, bitkisel yağ üretimi, rendering, kümes hayvancılığı, bira üretimi, atık su arıtımı ve maya üretimi gibi koku şikayetlerinin yoğun olduğu endüstriler üzerine örnekleme çalışmaları yapılmıştır. Belirlenen kaynaklardan numuneler alınarak Dokuz Eylül Üniversitesi Koku Laboratuvarı' nda dinamik olfaktometrik yöntem ile ölçülmüştür. Benzer bir ölçüm çalışması, bu tesislerdeki koku giderim ünitelerinin çıkışlarından alınan numuneler içinde yapılmıştır.

Yapılan ölçümler sonucunda bitkisel yağ üretimi, rendering, kümes hayvancılığı, bira üretimi, atık su arıtımı ve maya üretimi sektörleri için koku aralıkları belirlenmiştir. Ayrıca bitkisel yağ üretimi, rendering, terfi merkezi, kümes hayvancılığı ve bira üretimi için ıslak yıkama, atıksu arıtım ve çamur bertaraf ünitelerinde biyofiltreleme ve maya üretiminde ise ozon uygun koku giderim yöntemleri olarak belirlenmiştir.

Koku ülkemizde yeni bir konu olduğu için gerek kaynak gerekse tecrübe konularında büyük eksiklikler bulunmaktadır. Bu sebeple tez kapsamında elde edilen sonuçların hem uygulayıcı hem de denetleyici kurumlar için yol gösterici nitelikte olması beklenmekte, bu sayede sorunların daha doğru ve hızlı bir şekilde giderilmesi hedeflenmektedir.

**Anahtar kelimeler:** Koku, koku kontrolü, ıslak yıkama, ozon oksidasyonu, adsorpsiyon, biyofiltrasyon

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# CHAPTER ONE
# INTRODUCTION

The definition of odor can be explained as a sensation that results from the interaction of several chemical compounds, which are inhaled through the nose. Basically, the compounds including volatile organic compounds (VOC), and sulfur and nitrogen containing ones stimulate olfactory sense. After stimulation, odor perception occurs (Brancher, Griffiths, Franco, & de Melo Lisboa, 2016; Dincer , 2007).

In spite of the fact that odorous emissions have occupied a secondary role in the past due to their limited effect on human health and environment when compared with solid and liquid ones, odor problem is one of the biggest environmental concerns in our time (Lebrero, Bouchy, Stuetz & Munoz, 2011). However, continuous exposure to odor has many negative effects on human health, aesthetic and even causes economic issues (Atımtay, 2004). Due to increasing of complaints, sensitivity to environment, and developments on legislative regulations, odor management has played a prior role especially in the last years. Most of the countries have been trying to limit odorous emissions with strict environmental regulations (Dokuz Eylül Teknoloji Geliştime A.Ş. [DEPARK], 2014).

In the past, there was no limit value, a specific law or even regulation related to odor issues in our country. For that reason, legal authorities could not provide any concrete response or make evaluations about the complaints. In this regard, emissions of some compounds in the scope of ambient air quality were tried to be limited in order to provide partial precautions about the odor issue.

As Turkey's Environmental Legislation had to be harmonized with European Union Environmental Legislation in the scope of Turkey's European Union Full Membership Process, the lack of odor regulation in our country came to the forefront as an important deficiency. In this context, Turkey's Ministry of Environment handled this issue with a comprehensive study. In 2013, last version of odor regulation entered into force as ‘Koku Emisyonlarının Kontrolü Hakkında Yönetmelik’ (The Regulation on Odorous Emission Controlling). Also limit values are defined in the regulation.

Industrial activities are major sources of odor problem. Odorous emissions release as a result of many industrial activities, such as rendering, wastewater treatment, food processing, livestock operations, brewery production, petroleum refining, paint production, composting and so on. Due to the increasing complaints, characterization and abatement of the odorants has become a necessity (Atımtay, 2004; Dincer & Muezzinoglu, 2008).

Odorous emissions consist of mixture of numerous compounds, which occur as a result of industrial processes. According to their characteristics, each compound may be perceived in different concentrations. Also, determination of the concentration has vital importance in the odor management process. Measurement techniques are based on either chemical analysis of the compounds by using instruments or olfactometer analysis using human nose as a detector. Although each method has several advantages, olfactometer is the most prevalent one in order to determine odor concentrations. According to measured concentration, proper odor control method can be selected to decrease the concentration to acceptable levels indicated in the odor regulations (Dincer, 2007).

There are various methods to control of odorous emissions, including wet scrubbing, incineration, biofiltration, adsorption, chemical oxidation, UV applications and so on (Schlegelmilch, Streese, & Stegmann, 2005; Lewkowska, Cieslik, Dymerski, Konieczka, & Namiesnik, 2016). Although there are many applications of these systems on industrial and laboratory scale, it is highly required to do more research to find out the best control method  for different industries.

## 1.1 Aim of the Study

The main objective of this thesis is to find out odor sources in selected industries and investigation of proper odor control methods for them. In addition, specific objectives of this thesis are listed as follows:

- Determination of industrial odor sources
- Measurement of odor concentration of determined odor sources in the selected industries and odor control methods by olfactometry
- Calculation of average odor concentration for each industry by using olfactometric measurement results and removal efficiencies of odor control methods
- Evaluation of measurement data and decision of the best odor control methods for selected industries.

## 1.2 Scope of the Study

In this thesis, according to complaints and previous research studies, the most odor problematic industries were identified and their odor concentrations were investigated. Also, commonly used odor control techniques were examined and their outlet concentrations were measured in order to find out the best odor control technique for each industry according to Turkish Odor Regulation limit value. All the measurement activities were performed with dynamic olfactometric measurement method.

Odor concentration of six industries from selected sources, including oil deodorization unit for oil production, cooker unit for rendering, lift station, wastewater treatment and sludge disposal units for wastewater treatment, animal house for livestock operation, wort boiler for brewery and fermantor for yeast production were measured in the scope of this thesis. Moreover, similar measurement activities were performed for samples, which were collected from outlet of odor control units of these facilities, including wet scrubbing, ozone oxidation and bio-filtration systems.

### 1.3 Thesis Outline

This thesis consists of five chapters. Chapter One presents the introduction section in order to provide information, including odor issue, industrial odor sources, control methods, and regulations. The detailed information about regulatory issues, industrial odor sources and removing mechanisms of odor control methods are given in Chapter Two. Chapter Three describes the materials and methods used for odor measurement in this thesis. Measurement results for industries and outlet of odor control units and their evaluations are given in Chapter Four. In the final chapter, which is Chapter Five, the summary of all of findings, average odor concentration, and the most efficient odor control method on industrial base are provided.

# CHAPTER TWO
# LITERATURE REVIEW

## 2.1 Odor Regulations In The World

There are several regulations that applied by legal authorities in the world in order to control odorous emissions. Countries in Europe, in the United States and Canada have strictly limited odorous emissions on concentration and time percentage bases. Mostly, these limits are identified between 1-10 $OU/m^3$ for concentration and 80-99% for time percentage. Also, there are some differences on legal applications. For example, in some countries, odors are regulated by local authorities, while in other countries they are regulated by governments directly (Lebrero et al., 2011).

In the United States and Canada, odor limits are determined by local authorities, but not federally. In this regard, the limits can change state by state. In Canada, odor concentrations are measured by dynamic olfactometric method by using the standard EN 13725. Besides, maximum emission limit for facilities should not exceed 10 OU/M3 with 100% time percentages. Similarly, there is no federal regulation on odorous emissions in the United States. Regulations are under the responsibilities of state or local authorities. Differently, odorous emissions are measured by approach of fixing ambient odour dilution-to-threshold (D/T) limits. Field olfactometers are used to measure D/T values. While maximum allowable concentration limit is determined as 7 D/T for Colorado City, it is limited as 5 D/T in San Francisco (Brancher et al., 2016).

In European countries, odorous emissions are regulated by directives. Limits are determined with odor concentrations and percentage. For instance, in Germany, emissions are limited as 1 $OU/m^3$ for concentration. Besides, 15% in industrial areas and 10% in residential areas are identified for time percentages. In Austria, the maximum odor concentration limit is bounded to 1 $OU/m^3$ like in Germany. The exceedance probability cannot pass over 3%. In the UK, odorous emissions are limited on sectoral base in the range of between 1.5-6 $OU/m^3$. Also, exceedance time percentage is allowed only 2% over a year, which is respectively low (Brancher et al., 2016; Dincer, 2007).

For Turkey, there was no limit value, a specific law or even regulation related to odor issues in the past. However, the lack of odor regulation in Turkey came to the forefront as an important deficiency during the European Union harmonization process. In this context, Turkey's Ministry of Environment, and Turkish and European academic institutions organized meetings to handle this issue. In 2013, The Regulation on Odorous Emission Controlling entered into force. According to this regulation, terms and definitions about odor, industrial odor sources, odor control methods and emission limits are presented in detailed.

Within the scope of the Turkish regulation, three sets of odor emission limits are defined. Odor concentration below 1000 $OU/m^3$ is defined as an acceptable limit. If the concentration value is in the range of between 1000-10000 $OU/m^3$, precautions should be taken to decrease the emissions to acceptable limits in a short time, and then results should be reported. Odor emission with a concentration above 10000 $OU/m^3$ is unacceptable. In this situation, administrative sanction may be applied by legal authorities (Official Gazette, 2013).

## 2.2 Odor Causing Industries

As it is a fact that nations face with growing population and increasing demand of industrial production, shedding light on these issues has become prominent especially in the last two decades. As one of the issues of our century, odor problem is a growing concern in our day as a result of anthropogenic activities which are mostly industrial ones. Since industrial activities are increasing day by day and most of the odorous compounds are emitted from these activities, such as wastewater treatment, food and drink production, vegetable oil production, Slaughtering and rendering activities, livestock operations, brewery production, yeast production, oil refineries, pulp and paper mills, chemical industries and so on, the VOCs (Volatile Organic Compounds), ammonia ($NH_3$), sulfur compounds, mercaptans, organic acids, aldehydes and hydrocarbons are principal odor causing compounds. Besides, odor may cause following problems (Mudliar et al., 2010; Barbusinski, Kalemba, Kasperczyk, Urbaniec, & Kozik 2017).

- Deterioration of environment quality
- Interference with business activities
- Health and safety risks to living organisms
- Disturbance in the use of any property, plant or animal

In the aforementioned study, following industries were investigated:

- Vegetable oil processing industry
- Poultry Processing Wastewater treatment
- Livestock operations
- Brewery industry
- Yeast industry

#### *2.2.1 Vegetable Oil Processing Industry*

Vegetable oil production is one of the leading sectors in the food industry. Oil has been produced from seeds and other vegetable- based materials for a long time. According to latest research studies; vegetable oil production is based on ancient times in the Mediterranean area (Azbar et al., 2010).

Also vegetable oil production can be described as any activities to extract vegetable oil from seeds and other vegetable based materials, such as canola, cottonseed, palm, olive, soybean, sesame and sunflower and so on. There are several steps of the production activities, which cause atmospheric emissions like dust and VOC (European Commission 2008). Generally, oil seeds/fruit preparation activities include cleaning, screening and crushing, which may cause dust emissions. After physical preparation, raw materials are refined for oil production where most of the odor causing VOC emissions are released (World Bank Group, 2015).

Raw vegetable oil, which is produced with only physical methods, it cannot be consumed directly. The compounds, such as free fatty acids, aldehydes, ketones and other VOC give an unpleasant aroma that should be totally removed or decreased to acceptable levels. In a nutshell, these are main reasons of refining activities in oil production industry. Also, the steps of this process are listed below:

- Neutralization
- Bleaching
- Winterisation
- Deodorization

The aim of neutralization process is removing excess fatty acids from the oil by using alkaline solutions. At the end of this process, raw material for soap is acquired. Oxidized compounds, color pigments and other residuals are removed in bleaching phase by using bleaching earth. In winterization, other materials, which are provided from neutralization and bleaching, such as wax or strains, are removed. (Altınyag, 2013; Yemiscioglu, Ozdikicierler, Gumuskesen, & Sonmez, 2013).

The final step before marketing, deodorization is employed in order to remove all of the undesirable compounds for smell and taste from the product. Generally, this process occurs in the high temperature (220-240°C) and pressure (3-5 mBar), low volume of dry steam (approximately 0.5-1% of total volume), and vacuum systems. It continues nearly 20 or 30 minutes and most of the odorous compounds, such as aldehydes, ketones, alcohols, esters, carboxylic acids and many VOCs are taken away from oil. (Kalua et al., 2005; Yemişçioğlu et al., 2013). The flow diagram of whole process is given in Figure 2.1:

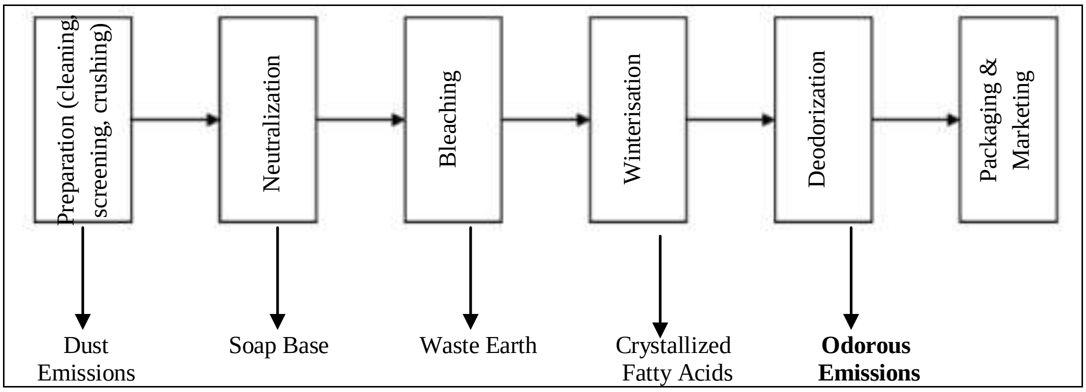


Figure 2.1 Vegetable oil production process

### *2.2.2 Rendering Processing*

Although rendering activities converts low economic value organic materials from the livestock activities, slaughter houses, farms, animal shelters, food services and related industries to convenient materials, it is one of the most irritating sectors. Rendering industry carries potential risks for environmental facts, including air, water and soil, but its most devastating effect is on odorous emissions (Sindt & Engineer, 2006; World Bank Group, 2007a).

Basically, animal by- product materials, such as grease, blood, feathers, offal, carcasses and other unnecessary parts of their bodies, are used to produce tallow, grease, high protein meat and bone meal. These organic matters are cooked in high temperature to separate high quality fat and protein from the mass. Meanwhile, the system is run under vacuum to remove moisture. Then these processes are followed by separation fat or protein material before drying for final preparation. In some cases, the need for employing sterilization at high temperatures may occur in combination with pressure for a couple of minutes in order to eliminate prion. All of these stages are followed, where odorous compounds intensively released. (Anderson, 2006). General rendering applications are indicated for different substances as follows:

- *Blood processing and drying;* Blood is recovered due to its high protein content. After the first step of heating, solid materials are coagulated. Then remaining blood solids and liquid phase are separated in a centrifuge and all solid materials are sent to dryer.
- *Poultry feathers and hog hair processing;* In this process; it is aimed that converting protein rich keratin matter into amino acids. These materials are processes in a cooker with high temperature and pressure nearly 30 to 45 minutes. The mixture which is called meat bone meal is dewatered; then solid part is dried before storage.
- Grease processing; collected grease material is heated in a cooker nearly 95 C. Then it is stored in a tank for 3 or 4 days to separate fine solid materials by gravity. After these steps four by-products are obtained; solids, water, emulsion matter and grease products. Settled materials are collected from the bottom while grease products are skimmed from the top layer. Then emulsion matter is centrifuged separate valuable materials (United States Environmental Protection Agency [USEPA], 2016).

As indicated below, even though there are several processes of rendering, cooking section is the most odorous one. Because of high temperature, degradations occur in animal tissues and as a result of this, many odorous compounds are released. In addition to other odor causing processes, if raw materials cannot be managed properly, it becomes another odor source due to the decomposition of organic materials (Sironi, Capelli, Centola, Del Rosso & Grande, 2006). In addition, many odorous VOCs are identified for rendering industry in several studies, such as aldehydes, ketones, aliphatic hydrocarbons, aromatic hydrocarbons, furans, sulphur containing compounds, alcohols and volatile fatty acids and esters and so on (Bhatti, Maqbool & Langenhove, 2013; Dincer, 2007)**.** Flow scheme of rendering industry is given in the Figure 2.2:

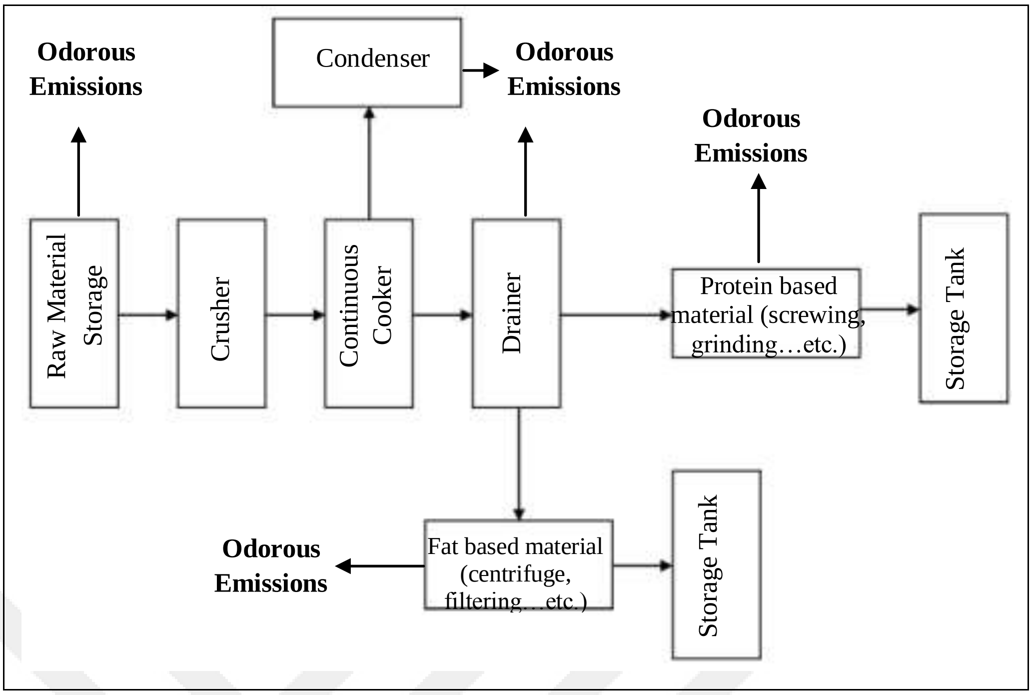


Figure 2.2 Flow scheme of rendering industries

### *2.2.3 Wastewater Treatment Process*

Wastewater treatment processes is one of the most outstanding sources that cause odor pollution. There are several compounds in the wastewater that come from several activities, such as domestic usage, industries, and so on. Odor nuisance occurs due to the degradation of these organic compounds to gases and vapors mostly in the anaerobic conditions (Onkal-Engin, Demir & Engin, 2005).

Although solid and gaseous emissions are of secondary importance in the past, as a result of increasing complaints, awareness of public, governments and companies, and enforcement of new regulations, odor management has become a priority in last decades (Estrada, Kraakman, Lebrero & Munoz 2015). Besides, odorous emissions, which are related with domestic wastewater treatment activities, have a larger domain when it is compared to other examined sources in this study. In addition to treatment activities, there are two more sections: transfer of wastewater and excess sludge disposal (World Bank Group, 2007b; Gostelow, Parsons & Stuetz, 2001).

Wastewater from household activities is transferred by sewer system and lifting stations through the WWTP. In some cases, pre-treated industrial waste water may be discharged into the system like in the Big Channel Project in İzmir. During the transfer, anaerobic degradation occurs in some points due to the insufficiency or absence of oxygen. Then odorous compounds are released into the atmosphere from cracks, manholes or lifting stations. It is stated that hydrogen sulfide is the major odor-causing compound in domestic wastewater treatment activities (Kapdan & Celebi, 2009). Also, existing of hydrogen sulfide causes another problem in the sewer system, which is called corrosion. Firstly, hydrogen sulfide is oxidized to elemental sulfur, and then sulfur is converted to sulfuric acid by metabolic activities of bacteria, which live on the wet surfaces of transferring systems. As a consequence, acidic corrosion occurs on the concrete or other materials (Chen & Szostak, 2013).

In the treatment process, generally these steps are followed:

- Physical treatment
- Chemical addition (if it is necessary)
- Biological treatment
- Sludge disposal

In the first step, little particles, undissolved materials and so on are removed with physical methods, such as screening and settling. After physical treatment, according to the water characteristic and requirements, chemical addition may be needed for pH balancing. More specifically, as a result of the excessive amount of domestic wastewater, which is collected from whole city, chemical treatment is not a feasible method due to the high rate chemical consumption.

Then the water is transferred in the aerobic pond/ponds, where most of the pollutants are removed by microorganisms. Microorganisms get together and create a living bulk, which is called *activated sludge*. Pollutants are used as food source by microorganism for their metabolic activities and reproduction. Then, mixture of activated sludge and water are passed in the final settling tank(s). In this section, treated water and activated sludge are separated from each other by the gravity, and then treated water is transferred into the discharge pipe system. (Kapdan & Celebi, 2009; Filibeli, 2013).

In biological treatment, sustainability of the treatment activities and removing efficiency highly depend on existence of microbial community. For this reason, while some of the settled activated sludge sending to disposal, other part is recirculated into the aeration tank. Excess sludge is one of the major problems in the aerobic treatment activities. (Liu, Gong Jiang Yan & Tian, 2016). There are several methods of disposing the sludge for example, drying, digestion, and incineration.

As indicated below, odor is a significant problem in all steps of treatment and sludge disposing, since most of the domestic WWTPs' units are open to atmosphere. Screens, settling tanks, aeration tanks and sludge process units are the major odorous emission sources. Also, it is stated in many studies that sludge operations make the biggest contribution to odorous emissions. (Gostelow et al., 2001; Laplanche, Bonnin, Darmon & du Gal Leclerce, 1994). All of the process is given with its details in the Figure 2.3.

Monoaromatics (i.e. benzene, toluene), halogenated compounds (i.e. chlorobenzene), aldehydes (i.e. hexanal, proponal), ketones (i.e. acetone), esters, terpenes, mercaptans, reduced sulfure compounds (i.e. hydrogen sulfide, diethyl sulfide), volatile fatty acids and various VOC are the odorous compounds are emitted through the aforementioned processes (Dincer, 2007; Dincer & Muezzinoglu, 2008; Estrada et al., 2015). Despite of the fact that most of the VOCs are highly odorous, reduced/volatile sulfur compounds, especially hydrogen sulfide, are the predominant groups as specified by authorities (Devai & DeLaune, 1999). Although removing all high priority VOCs would be the best solution in odor controlling, focusing reduced sulfur compounds would be easier and rapid way. (Sivret, Wang, Parcsi & Stuetz 2016).

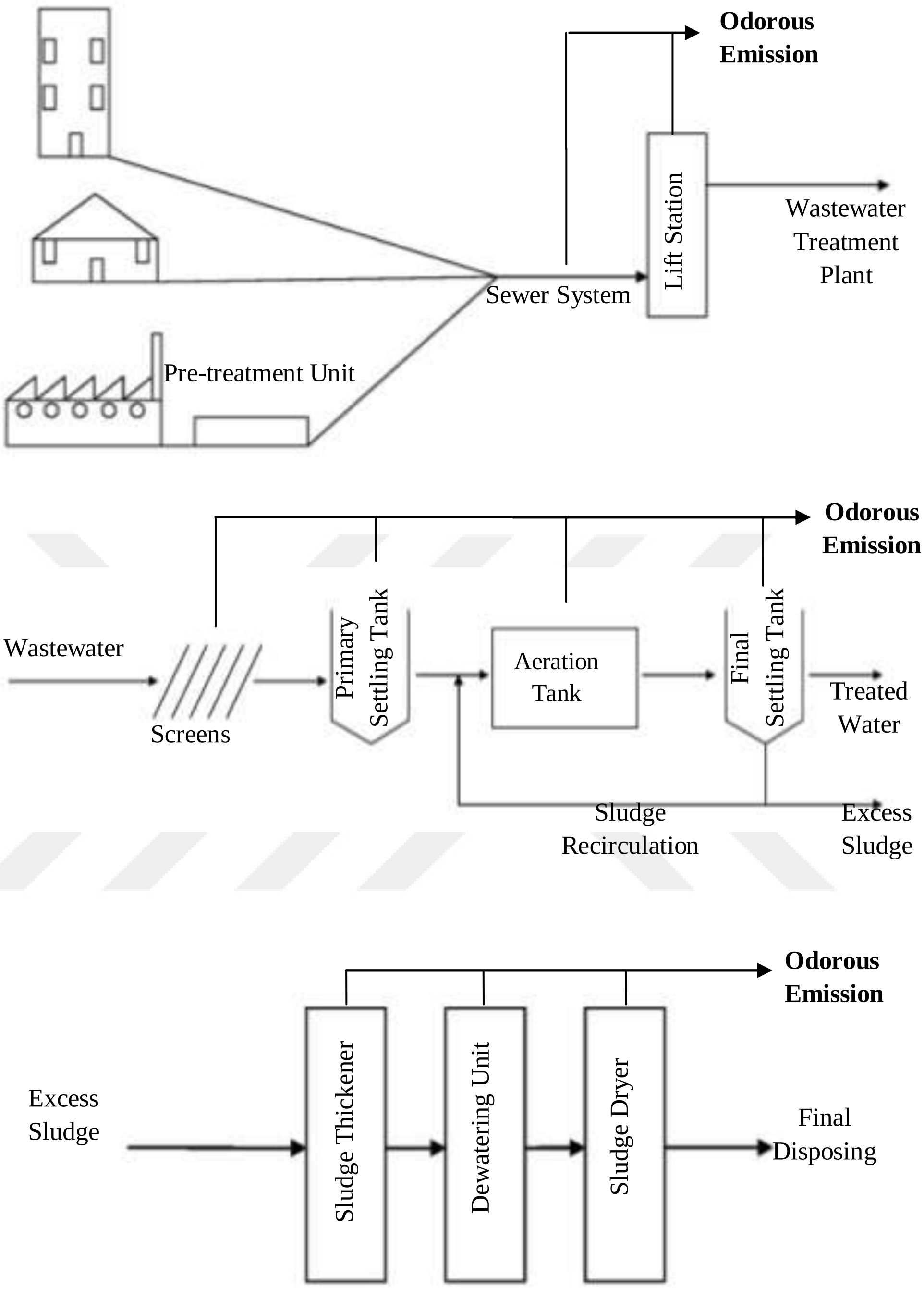


Figure 2.3 Wastewater transportation, treatment and sludge disposal processes. Most of the units are open to the atmosphere

### *2.2.4 Poultry Operations*

As a result of increasing consumption, livestock operations have been increased drastically in recent years. For meeting the demand, number and capacity of chicken broilers, pig barns, layers and diary barns are increased day by day. For example, from 1950s to end of the 1970s, total number of cattle is doubled in the United States (USEPA, 1978). For sure, these huge facilities have a positive effect on consumers to reach proper and non-expensive products. However, this has come at a price for environment due to huge amounts of wastes and odorous emissions (World Bank Group, 2007c; Traube et al., 2010).

Odor causing compounds are emitted into the ambient air because of decomposition of organic materials, which are in the litter, waste feed and manure and so on. So that, animal buildings, manure storage and treatment areas are the potential odor sources in the livestock operations (Murphy, Parcsi & Stuetz, 2014**;** Webb, Broomfield, Jones & Donovan, 2014). In addition to degradation of organic matter, there are several parameters, which effect indoor air quality and also odor nuisance in the animal buildings, such as manure handling, animal density, feed regime and ventilation. Additionally, ventilation plays the key role in dispersing malodorous air to the atmosphere. (Jin-Qin, 2015). Potential odor sources of livestock operations are given in the Figure 2.4.

There are several compounds, which cause odor nuisance in the livestock operations, such as carboxylic acids, hydrocarbons, alcohols, aldehydes, amines, aromatics, phenols, volatile fatty acids, S containing compounds, N containing compounds, ketones and indoles and so on. (Zhang et al., 2010). Although most of these compounds are found in operation areas, there are certain differences between different animals' livestock activities. For example, in one of the research studies conducting in a poultry facility, alcohols, ketones and volatile fatty acids were found as dominant groups (Traube et al., 2010), while sulfur compounds, volatile fatty acids, phenols and indoles were the abundant ones in most of the site (Jo et al., 2015).

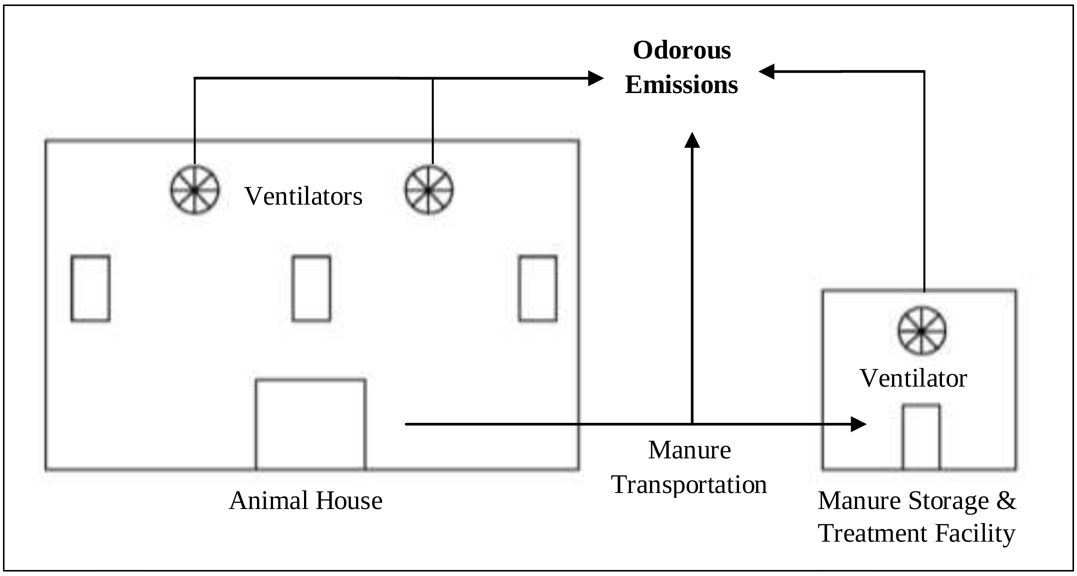


Figure 2.4 Odor sources in the livestock operations. Odorous emissions are released from ventilation points, cracks…etc. to the atmosphere. Also manure transportation can be another source unless it managed properly.

### *2.2.5 Brewery Industry*

Food and drink production industries are the major contributors to odorous emissions atmospheric contamination as well. Also, brewery industry one of the leading sector because of its vital economic position. After tea, carbonates, milk and coffee, beer is the fifth most consumed beverage in the world (Bergen, 1958; Olajire, 2012), and beer consumption has been increasing trend in the last years (Varnamkhasti et al., 2010). According to OECD 2011 data, average consumption of alcohol is 9.1 liters per capita and most of the countries have high rates for brewery consumption such as Germany, the Czech Republic and Poland…etc. (Organisation for Economic Co-operation and Development [OECD], 2011). Consumption details are given in the Figure 2.5.

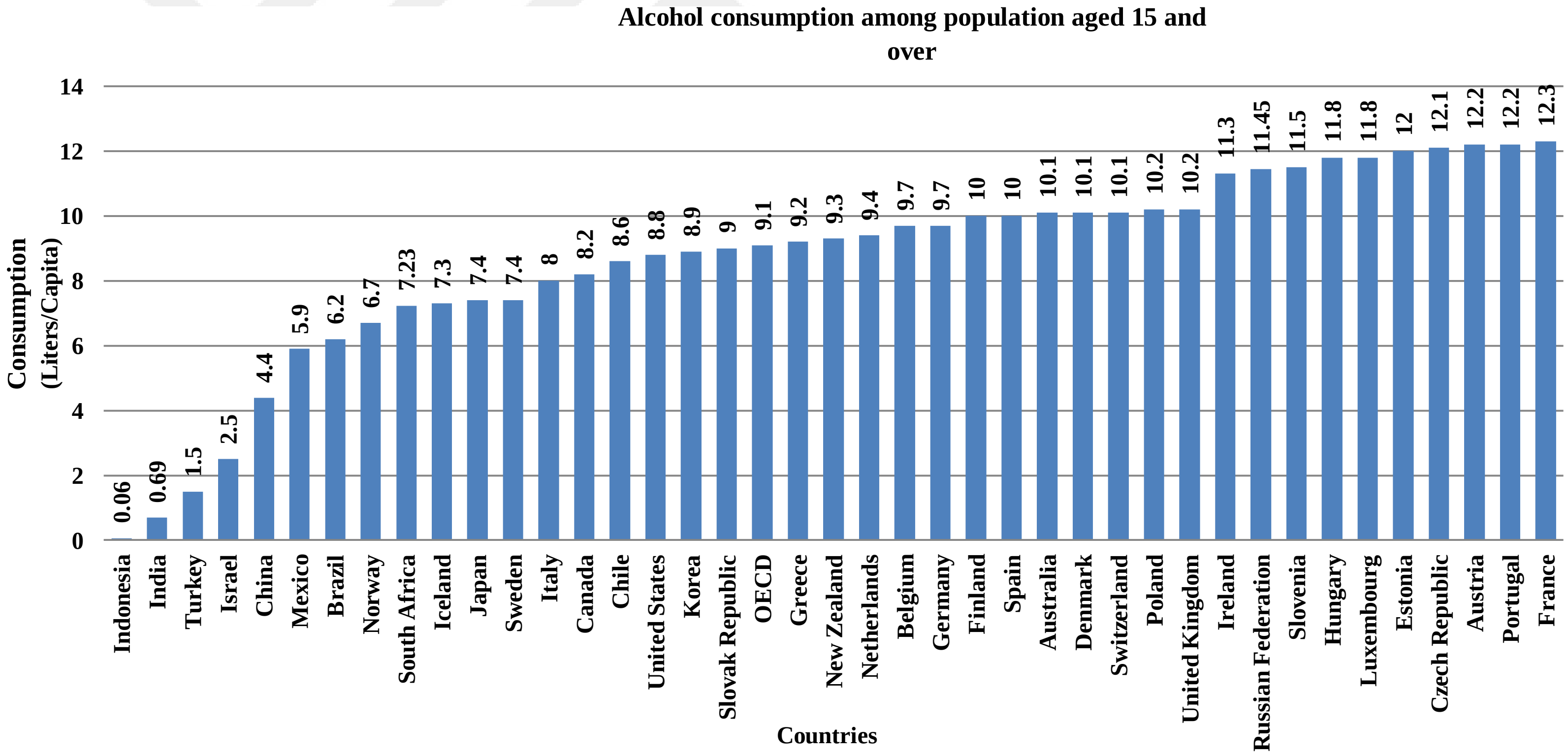


Figure 2.5 Alcohol consumption of OECD countries

There are different stages of brewery production and it can be classified in three categories (Gibson, Costigan, Swannell & Woodfield, 1995):

- Malting
- Wort Boiling
- Fermentation

In malting step, barleys are soaked for softening. Then, germination process is started in the germination tank. Typically, this period takes nearly one week and after that they are taken in a kiln for drying. After completing this process, malt is obtained in order to use it in other steps. Mashing is the following malting process that heats the malt for a while to break down complex compounds into simple ones, for instance, conversion of starch to glucose**.** After obtaining the product called 'wort', it is filtered for removing residuals (USEPA, 2016a). Secondly, wort is boiled with hops in a tank. Hops are the flavorant that give odor and taste to beer. During the boiling, hops give their bitter resins and essential oils, which give the beer its characteristic aroma (Olajire, 2012). Then, it is filtered again to remove undesirable grains.

As a result of boiling process, wort temperature can be reached to nearly 96-99°C, which is improper for fermentation activities. So, it is taken in a heat exchanger and cooled gradually until 7-12 Cs before transferring into the fermenter. (USEPA, 2016a).

Fermentation is the final process of conversion of simple sugars into alcohol (as ethanol), and carbon dioxide by yeasts. The yeasts are added while wort is transferring into the fermentation tank. There are two types of fermentation. In the first process, wort and yeast are stored nearly one week in the tank. In the second type, fermentation takes nearly three days. In both of these types, simple sugar is converted to ethanol as a result of metabolic activities of the yeast cells. Also, this is the process employed for giving the alcohol to the beer. After fermentation, beer is taken in the beer aging or condition tank, which is approximately on 1C. If the beer is fermented by using the first method, aging may take a few months. If the second one is chosen, it takes nearly few weeks. After aging, matured beer is filtered for the last time and sent to bottling in order to sell in markets (Sinci, 2009). Process is given in the Figure 2.6.

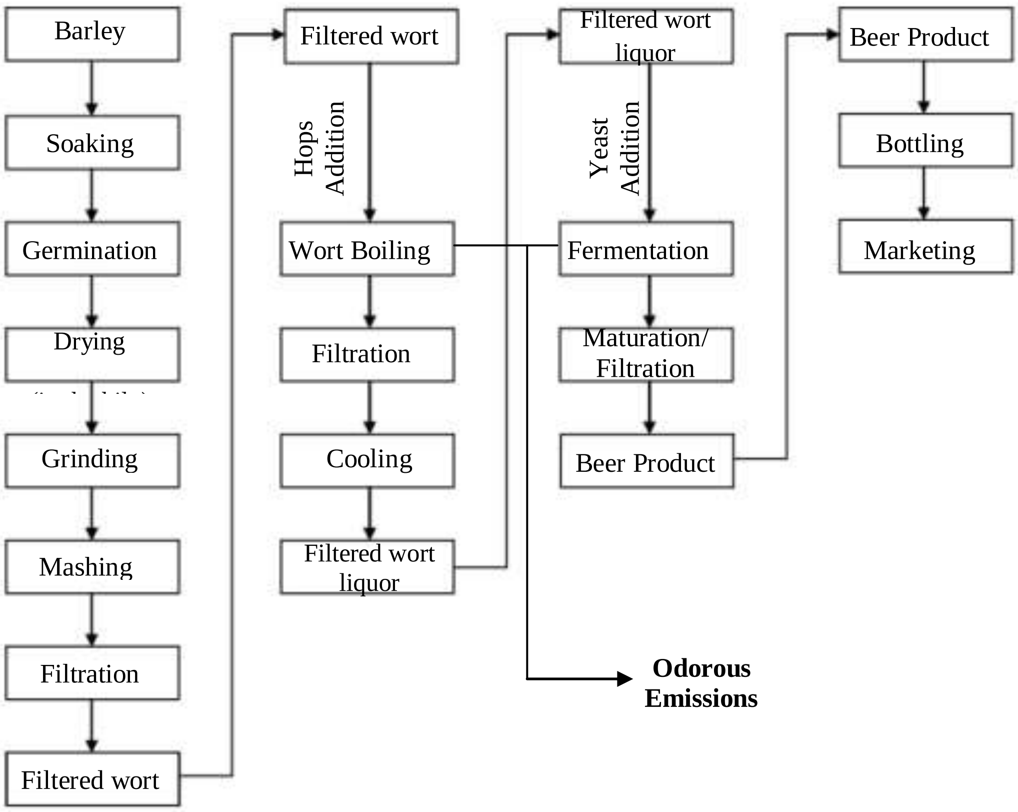


Figure 2.6 Brewery production process. In the whole process, wort boiling and fermentation have the major contribution of odorous emissions. Besides in the boiling process, odor causing compounds are released into the atmosphere as in the fermentation

Beside the dust emission, odor is one of the most important air emissions in brewery industry. Wort boiling makes the major contribution to odorous emission (World Bank Group, 2007d). As a result of processing in the high temperature, many aromatic compounds in the hops occur. While some of them are giving the beer its taste and characteristic aroma, others are released as odorous emission. Also, during the fermentation, several odorous compounds are generated as well. Most of the alcohol -possibly in ethanol form- is dominant odorous compound produced in the fermentation. Additionally, volatile fatty acids, sulfuric and carbonyl groups are the other compound groups (Sinci, 2009; USEPA, 2016b). Esters, alkenes and other forms of alcohol are emitted in other VOCs, which are smaller concentrations. (Gibson et al, 1995).

### *2.2.6 Yeast Industry*

Baked products, especially bread, are one of the most consumed foods in the world. Bread is a kind of food made from the mixture of water, salt, flour and yeast in the right proportions. In spite of the fact that consumption depends on the country, each year over 9 billion kg of bread is consumed worldwide. Also, it is stated in the Figure 2.7, Turkey has the highest bread consumption among European countries (Pico, Bernal, & Gomez, 2015; The Statistics Portal, 2013).

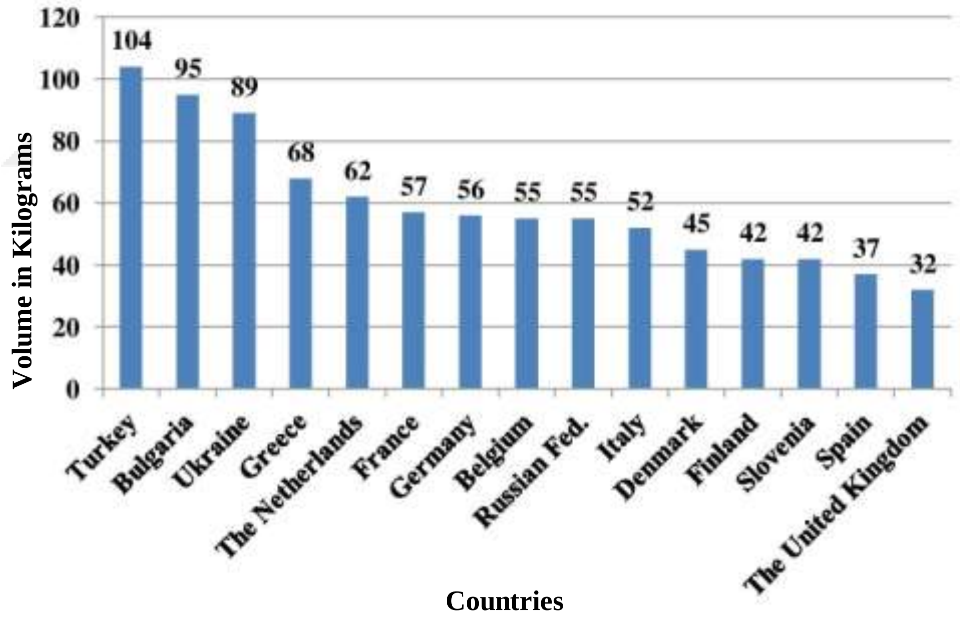


Figure 2.7 Volume of bread consumed per person per year in selected European countries in 2013

Because of the facts indicated above, yeast industry plays a crucial role in meeting increasing food demand. It is one of the most odor-problematic sectors because of its production processes. Fermantation is the main process in which many odor- causing compounds are released into the atmosphere (Turker, Karadag, Isık, & Ertan, 2015). During the yeast production, there are mainly four steps of fermentation:

- Pre culture fermentation
- Mother yeast fermentation
- Seed yeast fermentation
- Commercial yeast fermentation

Pre-culture fermentation is the step that provides yeast cells for whole process. Before starting to fermentation, yeast culture is sterilized nearly 120°C to kill all of the other microorganisms. Then, fermentation is started in a batch system. This process is of vital importance due to the final production quality. Following pure yeast culture, it is transferred to mother yeast fermentation tank. The fermentation is continued in 29-31°C with the addition of trace elements. In addition to these elements, molasses, which is the by-product of sugar production, is used as food source for all fermentation steps. Before commercial production, yeasts are fermented in seed yeast fermentation tank in approximately 28-32°C. Undesirable materials are separated by sedimentation, and then filtration is employed. Finally, it is transferred to commercial yeast fermentation tank for final fermentation. This process is performed in higher temperature (30-36°C). As a last stage, it can be dried or directly packaged for the market (Akmırza, 2012, Zhang, Song, Li, Yao & Xiong, 2017).

During the fermentation and drying processes, various emissions are emitted. As it is stated in the previous brewery industry section, alcohol is the most dominant malodor compound in the fermentation process. (Akmırza, 2012). Besides alcohol, other VOCs, such as aldehydes, volatile acids, esters, ketons are other groups, which cause odor nuisance. Also, most of these emissions are released during the drying process as well. In the drying process, excess moisture is removed from fresh yeast by heating in order to increase solid material content. By this way, some of these compounds are released to the open atmosphere (Turker et al., 2015; Guler, 2015). Detailed process information and emission sources are shown in Figure 2.8.

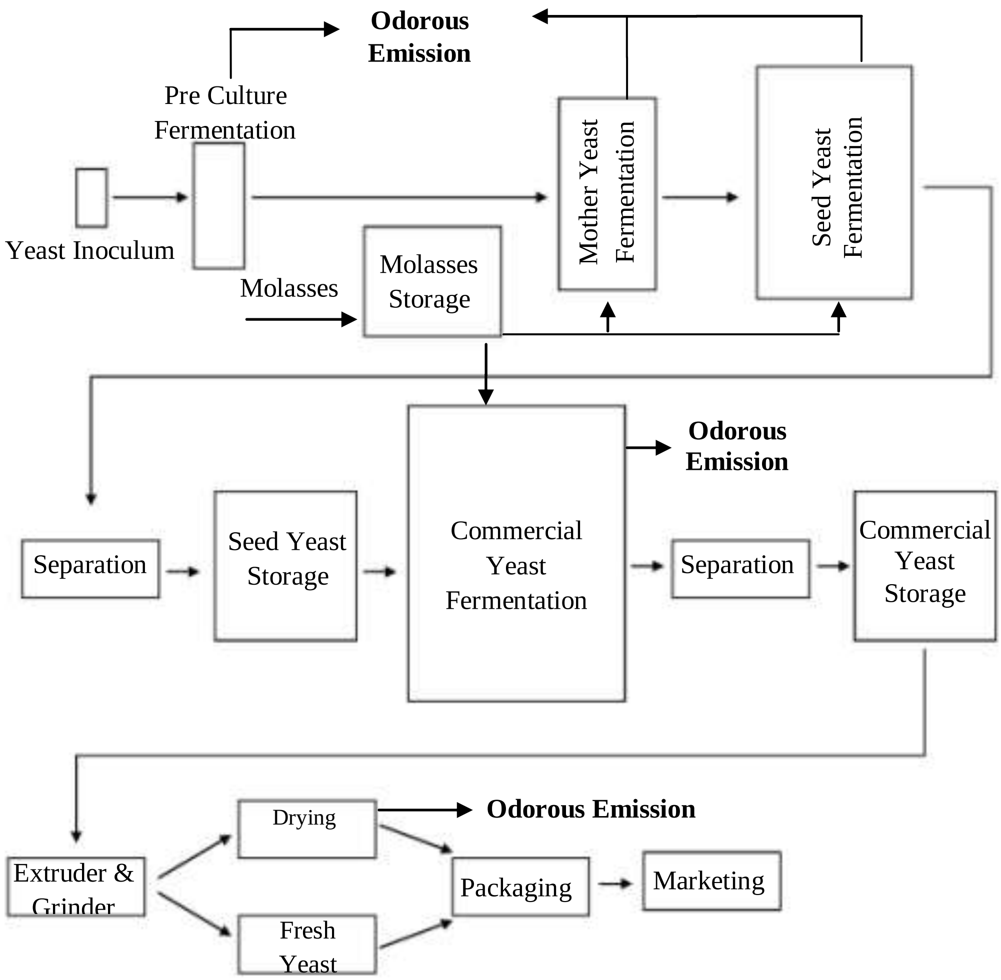


Figure 2.8 Yeast production flowchart

## 2.3 Odor Control Methods

### *2.3.1 Biofiltration*

Waste gas is one of the most important emission sources for industrial and production activities. These emissions are not stable on a specific point and they can move in the atmosphere easily. Depending on their properties and concentrations, they may cause some problems related to environment and public health. Additionally, gaseous emissions have been in the second position in environmental aspects for a long time when they are compared to solid and liquid ones. However, as a result of increasing public awareness and complaints, legal regulations became stricter. In accordance with these regulations, certain precautions were taken in most of the areas (Schlegelmilch et al., 2005; Stuetz & Frechen, 2001)

In addition to traditional physico-chemical systems, biological processes are commonly used in waste gas treatment and odor control. Basically, the process can be described as a reactor -generally a column- populated with microorganisms. In this process, the gas is treated by them while passing through. Microorganisms form the biofilm where most of odor-causing compounds are absorbed and transformed to odorless ones, such as carbon dioxide, water vapor and so on (Schlegelmilch et al., 2005). Also, this method is widely used in many industries successfully such as, petrochemical, tobacco, and meat (McNevin & Barford, 2000).

There are several applications for biological processes. One of them is bio filter. It consists of an organic fixed bed that microorganisms attach on its surface and form biofilm (Lebrero et al., 2011). Besides, the other one is bio-tricking filter. In spite of the fact that working principle is similar with biofilters, microorganisms attach on a backfill material. The backfill material can be chosen from inert ones, i.e. wood chips, granular activated carbon, plastic packing or crushed oyster shell. (Kim, Kim, Chung &, Xie, 2002; Schlegelmilch et al., 2005; Ergas, Schroeder, Chang & Morton et al., 1995). Examples are given in the Table 2.1.

Bio-scrubber is another abundant example for biological treatment of waste gas (Kennes & Thalasso, 1998). Microorganisms grow in an aqueous solution containing nutrients. In these systems, odorous compounds are eliminated both mechanism. Some of the odorous compounds are held by liquid, while others, which are dissolved in the solution, are used by microorganisms as a nutritional source (DEPARK, 2014).

Concerning the working mechanisms for all three systems, air containing odorous compounds is sprayed from the bottom of reactor, while liquid is coming from the top. For bio-scrubbers, the scrubbing liquid is drawn away and continuously cycled. Detailed drawings can be seen in the Figure 2.9.

Table 2.1 Examples for different filling materials specifications in biofiltration applications

| **Process** | **Filling Material** | **Pollutant** | **Empty Bed Retention Time (EBRT) (s)** | **Efficiency (%)** | **Reference** |
|---|---|---|---|---|---|
| Biofiltration | Peat | $H_2S$ | 60 | 90%-99% | (Omri et al., 2013). |
| Biofiltration | Manure Fertilizer and Bagasse | $NH_3$ | 78 | 71.86%-89.9% | (Kaosol & Pongpat, 2011). |
| Biotrickling | Polyurethane foam | $H_2S$ | 1.6-2.2 | 90%-95% | (Gabriel & Deshusses, 2003). |
| Biofiltration | Polyamide fibres | Nicotine | 2-6 | 95.2% | (Zagustina et. al., 2012) |
| Biofiltration | Structured plastic packing | $H_2S$ | 11 | 85%-99% | (Cox & Deshusses 2002) |

Some parameters, such as nutrient content, moisture, pressure, surface area, and porosities have vital importance in designing and operation (Morgan-Sagastume & Noyola, 2005; Lebrero et al., 2011). In order to grow, microorganisms need some nutrients, which are absent in the waste air. Organic backfill materials can provide them nutrient content in an easy and inexpensive way (Ortiz, Revah & Auria 2003). For inorganic backfill and aqueous solution for bio-scrubbers, nutrients are supplied with an external system.

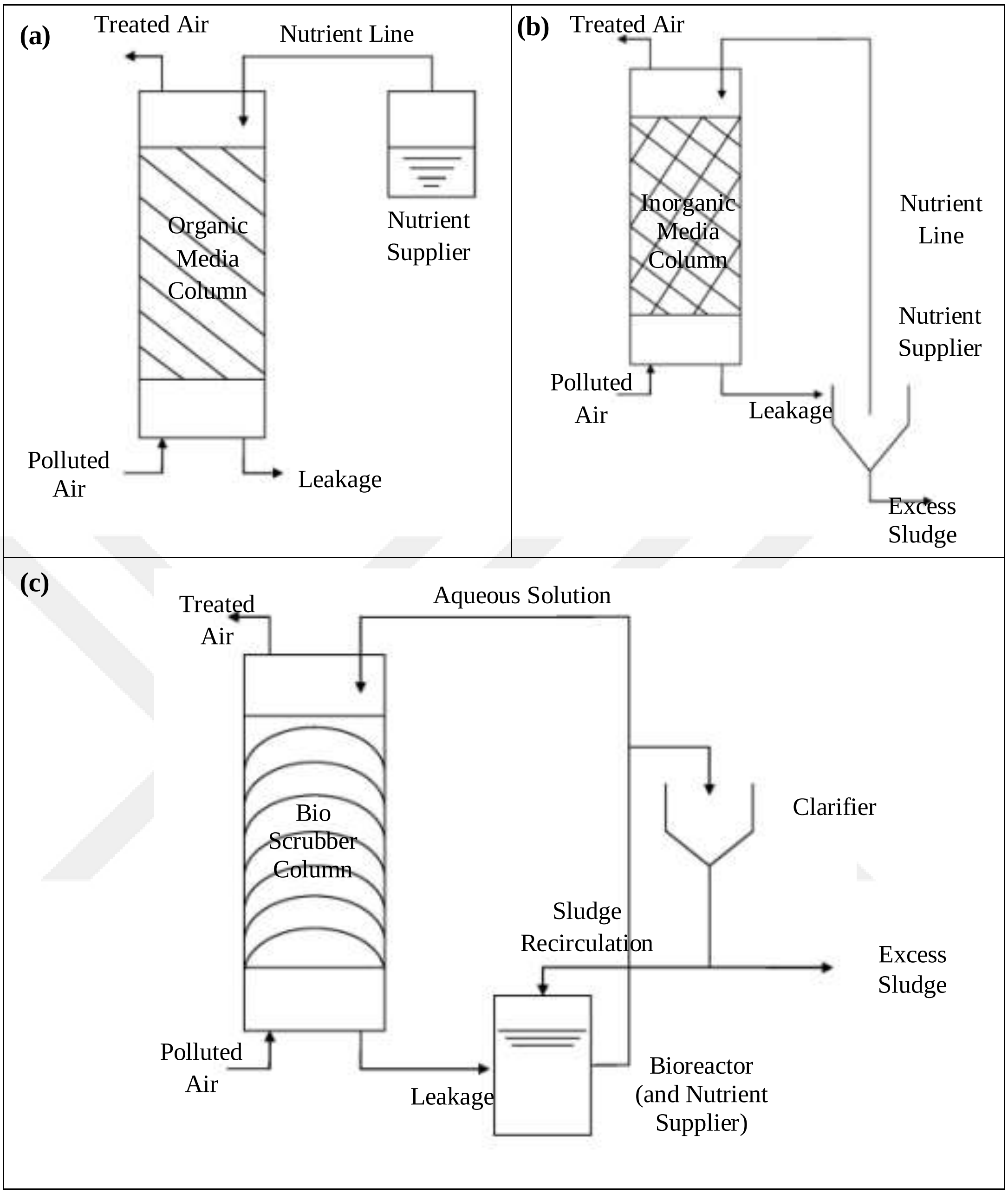


Figure 2.9 **(a)** Biofilter, **(b)** bio-trickling filter and **(c)** bioscrubber

Optimal moisture content has the key role in biodegradation activities. Although proper moisture content is given as between 20% and 60% in one of the research studies (McNevin & Barford, 2000), it is operated with nearly 80% moisture content with high efficiency (~%99) in another research study (Omri, Bouallagui, Aouidi, Godon & Hamdi, 2011). Moisturizing is not important for only mineralization of compounds, but also it is necessary for microorganisms' own metabolic activities.

So, biofilters are always left in humid even they are not used. Irrigation for moisture is highly related with pressure drop. If too much water is added, it results in clogging problems, and then increasing pressure drop. This situation causes limitation of mass transfer and consequently decreasing efficiency (Kennes & Thalasso, 1998).

Surface area is another important criterion for microorganism growth. Like surface area, porosities is a criterion playing key role for water-air distribution for biofilters (Song & Kinney, 2000). The other physical parameters, such as temperature and pH, depend on microorganism structure and diversity in both biofilters and bio scrubbers. Besides, identifying microorganism diversity is significant to determine undesirable ones. In recent times, many molecular techniques have been developed analyzing on DNA base. One of these methods, which is called ‘single strand conformation polymorphism’ (SSCP), is a very useful example for identification of microorganism diversity (Khelifi, Bouallagui, Touhami, Godon & Hamdi, 2009).

As it is mentioned below, there are many drastic implementations for elimination of odorous compounds in both laboratory and industrial scales for tobacco, livestock farming, hardboard production, waste-water treatment and many sections (Barford & McNevin, 2000;Zagustina et. al., 2012; Chung, Huang, & Tseng, 1996; Rabbani, Charles, Kayaalp, Cord-Ruwisch & Ho, 2016). In these sectors, many VOC compounds are essential source of odor.

One of them is ammonia ($NH_3$), which is highly odorous and corrosive gas, becomes degradation of protein, urea or uric acid (La Pagans, Font & Sanchez et al., 2005). Basically, $NH_3$ degradation follows the steps which are shown in the equations 2.1, 2.2 and 2.3 in microorganisms:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2- + 2H_2O + 4H^+ \quad (2.1)$$
$$2NO_2^- + O2 \rightarrow 2NO_3^- \ NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^- \quad (2.2)$$
$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \quad (2.3)$$

In the first research study, ammonia in the composting exhaust gases were tried to remove in a pilot scale reactor. Different organic materials (i.e. from a municipal composting plant, wastewater treatment facility, poultry animal body parts) were used to create the compost mass in composter, which was connected to bioreactor. Also, the biofilter was filled with organic based media that was used in different studies and proved that it is a proper option for filling material (Kaosol & Pongpat, 2011). The system was run nearly 2 months continuously with the sample gas obtained from the composter. In fact, no additional nutrients were needed because of the existence of organic media. Inlet and outlet gases were monitored periodically and at the end of the experiment, the efficiency of ammonia removal was found as approximately 95%. In addition, it was reported that ammonia removal was performed not only with microorganisms, but also it was adsorbed by organic media (La pagans et al., 2005).

As another example, some of volatile organic compounds (VOCs) obtained from leaf tobacco were removed with the same process. A column, filled with inert fibers, was used as a bioreactor. Selected microorganisms were placed in the reactor and fed with a circulation fluid for additional nutrient and moisture. VOC compounds were obtained from fermentation of selected tobacco leaves and they were given to the system with airflow. Inlet and outlet air were measured periodically. Although the groups of VOCs: C4–C20 organic acids were revealed among organic acids, a huge number of branched and normal hydrocarbons, aliphatic and aromatic aldehydes and ketones, and alcohols, nicotine had the higher content among all. According to measurement results, most of the VOC compounds were removed successfully (Zagustina et. al., 2012). The detailed results are given in the Table 2.2.

Despite of experimental applications, biofilters are used in industrial scale (DEPARK, 2014). The gases such as $H_2S$, $NH_3$, $CO_2$ and $CH_4$ are produced as a result of degradation of organic pollutants in the wastewater. Among these gases, $H_2S$ is the predominant odorant and it is recognizable with its characteristic rotten egg smell (Dincer and Muezzinoglu, 2008; Omri, Aouidi, Bouallagui, Godon & Hamdi et al., 2013).

Table 2.2 Elimination rates on some of VOC compounds in tobacco leaves after biofiltration

| **Compound** | **Compound Elimination (%)** |
|---|---|
| Nicotine | 95.2 |
| Octadecanoic acid, propyl ester | 100 |
| Valeric acid, 2,2,4 trimethyl 3 carboxyiso propyl, isobutyl ester | N/A [a] |
| 9 Octadecenamide | 100 |
| Octadecanamide, N butyl | 100 |
| 3,7,11,15 Tetramethyl 2 hexa decen 1 ol | 92.8 |
| Palmitic acid, pentadecyl ester | 100 |
| Palmitic acid | 66 |
| Palmitic acid, dihydroxypropyl ester | 100 |
| Oleic acid | 94.6 |
| Stearic acid | 3.5 |

[a] *The outlet peak area exceeds the inlet one*

In this scope, biofilter is chosen as a controlling unit for a wastewater treatment plant, which can treat 100 000 $m^3$ wastewater per a day in Turkey. Plant units, whose surfaces are open to the atmosphere, are covered and gases are collected with a pipe system that can be seen in the Figure 2.10, in order to deliver biofilter columns to remove of $H_2S$ and other VOCs.

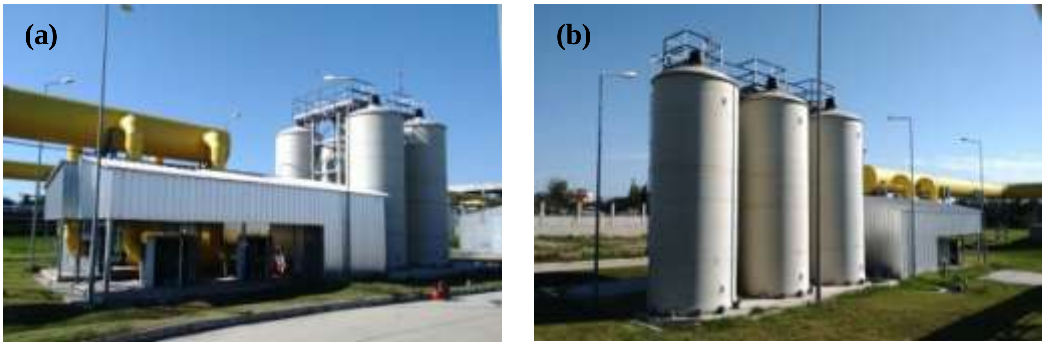


Figure 2.10 Biofilters in a municipal wastewater treatment plant. **(a)** Collected gases from plant units (i.e. settling tanks) are delivered to biofilters by yellow line. **(b)** Gases are treated in the columns from pollutants

### *2.3.2 Wet Scrubbing*

With the passage of the 1971 Clean Air Act in the United States of America, industries are supposed to reduce their air pollutants. For this reason, many odor control technologies were used to reduce odorous emissions. One of the technologies is a wet scrubber, which is used by most of the publicly owned treatment works in that country (Gabriel, Cox, & Deshusses 2004).

Although many scrubber applications are available to remove particulate matters, wet scrubbers are preferable for gaseous/soluble compounds. Operation is simply based on spraying of aqueous solution (or pure water) from the top, while foul airflow is passing counter currently through of the reactor. Besides, the solution is generally recirculated from bottom to the top. (Rajmohan, Reddy, & Meikap 2008).

Spray and packed bed tower wet scrubbers are mostly preferable for odor elimination. Basically, spray scrubbers are designed as packed bed ones without backfill material. The aqueous solution is sprayed by nozzle or atomizers from the top to form it as small droplets in order to provide bigger surface area. (Wet Scrubbers, (n.d.); Velhov, 2015). In packed bed towers, packings are used, such as Raschig ring, saddle, and so on. These packing materials are made from a number of inert materials, for instance, metal, plastic or ceramic. These small materials make surface area bigger for packed bed scrubbers (Chien, Tsai, Sheu, Cheng,& Starik 2015). Two types of the wet scrubbers can be seen in the Figure 2.11.

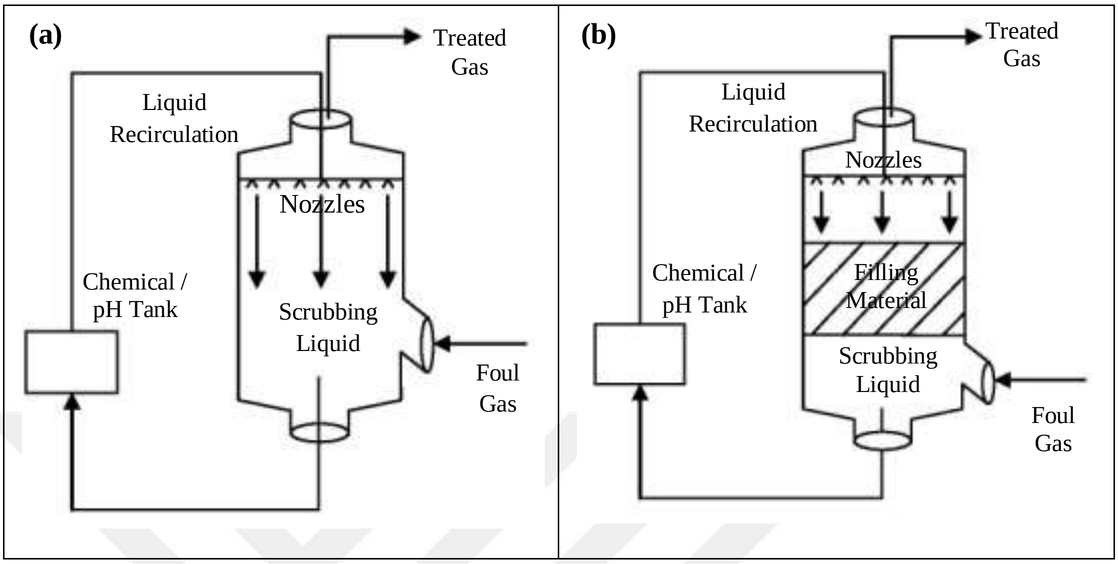


Figure 2.11 (a) Spray tower scrubber, (b) packed bed tower scrubber

In scrubbing processes, odorous compounds are eliminated by two mechanisms,

- Absorbing by the scrubbing solution,
- Oxidizing or neutralization by chemical agents,

Absorbing is the primary removing mechanism for contaminants. In some cases, pure water may be inadequate to remove contaminants, so proper chemicals should be added into the water, such as caustic, organic acids and so on to enhance the efficiency of removal (DEPARK, 2014).

Although adding chemicals to the scrubbing liquid has a powerful effect on the efficiency, solution requires to be regenerated or disposed in suitable manner (USEPA, 1991). Compounds are absorbed by the liquid until it becomes saturated, and then some regeneration activities can be employed for proceeding of removal process. For instance, stripping is an acceptable method for VOC separation. While VOCs are recovered by the condensation, treated solution is fed back into the recirculation system. On the other hand, it is feasible to dispose the waste scrubber solution and feed the system with the fresh one (USEPA, 1995).

Generally, waste scrubber solution is categorized as hazardous waste due to the fact that it includes chemicals. In some cases, it is used as commercial goods instead of waste**.** In this context, researchers conducted relevant studies about ammonia recovery (Schlegelmilch et al., 2005). For instance, air from the pig stable is passed through two- stage deodorization system including acidic wet scrubber and biofilter to degrade ammonia compounds. In consequence of chemical reactions between the target compound and acidic washing solution, ammonium sulphide is formed and it can be used as a fertilizer (Hahne and Vorlop, 2001). The schematic diagram of the reaction is provided in Figure 2 .12.

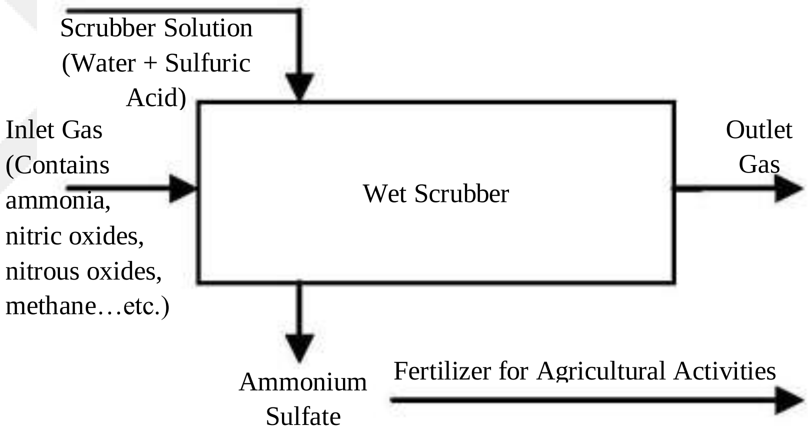


Figure 2.12 Schematic shown of fertilizer production from acidic waste scrubbers

As indicated below, in order to strengthen removing effect, some additives should be put into the solution (J. Vehlow, 2015). The most known chemicals are alkaline hypochloride (NaOCl), hydrogen peroxide (H2O2) and caustic, which are highly effective to enhance removing efficiency of malodor compounds. In recent years, ozone (O3) is used as oxidizer because of its high reactivity (Kastner, Das, Hu, & McClendon, 2003). Generally, the reaction between these chemicals and odorants is neutralization. The significant point of neutralization is salt formed by-products. Although these salt formed compounds are dissolved in the scrubbing liquid, they can be crystallized due to changing environmental conditions, which causes clogging problems in backfill material or equipments of recirculation unit (DEPARK, 2014). In addition to this, the other reaction oxidation is very strong for eliminating most of the odorants (Kastner & Das, 2002; Uresin, Sarac, Sarıoglan, Ay, & Akgun 2015).

There are some design parameters for wet scrubbers, such as L/G flow ratio, residence time, pH, and temperature. L/G flow ratio is an important parameter of removal of compounds. The more liquid flow rate is increased, the more it affects the efficiency of removal positively (Rajmohan et al., 2008). Liquid flow rate plays a crucial role in operation phase as well. Even though increasing liquid flow rate has a positive effect on the efficiency of removal, trying to recirculate more solution than scrubber's capacity causes flooding or clogging problems. For these reasons, it is acceptable having 50-70% L/G ratio for designing (DEPARK, 2014).

The next parameter, residence time, is similar to other control technologies. Proper time should be provided for absorption and reaction between odorants and chemicals. Many parameters can be decisive for the residence time, such as reactivity of the chemicals, dimensions of reaction and so on. As indicated in the research studies, while optimum residence time is 1.4 second for a wet scrubber system, it is 3 second for the other wet scrubber system **(**Kastner & Das, 2002; Uresin et al., 2015).

Large interfacial surface plays a critical role in chemical reactions. In order not to face with any undesired situation during the operation, the contact surface area of wet scrubber should be maximized in designing process (Schlegelmilch et al., 2005). Apart from designing, larger surface area can be provided by using nozzles or atomizers in order to form scrubber liquid into the little droplets. In addition to using nozzles or atomizers, backfill material can provide extra surface area in the packed bed scrubbers (Velhov, 2015).

pH, temperature and proper chemical usage are other parameters, which are important in the operation phase. Although these parameters' values depend on reaction characteristics (acidic, basic scrubbing, oxidation and so on), optimal values are indicated as 3.5–11 for pH and 23–40°C for temperature (Kastner et al., 2011).

As a result of ability of removing both gaseous and particulate air pollutants, wet scrubbers are preferred in many sectors. According to composition of odorous compounds, many chemicals, such as acid, base, oxidant or ozone can be selected to enhance reactions. Moreover, wet scrubbers can be easily converted to multi stage systems in compliance with the necessities. Thanks to these features, wet scrubbers can be defined as one of the leading odor control technologies (Kastner & Das, 2002 ; Talaiekhozani, Bagheri, Goli, & Khoozani, 2016).

Elimination of different odorous compounds with wet scrubber systems were investigated by many experimental scales. Hydrogen sulfide is one of the selected compounds, which is predominant and released from WWTP in the large amount. Also, it is the chemical compound that causes odor nuisance (Lewkowska et al., 2016; Alfonsin et al., 2015).

Under proper conditions, the expected reaction between $H_2S$ and NaOCl is given in equation 2.1.

$$H_2S + 4NaOCl + 2NaOH \rightarrow Na_2SO_4 + 4NaCl + 2H_2O \qquad (2.1)$$

$H_2S$ removing from the foul air with a wet scrubber system was examined in one of the experimental studies (Biard, Couvert, Renner, & Levasseur 2010). A packed bed tower system was used during this experiment. Two chemicals, NaOCl and NaOH, were added into the scrubbing liquid. While NaOH was added for balancing the pH, NaOCl was added for enhancing the efficiency. Polluted air was provided from the extraction pipe of the WWTP, which was diluted with fresh air for concerning various concentrations. The system was operated with different inlet $H_2S$ concentration from 6 to 80 ppmv and pH range between 10 and 10.5. The removal efficiency reached approximately 96%.

Also, another experimental study was employed about rendering emissions to remove odorous VOC compounds, such as methanethiol, hexanal, heptanal and octane (Kastner & Das, 2002). In this study, vapors from cooker and hydrolyzer units were condensed. Then, the condensed air was transferred through two -stage packed bed tower wet scrubber system. ClO2 enriched aqueous solution was used whose pH is stable at 3.04. While average removal efficiency was 60%, some sulphur compounds, such as methanethiol, were removed 100% (Kastner & Das, 2002)**.**

Besides, there are many applications of wet scrubbers on industrial base, which can be seen in the Figure 2.13 (Envirotek, 2013).

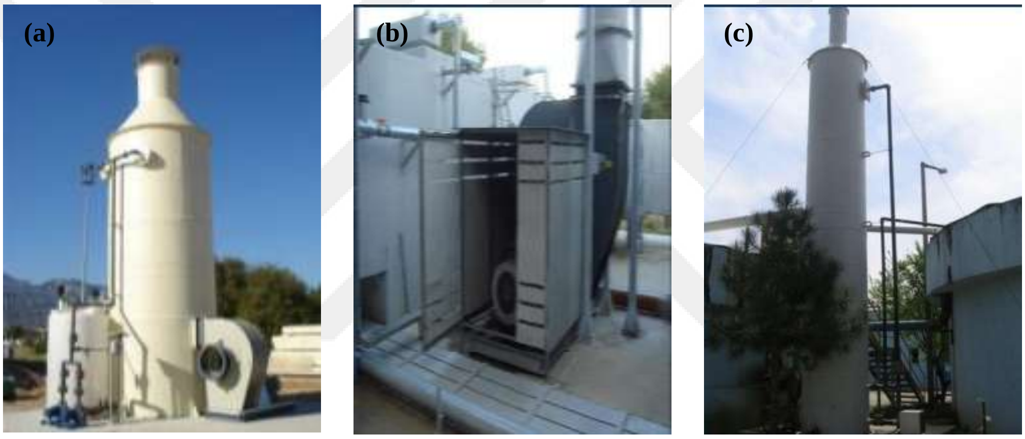


Figure 2.13 Wet scrubbers from different sectors **(a)**, **(b)** from wastewater treatment plants, **(c)** alcohol production

### *2.3.3 Adsorpion*

Adsorption method is another control technology, which has been used for many years. Several materials are used to adsorb pollutants from waste air, such as activated carbon, alumina, silica gel and zeolite. Besides, due to the high surface area, the easiness to produce, adsorption capacity, high surface reactivity and regeneration ability, zeolite and activated carbon (AC) are the most selected materials for adsorption systems (Chen, Pan, & Chen, 2013; Schlegelmilch et al., 2005).

Zeolite is a kind of mineral that has advantageous properties including adsorption potential, polarity, and porosity. Also more than 50 types of zeolite can be found in the nature (Nuernberg, Moreira, Ernani, Almeida, & Maciel, 2016). It is widely used in the systems to remove odorous compounds due to its cheapness and accessibility. Several odorous compounds are removed with zeolite adsorption method easily (Cai, Koziel, Liang, Nguyen, & Xin, 2007).

As a result of being carbon based material, it can be produced by organic materials by physical or/and chemical processes. Some materials, such as wastes, ignocellulosic material and activated sludge, were examined to produce AC in some research studies (Simitzis & Sfyrakis, 1994; Anfruns et al., 2008). Satisfactory results were obtained in these experimental studies, which are indicated in Table 2.3.

Generally, there are two types of AC carbons used for odor removing, virgin AC and impregnated AC. Virgin AC is produced by using simple methods, such as processing of carbon based materials in high temperature (mostly pyrolysis). And then, it is activated with steam or gases like $CO_2$ (Al-Rahbi & Williams, 2016). Distinctly, impregnated AC is designed to remove selective compounds by using chemicals. After virgin AC production, the char is mixed with chemicals, such as caustic, metal oxides, salts and various chemical agents accordingly target odorous compound. As an example, virgin AC is impregnated with caustic or other high pH chemicals in order to adsorb hydrogen sulfide (Bandosz, 2006; Shammay et al., 2016).Adsorption columns can be seen in the Figure 2.14.

Most of the adsorption process occurs on the porous. Firstly, physical adsorption, called *physisorption*, follows the steps on the porous indicated below;

- Odorant molecule approaches to the edge of AC porous
- The molecule diffuses into the porous
- The molecule adheres to pore with physical/chemical bounds

Table 2.3 AC production from different materials

| Material | Production Temperature (°C) | Impregnation/Activation Temperature | Surface Area ($m^2/g$) | Reference |
|---|---|---|---|---|
| Waste Tyre | 600 | KOH (in 900°C) | 621 | (Al-Rahbi & Williams, 2016) |
| Coconut shell | 500 | NaOH (in 700°C) | 1726* | (Cazetta et al., 2013) |
| Activated Sludge | 700 | KOH/NaOH (in 700°C) | 1757 | (Montes-Mor´an et al., 2008) |
| Acrylic textile waste | 800 | Steam (in 900°C) | 619 | (Nahil & Williams, 2010) |
| Almond shell | 750 | $ZnCl_2$ (in 750°C) | 736 | (Aygun, Yenisoy-Karakas & Duman, 2003) |

* After regeneration

Secondly, for chemical adsorption (chemisorption), the bounds occur as a result of chemical reactions between adsorbate and adsorbent molecule, while the bounds occurring as a result of van der Waal's forces in the physisorption. Chemical bounds hold the odorous compound on the surface more powerful than physical connection (Shammay et al., 2016).

Although chemical adsorption is advantageous in terms of the efficiency, it causes some problems for regeneration of used AC due to its strong bounds. Depending on its adsorption capacity, AC has to become saturated and needs to be regenerated or replaced with the fresh one (Chen et al., 2013). Replacing with the fresh one is not a preferable method. Instead of reusing, pollutant-carrying AC is sent to landfill or incineration for disposing, which may cause some environmental problems.

However, regeneration reduces the amount of pollutants, which are mostly hazardous and make it possible to reuse same AC in several times. Chemical, microwave, non-thermal plasma and thermal regeneration techniques have been widely used, but due to its easiness of application, thermal regeneration is the most preferable one (Cazetta et al., 2013; Chen et al., 2013; Lu, Lin,Yu, & Chern et al., 2011; Foo & Hameed, 2012).

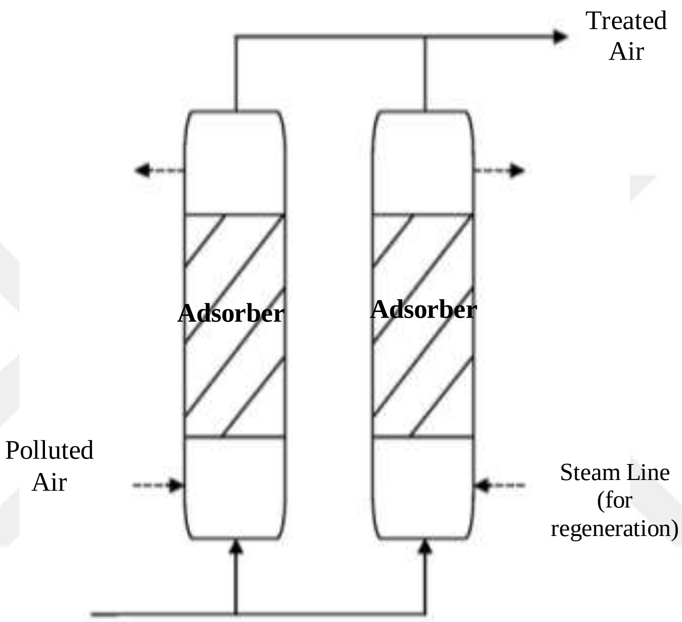


Figure 2.14 Adsorption columns. As a result of regeneration requirements and short lifetime; it is a proper solution to design the adsorption systems in two stages

Even if it is produced from various solid materials, and useful for most of odorants, continuous regeneration necessity limits the removing process on AC adsorbtion (Al-Rahbi & Williams, 2016). Comparing with the other control technologies, AC systems' lifetime is prominently lower than other control technologies. For this reason, they are designed as two-stage or placed secondary treatment unit after the main ones (bio scrubbers, ozone units or wet scrubbers) for polishing (DEPARK, 2014).

One of the designing parameters surface area is related with the porous. Although porous are too small, they provide enormously high surface area for AC (Bandosz, 2006). They are categorized as macro, meso and micro depending on their radius dimensions. The radiuses were indicated in this study as follows (Henning & Schafer, 1993):

- Macropore: r>25 nm
- Mesopore: 25>r>1 nm
- Micropore: 1>r>0.4 nm.

Thanks to their tiny dimensions, most of the micropores can fit to the maximum number of per unit area of AC. This situation provides more surface area to attach for contaminants. The more surface area helps capture higher removal efficiency. In many studies, high removal efficiency was acquired with AC, which has nearly 1000 $m^2/g$ surface area (Guo, Xie, Hong, & Kim, 2001; Al-Rahbi & Williams, 2016). Also, 1000 $m^2/g$ is accepted as minimum surface area by Sydney Water Authority (Sydney Water, 2011). Other parameters, such as temperature (e.i. room temperature is preferable), pH (mostly neutral, but it depends on AC and target compounds characteristics), humidity (having negative effect adsorption capacity), retention time (between 1-6.5 second) should be monitored in operational phase (Bandosz, 2006; Smet, Lens, & Langenhove, 1998).

As it is easy to produce AC from several carbon contained materials, it has been used in many experimental and industrial practices. In one of the research studies, AC production capability from lignocellulosic biomass (i.e. durian shell, wood, palm kernel shell, cotton stalks, and so on) and removing of various compounds from the foul air were investigated. In this study, it is indicated that most of the odor-causing compounds, such as $H_2S$, VOCs (benzene and toluene) were eliminated successfully by ACA in the industrial base as well. For example, one of the industrial base applications is usage of wastewater treatment plants (Nor, Lau, Lee, & Mohamed 2013).

### *2.3.4 Ozone Oxidation*

Ozone has been used in many countries for a long time for many purposes. For instance, while it has been used for water reclamation, such as disinfection, removal of odor and taste, turbidity and color reduction in Switzerland and in the United States, it has been used for odor control in France. (Geering, 1999; Rice, 1999 ; Le Pauloue & Langlais 1999).

Ozone is a mighty oxidant, which can eliminate odorous compounds, such as hydrogen sulfide, mercaptans, indole, skatole and several VOCs easily. In addition, it has certain advantages while comparing to other control methods. For example, in the chemical scrubbers, which are mostly hazardous substances, are used in the scrubber liquid for elimination. These chemicals are expensive and they may cause safety risks in transportation and handling activities. In addition, they react with the odorous compounds and generate solid products (i.e. salts), which may cause clogging problems in the nozzles.

Unlike wet scrubbers, as ozone cannot be stored or transported, it has to be consumed quickly after production. Moreover, after it reacts with odorous compounds, simple products are formed, such as $CO_2$ and $H_2O$. Another example can be given for bio-filters. There are numerous parameters, which should be monitored during bio-filter operation, such as media porosity, pH, nutrient supply and humidity. Unlike bio-filter operation, ozone systems require none of these parameters (Zhang & Pagilla, 2013).

As a first step, what needed to produce ozone is that an oxygen molecule, which should be separated into two unstable oxygen atoms. Then, each single oxygen atoms react with other oxygen molecules in order to produce ozone. Energy is required for the separation process. The separation process can be performed in two ways: Electrical discharge and Irradiation. If pure oxygen gas or air is passed through a high voltage area, electrical discharge is performed. Irradiation is performed, if the gases pass around the UV lamps. Since ozone oxidation was an expensive technology, it was not a preferable way in the past. Additionally, due to unreliable working conditions and low ozone production capacity, it was not a preferable method for odor control (Christensen, Yonar, & Zakaria, 2013; Noordally, Richmond, & Drumm, 1994).

The ozone application can be done in two ways. It can be applied as a direct gas or it can be mixed with a liquid solution. In order to remove odorous compounds, packed column reactor is used for ozone application when ozone is applied to a liquid solution. Although pure or chemical added water is used as scrubbing liquid in some research studies, the system was operated special liquids, such as silicone oil and so on (Smet et. al, 1998). A drawing of a simple ozone system is given in the Figure 2.15. Compared to several scrubber chemicals, ozone is highly corrosive reagent, which needs to be paid attention while designing the reactor. Basically, scrubber units are given in the following list: (Laplanche et al., 1994).

- Column with inert packing material
- Foul gas distribution system
- Liquid distribution and recirculation systems
- Ozone reactor and distribution system
- pH control system
- A tank in the bottom section
- Mist trap
- ACA Column (For unpleasant compounds)

Parameters, such as ratio of ozone and odorous compounds, pH, temperature and retention time, are important for the ozone system. For pH, there is no remarkable effect on ozone consuming. However, adding chemicals for into the scrubber liquid pH balancing may have an increasing effect on removing efficiency. Although, room temperature (i.e., 25°C) condition is appropriate while operating these systems, in one of the research studies, an ozone system was operated in 28°C and most of VOC compounds were eliminated successfully (Lawson & Adams, 1999). For concentrations, sufficient amount of ozone should be provided by using stoichiometric ratios, which depends on the compound characteristic (Laplanche et al., 1994; Mok & Lee, 2006).

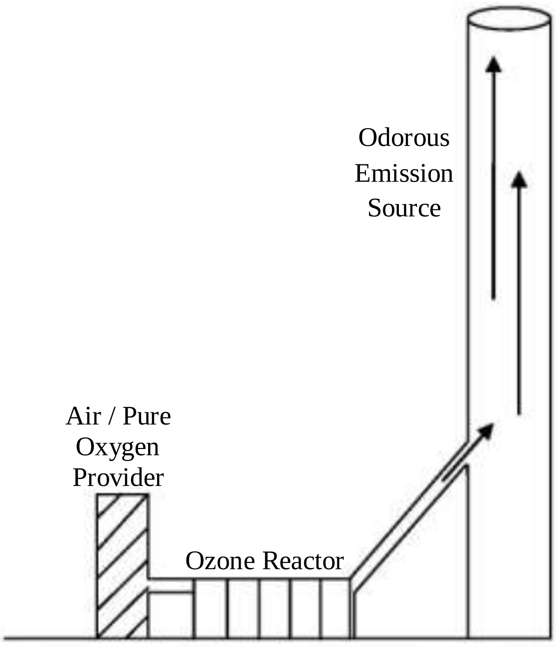


Figure 2.15 Simple ozone oxidation system. Ozone is generated by a reactor and directly sent to odor source. In this process, Air / Pure Oxygen Provider has vital importance for efficiency. Because if ozone is produced by using pure oxygen, five times higher ozone is produced than by using air

Parameters, such as ratio of ozone and odorous compounds, pH, temperature and retention time, are important for the ozone system. For pH, there is no remarkable effect on ozone consuming. However, adding chemicals for into the scrubber liquid pH balancing may have an increasing effect on removing efficiency. Although, room temperature (i.e., 25°C) condition is appropriate while operating these systems, in one of the research studies, an ozone system was operated in 28°C and most of VOC compounds were eliminated successfully (Lawson & Adams, 1999). For concentrations, sufficient amount of ozone should be provided by using stoichiometric ratios, which depends on the compound characteristic (Laplanche et al., 1994; Mok & Lee, 2006).

Ozone is a kind of molecule, which cannot be stored and, therefore should be consumed promptly. For this reason, total amount of ozone should be calculated and the system should be installed. As an example for the calculation of ozone amount, one of the research studies achieved an equation for specifically removing of $H_2S$ compound in 2.5 (Zhang & Pagilla, 2013):

$$H_2S_{(out)} = 0,92 + 0,54H_2S_{(in)} - 0,09O_{3(in)}-0,015t \qquad (2.5)$$

According to equation, required parameters can be found if other parameters in the equation are identified. As indicated below, if the scrubber's retention time and inlet $H_2S$ value are known, a value for $H_2S_{(out)}$ can be chosen, which is under the legal limit and sufficient ozone amount can be calculated. If $H_2S$ $_{(in)}$, $H_2S_{(out)}$, and production capacity of ozone generator values are known, retention time can be calculated. Then, the scrubber can be designed by using these results.

Thanks to the improvements in ozone systems, they have been used in many industries, including wastewater treatment, rendering, paper pulp production, and petroleum refinery activities (Smet et. al, 1998). In one of the research studies, a packed bed wet scrubber system, which is pilot scale, was operated in a municipal wastewater treatment facility. The foul air was taken from sludge storage tank that contains most of the odorous compounds by a blower. Also, as indicated in previous sections, since $H_2S$ is accepted as the target compound, caustic was added in scrubbing liquid in addition to ozone for redounding removing efficiency. Probable neutralization and oxidation reactions are indicated as following equations 2.6, 2.7 and 2.8.

$$H_2S + O_3 \rightarrow S + H_2O + O_2 \qquad (2.6)$$
$$H_2S + 2O_3 \rightarrow H_2SO_4 + O_2 \qquad (2.7)$$
$$2NaOH + H_2S \rightarrow Na_2S + 2H_2O \qquad (2.8)$$

Although full capacity of ozone reactor was nearly 50 g/h, it was operated 25, 50 and 75% ranges. In addition, different combinations were applied, such as only ozone, only caustic and both caustic, and ozone. With range of between 5 and 15 seconds, 99% efficiency was achieved (Kerc & Olmez, 2010).

Additionally, as other example, VOC compounds, which are gathered from rendering, were removed by ozone. Several VOC compounds, such as methanethiol, octane, hexanal, 2-methylbutanal, and 3-methylbutanal were eliminated in the efficiency range of between 40 and 100%. In this example, it was observed that efficiency was affected from temperature changes. In consequence of increasing scrubber liquid's temperature, ozone solubility decreased. This situation was resulted in transformation of fewer amounts of odorous compounds to non-odorous ones (American Society of Agricultural and Biological Engineers [ASABE], 2003).

# CHAPTER THREE
# MATERIAL METHOD

There are different applications to measure odor concentration. These methods are Chemical Analysis (GS-MS), Electronic Nose Technology, Dynamic Olfactometry (Capelli, Sironi, Del Rosso, Centola & Grande, 2008). It is stated by some authorities that dynamic olfactometric measurement method is quite efficient for prompt response comparing to other applications (Giungato et al., 2016).

In this thesis, all of the samples, which were collected from several industries, were measured by dynamic olfactometric measurement method. This method makes use of human nose as a detector to determine odorant concentration. Basically, the method bases on Yes/No principal and provides the measured concentration in odor unit per cubic meter ($OU/m^3$).

## 3.1 Studied Industries

Within the scope of this thesis, samples were collected from various industries, which are given in the Table 3.1 with their NACE codes:

Table 3.1 List of the industrial activities with their NACE codes

| NACE(*) Code | Industry |
|---|---|
| C10.4.1 | Oil Production |
| C10.1.2 | Rendering |
| E37.0.0 | Wastewater Treatment |
| A1.4.7 | Livestock Operations |
| C11.0.5 | Brewery |
| C10.8 | Yeast |

(*)NACE: Nomenclature of Economic Activities

These industries were chosen, since they mostly cause odor problems. Additionally, complaints related to their highly odorous processes were the other reason to choose these industries in this thesis. Samples were taken from selected process exhaust stacks, which were identified as odor source in the Section (1) Odor-Causing Industries. Industrial activities and sampling units are given in the Table 3.2.

Table 3.2 Industrial activities and sampling units

| Industry | Emission Measurement Point |
|---|---|
| Oil Production | Deodorization |
| Rendering | Cooker |
| Wastewater Treatment | Air Collection Line |
| Livestock Operations | Ventilation Point |
| Brewery | Boiling |
| Yeast | Fermantor |

### 3.2 Sampling Method

During this thesis, samples were collected from exhaust stacks of selected industries, which were indicated in the previous sections. Also previous studies were evaluated which were done by laboratory before. Three samples were collected for each sampling point with 5-liter capacity of Nalophan bags, which were odor and taste free. These bags were used only once.

A vacuum sampling device was used to collect odorous air from the sampling points. Each Nalophan bag was combined with a tube made of stainless steel. Nalophan bag was inserted to the inside of vacuum sampling device and filled with the required sample. Then, the top of the tube was closed with a rubber stopper. The tubes and stoppers were used many times after washing with Merck acetone and hexane in order to remove odorous residuals. In some cases, for sampling, it was required to use an extension tube made of Teflon. Unlike the previous ones, these tubes were used only once. In Figure 3.1, vacuum sampling device can be seen in detailed. As the final step, samples were transported to the Air Pollution Laboratory of Dokuz Eylül University and were measured within 24 hours.

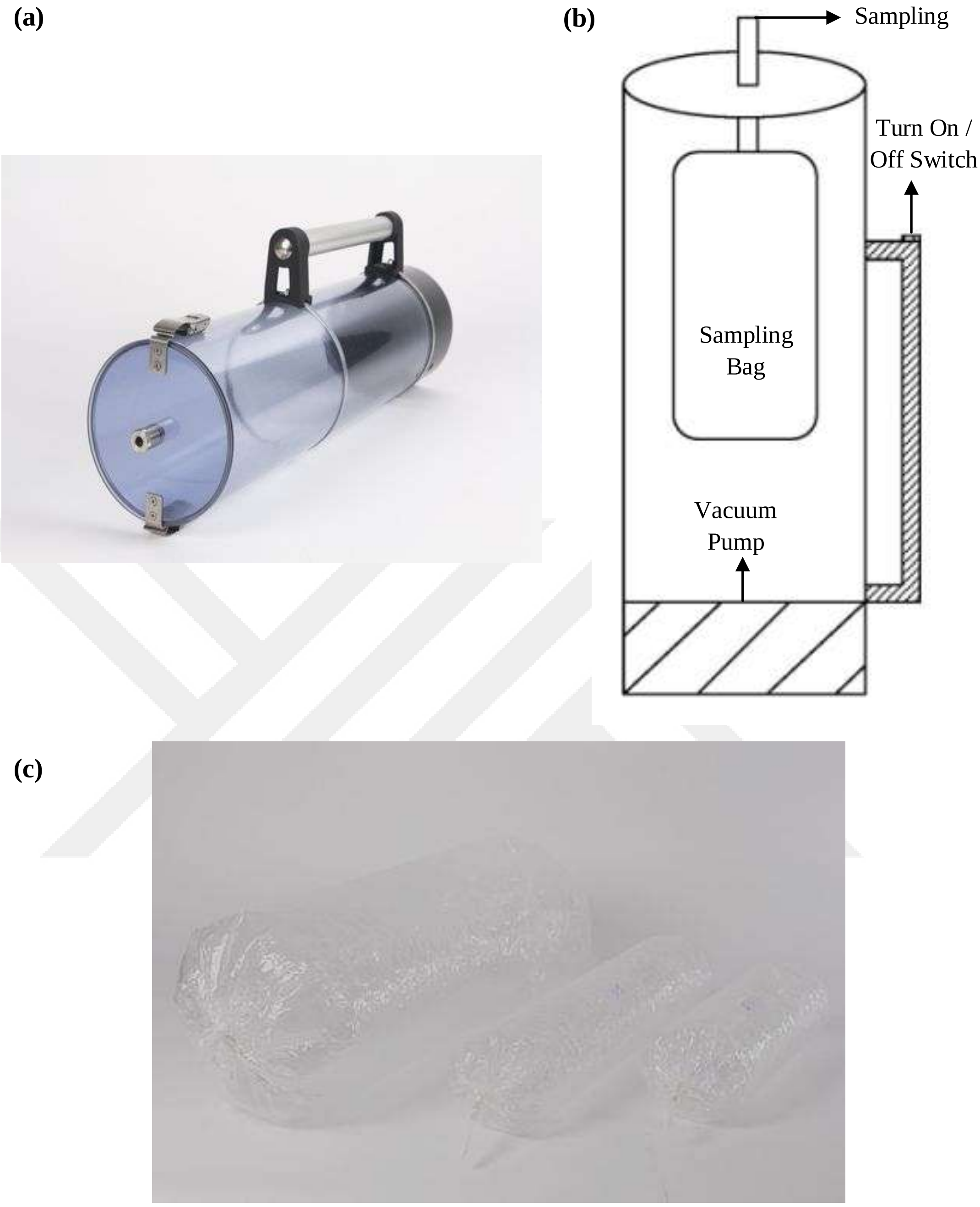


Figure 3.1 (a) Vacuum sampling device (b) its schematic show (c) nalophan bags

### 3.3 Olfactometric Analysis

The samples were measured in order to determine odor concentration by a dynamic olfactometry. An *ECOMA (Emission Measurement Technique and Consultation Mannebeck) TO7 Yes/No Olfactometer* was used which can be seen in the Figure 3.2. This device was purchased by LIFE program, which was supported by European Union. This program can be defined as European Union’s financial instrument to support environmental, nature conservation and climate action projects. The measurement activities were performed in accordance with the protocols described in European Standard EN 13725 (European Committee for Standardization [CEN], 2003). The tests were carried out in the Air Pollution Laboratory of Dokuz Eylül University, which was odor free with trained panelists.

Figure 3.2 ECOMA TO7 Olfactometry

Each panelist candidate is taken ‘n butanol test’ before selection as a‘panelist’. In the test, gas is given in the system with different dilution. It is expected that compatible responses should be given for each dilution level by the panelist candidate. In addition, a panelist does not smoke to avoid any effect on his/her sense of smell. Besides, if one of the panelists has a respiration illness, such as influenza on the panel day, he/she cannot join. One of the substitute panelists join the panel instead of he/she.

Basically, the working principal of the olfactometer is based on the dilution system. This system dilutes odorous air by using fresh air. The air is supplied by a compressor fitted with carbon filters and silica gels.

The olfactometer runs with four panelists and a panel leader. It computes the odor concentration by means of a specific computer program based on the panelists' perception response data. This method is based on a Yes/No technique and specifies how many times that a sample must be diluted with odor-free air. The threshold of detection must be by 50% of the panel in order to get a response. The essential number of dilution with fresh air refers to odor concentration in odor units per cubic meter ($OU/m^3$).

As indicated below, the sucked odorous air from sampling bag is diluted with fresh air. The presence of odor in the diluted samples are judged by panelists. The flow rate of odorous air is controlled in steps by needle valves, which are adjusted by the panel leader.

The panelists smell the air from sniffing ports. While a panelist is provided with air, which is diluted, the opposite ones receive fresh air. Also, the measurement starts with low threshold concentration and increases. With the first odor interaction, the button has to be pushed to indicate 'Yes, it smells'. This action states that the odor concentration is reached. The concentration of each sampling bag is calculated by olfactometer' s software for four panelists in three rounds. The software expresses the odor concentration as Z50, which is the value of panellists' odour thresholds geometric mean and displayed in terms of $OU/m^3$.

An output is given in the Figure 3.3, which is one of the results of measured samples in Air Pollution Laboratory of Dokuz Eylül University.

Panel members' response to different dilution levels are determined automatically by the software, which are given in 'Result of the Panelists' part in red circles. Also, the result of Panelist can be seen in Table 3.3 clearly:

TO7 by ECOMA GmbH — Software (0.9c) by Consult Smyth

Olfactometric measurement according to VDI-RL 3881, 3882 and prEN13725

**Measurement** : (User defined)
**Date** : 2016,
**Sample** : (User defined)
**Blanks** : 20%

Results of the Panelists

| Measuring | Start step | Pre-dilution | Pre-dilution | Panelist 1 | Panelist 2 | Panelist 3 | Panelist 4 |
|---|---|---|---|---|---|---|---|
| 1 | 640 | 1 | 1 | 320 | 320 | 320 | 320 |
| 2 | 640 | 1 | 1 | 640 | 640 | 320 | 320 |
| 3 | 640 | 1 | 1 | 640 | 320 | 320 | 640 |

Z50 = 570 GE/m³ 27,6 dB ± 1,0 dB

Z16 = 800 GE/m³ ZII = 720 GE/m³
Z84 = 410 GE/m³ Zul = 450 GE/m³

Error report of the panelists
Reference air errors

| Measuring sequence | Panelist 1 | Panelist 2 | Panelist 3 | Panelist 4 |
|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 |
| 2 | 0 | 0 | 0 | 0 |
| 3 | 0 | 0 | 0 | 0 |

Errors on blanks

| Measuring sequence | Panelist 1 | Panelist 2 | Panelist 3 | Panelist 4 |
|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 |
| 2 | 0 | 0 | 0 | 0 |
| 3 | 0 | 0 | 0 | 0 |

Figure 3.3 An output, which is one of the results of measured samples in Air Pollution Laboratory of Dokuz Eylül University

Table 3.3 Panelists response dilution levels

| Measurement Set | Panelist 1 | Panelist 2 | Panelist 3 | Panelist 4 |
|---|---|---|---|---|
| 1 | 320 | 320 | 320 | 320 |
| 2 | 640 | 640 | 320 | 320 |
| 3 | 640 | 320 | 320 | 640 |

According to Table 3.3, Panelist 1 was given the answers at related dilation levels,

| Dilution Factor | | Panelist 1 Answer |
|---|---|---|
| 640 | ⟶ | No |
| 320 | ⟶ | Yes |

As indicated Figure 3.3, in the starting dilution 640, Panelist 1 had no response. When the concentration was increased, Panelist 1 gave answer 'Yes'. After two consecutive 'Yes', the measurement ends for it. Same steps are followed for the other panelists.

Then, logarithm values of all panelists' 'Yes/No' answers are calculated in order to calculate Z50 value, which can be identified as threshold concentration level. Also, Z50 means the odor impression of 50 % of the defined group. Logarithm values of 'Yes/No' answers, which are calculated according to sample output, is given in the Table 3.4:

Table 3.4 Logarithm values of panelists' Yes/No answers

| Measurement Set | Panelist 1 | Panelist 2 | Panelist 3 | Panelist 4 |
|---|---|---|---|---|
| 1/No | Log640=2.806 | Log640=2.806 | Log640=2.806 | Log640=2.806 |
| 2/No | Log1280=3.107 | Log1280=3.107 | Log640=2.806 | Log640=2.806 |
| 3/No | Log1280=3.107 | Log640=2.806 | Log640=2.806 | Log1280=3.107 |
| 1/Yes | Log320=2.505 | Log320=2.505 | Log320=2.505 | Log320=2.505 |
| 2/Yes | Log640=2.806 | Log640=2.806 | Log320=2.505 | Log320=2.505 |
| 3/Yes | Log640=2.806 | Log320=2.505 | Log320=2.505 | Log640=2.806 |

The arithmetic means of logarithmic values in the Table 3.5 is called as ‘M’, which is the geometric mean value of panelists’ responses. In the final step, the antilogarithm of M is taken in order to calculate concentration Z50. Also, odor threshold values are calculated for each panelist. The calculation steps are given in Table 3.6.

Table 3.5 Calculation of panelists’ odor threshold values

| | **Panelist 1** | **Panelist 2** | **Panelist 3** | **Panelist 4** |
|---|---|---|---|---|
| Total of Logarithm Values | 17.137 | 16.535 | 15.933 | 16.535 |
| Average of Total | 17.137/6=2.856 | 16.535/6=2.756 | 15.933/6=2.656 | 16.535/6=2.756 |
| Panelists’ Odor Threshold Values (OU/M3) | 10^2.856=718 | 10^2.756=570 | 10^2.656=453 | 10^2.756=570 |

Table 3.6 Calculation of odor value of sample

| | |
|---|---|
| Total of Panelists’ Logarithm Values | 17.137+16.535+15.933+16.535=66.14 |
| Arithmetic Means of Logarithmic Values (M) | 66.14/24=2.756 |
| Odor Concentration of Sample, OU/M3, (Z50) | 10^2.756=570 |

Z50 value is calculated with same method for each sample. Then, arithmetic mean value is calculated for three samples to find odor concentration of stack.

### 3.4 QA/QC Analysis

As being in the each measurement activities, uncertainty is an important factor that effect measurement result directly. Uncertainty sources may be anthropogenic or device related in the olfactometric method.

Anthropogenic ones are related with panelists. All panelists should pass n butanol test successfully to be a member of panel team. As indicated in the Olfactometric Analysis section; they are selected who do not smoke due to decreasing effects on their sense of smell. Also if there is any situation which effect sense of smell; for example flu and so on, they cannot join the panel. Substitute members join these measurements instead of him/her.

The olfactometer is calibrated regularly by an accredited laboratory due to requirements of TS EN 13725. Additionally the system is tested by Dokuz Eylül Laboratory personnel regularly with propan too. In this case concentration of propan and flow meters' dilution rates are known. The gas is diluted several times and collected as samples. Then the samples are analyzed in an accredited GS-MS in another laboratory of Dokuz Eylül University to determine propan concentration. If there is no problem in the device, the results should be compatible with dilution rates.

# CHAPTER FOUR
# RESULTS AND DISCUSSION

In this section, olfactometric measurement results are given for each sector and control methods. All of the samples were measured with olfactometric method, which is identified in the previous section.

Sampling points, which were identified in Odor Causing Industries section, were chosen. Also, average odor concentrations were calculated for each sector by using olfactometric measurement results. Also, similar measurement activities were performed for other samples, which were collected from outlet of odor control units.

## 4.1 Results of Oil Production Industry

### *4.1.1 Sectoral Odor Concentrations*

In oil production industry, oil deodorization process makes the major contribution to odorous emissions. Samples were collected from this process stacks from two different facilities, which are used wet scrubber and wet scrubber and ozone combination systems for deodorization. Then they were measured in the laboratory with dynamic olfactometric method. Concentration range was calculated between 2580-5050 OU/m$^3$. Measurement details are given in Table 4.1.

Table 4.1 Odor concentrations for vegetable oil production industry

| Sector | Sampling Unit | Facility No | Outlet Odor Concentration (OU/m$^3$) |
|---|---|---|---|
| Vegetable Oil Production | Oil Deodorization Unit | 1 | 4669 |
| | | | 5050 |
| | | 2 | 3180 |
| | | | 2580 |

### *4.1.2 Selection Of Proper Odor Control Method*

In this sector, wet scrubber and combination of wet scrubber and ozone oxidation methods were used for odor removing. Results are given in Table 4.2.

Table 4.2 Outlet Concentration from each Odor Control Units

| **Facility No** | **Inlet Odor Concentration ($OU/m^3$)** | **Odor Control Method** | **Odor Concentration ($OU/m^3$)** | **Removal Efficiency (%)** |
|---|---|---|---|---|
| 1 | 4669 | Wet Scrubber | 603 | 87 |
| | 5050 | Wet Scrubber | 640 | 87 |
| 2 | 3180 | Wet Scrubber + Ozone | 605 | 81 |
| | 2580 | Wet Scrubber + Ozone | 550 | 79 |

As seen in Table 4.2, all selected odor control methods were reduced to the outlet concentrations, which are less than 1000 $OU/m^3$. 1000 $OU/m^3$ is the limit indicated in the Turkish Odor Regulation. In addition to outlet concentrations, efficiency values are in the range of 79-87% for all selected methods. These values are compatible with wet scrubbing (60-100%) and ozone oxidation (40-100%) methods as indicated in the research studies of Kastner and Das (2011), Biard (2010) and ASABE (2013). It can be extracted from these results that even though wet scrubber and ozone oxidation methods were applied in different industries, the efficiency of odor removal was detected approximately in the same range. So, it might be said that this control technology can be efficient in different industries.

Even though all of the efficiency values are close to each other, wet scrubbing applications have higher removal efficiencies. In both applications same removal efficiency values are detected. It is seen that using wet scrubbing has more powerful effect on removing odorous compounds.

In the normal conditions, it is expected that wet scrubber and ozone combination have more powerful effect than only wet scrubber application. In this study wet scrubber have higher removal efficiency. Improper design and chosen lower capacity odor control units are several reasons for the situation.

## 4.2 Results of Rendering Industry

### *4.2.1 Sectoral Odor Concentrations*

There are several odor sources in rendering industry. Cooking is the process, where the most of the odorous emissions are released due to the disintegration of organic matter in high temperature. Samples were collected from this process stacks from three different facilities, which are used wet scrubber systems for deodorization. Then they were measured in the laboratory with the dynamic olfactometric method. Concentration range was calculated between 9583-33410 OU/$m^3$. Measurement details are given in Table 4.3.

Table 4.3 Odor concentrations for rendering industry

| Sector | Sampling Unit | Facility No | Outlet Odor Concentration (OU/$m^3$) |
|---|---|---|---|
| Rendering Industry | Cooker | 1 | 33410 |
| | | | 24328 |
| | | 2 | 9583 |
| | | 3 | 14000 |
| | | | 14280 |

### *4.2.2 Selection of Proper Odor Control Method*

In this sector, wet scrubbing methods were used for odor removing. Results are given in Table 4.4.

As seen in Table 4.4, all selected odor control methods were reduced to the outlet concentrations, which are less than 1000 $OU/m^3$. 1000 $OU/m^3$ is the limit that indicated in Turkish Odor Regulation. In addition to outlet concentrations, efficiency values are in the range of 96-98% for all application. These values are compatible with Biard' s (2010) study which defined as 96%. In this context, the efficiency range is highly related to odor control method, regardless of industry type. Also, in the first facility outlet concentration was reduced from 24328 to 515 $OU/m^3$ with the highest efficiency value, 98%.

Table 4.4 Outlet concentration from each odor control units

| **Facility No** | **Inlet Odor Concentration ($OU/m^3$)** | **Odor Control Method** | **Odor Concentration ($OU/m^3$)** | **Removal Efficiency (%)** |
|---|---|---|---|---|
| 1 | 33410 | Wet Scrubber | 986 | 97 |
| | 24328 | Wet Scrubber | 515 | 98 |
| 2 | 9583 | Wet Scrubber | 371 | 96 |
| 3 | 14000 | Wet Scrubber | 417 | 97 |
| | 14280 | Wet Scrubber | 360 | 97 |

## 4.3 Results of Wastewater Treatment

### *4.3.1 Sectoral Odor Concentrations*

As stated in the previous sections, there are three main stages of wastewater treatment activities, including wastewater transportation, treatment and sludge disposal which are odor-causing processes. Samples were collected from two sources from two different facilities several times and measured in the laboratory with dynamic olfactometric method. Sources are listed as:

- Lift stations
- Wastewater treatment and sludge disposal units (from the common line, which collects all units odorous emissions)

Also, concentration range was calculated between 3795-11385 OU/m$^3$for lift stations, and 2754-13325 OU/m$^3$ for wastewater treatment and sludge disposal units. Measurement details are given in Table 4.5.

Table 4.5 Odor concentrations for wastewater treatment activities

| Sector | Sampling Unit | Facility No | Outlet Odor Concentration (OU/m$^3$) |
|---|---|---|---|
| Wastewater Treatment | Lift station | 1 | 3795 |
| | | 2 | 11385 |
| | Wastewater treatment and sludge disposal units | 1 | 3795 |
| | | | 8385 |
| | | | 13325 |
| | | 2 | 11921 |
| | | | 11075 |
| | | | 7247 |
| | | | 13658 |
| | | | 2754 |

### *4.3.2 Selection of Proper Odor Control Method*

Wet scrubbers were used in order to remove odorous emissions in lift stations. In addition to wet scrubbers, bio-filters were used in order to remove odorous emissions in the wastewater treatment and sludge disposal units. Results are given in Table 4.6 and Table 4.7.

Table 4.6 Outlet concentration from each odor control methods for lift stations

| Facility No | Inlet Odor Concentration (OU/m3) | Odor Control Method | Odor Concentration (OU/m$^3$) | Removal Efficiency (%) |
|---|---|---|---|---|
| 1 | 3795 | Wet Scrubber | 370 | 90 |
| 2 | 11385 | Wet Scrubber | 1400 | 88 |

Concentration ranges were calculated differently for each sampling unit. 3795-11385 was found for lift stations, while it was found 2754-13325 OU/m$^3$ for wastewater treatment and sludge disposal units. The difference might be explained with the decomposition of organic materials in the aeration tank by the microorganisms and sludge disposal activities, since these activities make major contribution to odorous emissions.

Table 4.7 Outlet concentration from each odor control units for wastewater treatment and sludge disposal units

| Facility No | Inlet Odor Concentration (OU/m3) | Odor Control Method | Odor Concentration (OU/m$^3$) | Removal Efficiency (%) |
|---|---|---|---|---|
| 1 | 3795 | Wet Scrubber | 400 | 89 |
| | 8385 | Wet Scrubber | 380 | 95 |
| | 13325 | Wet Scrubber | 330 | 98 |
| 2 | 11921 | Biofiltration | 425 | 96 |
| | 11075 | Biofiltration | 170 | 98 |
| | 7247 | Biofiltration | 285 | 96 |
| | 13658 | Biofiltration | 196 | 99 |
| | 2754 | Biofiltration | 110 | 96 |

It can be seen in the Table 4.6, wet scrubbing methods were used for removing odorous compounds for lift stations. In the first application, outlet concentration was reduced to less than 1000 OU/m$^3$, which is the limit indicated in Turkish Odor Regulation. In addition to the outlet concentration, efficiency value was found as 95%. The efficiency was similar within Biard's study (2010), which was performed to remove odorous emissions in WWTP with a pilot scale reactor. Despite of the fact that efficiency value was in determined range in the second application, outlet odor concentration could not be reduced to under the 1000 OU/m$^3$. In order to solve the problem related to the second application, improper operation conditions, incorrect design, insufficient capacity and inappropriate chemical usage situations can be investigated.

The results for wastewater treatment and sludge disposal units are given in Table 4.7. All selected odor control methods were reduced to the outlet concentrations less than 1000 OU/$m^3$. 1000 OU/$m^3$ is the limit indicated in the Turkish Odor Regulation. In addition to outlet concentrations, efficiency values are in the range of 95-99% for selected methods. These values are compatible with Pagan' s (1995) and Biard's (2010) studies. When comparing these two methods' efficiencies, the highest values were obtained in bio-filtration applications. In the second facility, last bio-filtration application indicated in Table 4.7, the efficiency reached to 99%, which is the highest value. In the normal conditions, it is expected that operation of a biological system is relatively harder than a system like wet scrubber. However, as seen in this study, it is possible to achieve high removal efficiency if these systems are properly managed.

## 4.4 Results of Livestock Operations

### *4.4.1 Sectoral Odor Concentrations*

Animal houses, manure transportation, storage and disposal activities are the major odor sources in the livestock operations. Samples were collected from ventilation stack of animal house from only one facility. Also, collected samples were measured in the laboratory with dynamic olfactometric method. The concentration was calculated as 3600 OU/$m^3$. Measurement details are given in Table 4.8.

Table 4.8 Odor concentration for livestock operations

| Sector | Sampling Unit | Facility No | Outlet Odor Concentration (OU/$m^3$) |
|---|---|---|---|
| Livestock Operations | Animal house | 1 | 3600 |

### *4.4.2 Selection of Proper Odor Control Method*

In this facility, wet scrubbing method was used for odor removing. The result is given in Table 4.9.

Table 4.9 Outlet concentration from odor control unit

| **Facility No** | **Inlet Odor Concentration (OU/m3)** | **Odor Control Method** | **Odor Concentration (OU/m$^3$)** | **Removal Efficiency (%)** |
|---|---|---|---|---|
| 1 | 3600 | Wet Scrubber | 305 | 92 |

As seen in Table 4.9, wet scrubbing method decreased outlet concentrations to less than 1000 OU/m$^3$, which is the limit indicated in Turkish Odor Regulation. In addition to outlet concentration, efficiency value was found 92%, which is compatible with wet scrubbing methods' efficiency range (60-100%) as indicated in the research studies conducted by Kastner and Das (2011) and Biard (2010). It can be extracted from these results that this control technology can be efficient in different industries and compounds.

## 4.5 Results of Brewery Industry

### *4.5.1 Sectoral Odor Concentrations*

There are several processes for beer production. Wort boiling and fermantation are two of these processes that most of the odor emissions are emitted. In this thesis, samples were collected from wort boiling units from different facilities and measured in the laboratory with dynamic olfactometric method. Concentration range was calculated as 13976-55360 OU/m$^3$. Measurement details are given in Table 4.10.

### *4.5.2 Selection of Proper Odor Control Method*

In this sector, wet scrubbing methods were used for odor removing. Results are given in Table 4.11.

Table 4.10 Odor concentrations for brewery industry

| Sector | Sampling Unit | Facility No | Outlet Odor Concentration (OU/m$^3$) |
|---|---|---|---|
| Brewery Industry | Wort boiler | 1 | 30000 |
| | | | 13976 |
| | | 2 | 31880 |
| | | | 48031 |
| | | | 55360 |

Table 4.11 Outlet concentration from each odor control units

| Facility No | Inlet Odor Concentration (OU/m3) | Odor Control Method | Odor Concentration (OU/m$^3$) | Removal Efficiency (%) |
|---|---|---|---|---|
| 1 | 30000 | Wet Scrubber | 7070 | 76 |
| | 13976 | Wet Scrubber | 580 | 96 |
| 2 | 31880 | Wet Scrubber | 627 | 98 |
| | 48031 | Wet Scrubber | 590 | 99 |
| | 55360 | Wet Scrubber | 560 | 99 |

With the value of 55360 OU/m$^3$, highest concentration was found in brewery industry in this thesis. During the wort boiling process, many aromatic compounds are released from hops that make a huge contribution to odorous emissions.

In Table 4.11, except the first one, all wet scrubber applications decreased the outlet concentrations, which is less than 1000 OU/m$^3$ as indicated in Turkish Odor Regulation. In addition to outlet concentrations, efficiency values are in the range of 96-98% for all application. Although the first one' s efficiency value, which is 80%, is in the determined range, outlet odor concentration could not be reduced under the 1000 OU/m$^3$. In order to solve this problem, improper operation conditions, incorrect design, insufficient capacity and inappropriate chemical usage situations can be investigated. In the last one, outlet concentration was reduced till 560 OU/m$^3$ with the highest efficiency value, which is 98%. This value is parallel with Biard' s (2010) study. Although brewery industry' s average odor concentration is much more than

WWTP's, efficiency is highly related with odor control method, regardless of industry type.

Also it should be noted that, in some cases only one control method or control unit cannot be adequate reduce odor concentration limit value due to high odor concentration. For this reason; two or more control units or combination of different control methods; for example; wet scrubbing and ozone oxidation can be used in brewery industry.

## 4.6 Results of Yeast Industry

### *4.6.1 Sectoral Odor Concentrations*

In the yeast industry, most of the odorous compounds are originated from fermentation and drying processes. During the fermentation, dominant odorous compounds release. In this thesis, samples were collected from fermentation units of different facilities and measured in the laboratory with dynamic olfactometric method. Concentration range was calculated as 9095-15305 OU/m$^3$. Measurement details are given in Table 4.12:

### *4.6.2 Selection of Proper Odor Control Method*

In this sector, ozone oxidation methods were used for odor removing. Results are given in Table 4.13:

Table 4.12 Odor concentrations for yeast industry

| Sector | Sampling Unit | Facility No | Outlet Odor Concentration (OU/m$^3$) |
|---|---|---|---|
| Yeast Industry | Fermantor | 1 | 15305 |
| | | | 12000 |
| | | | 13000 |
| | | | 13000 |
| | | | 9095 |

Table 4.13 Outlet concentration from each odor control units

| Facility No | Inlet Odor Concentration (OU/m$^3$) | Odor Control Method | Odor Concentration (OU/m$^3$) | Removal Efficiency (%) |
|---|---|---|---|---|
| 1 | 15305 | Ozone Oxidation | 640 | 96 |
| | 12000 | Ozone Oxidation | 480 | 96 |
| | 13000 | Ozone Oxidation | 460 | 96 |
| | 13000 | Ozone Oxidation | 592 | 95 |
| | 9095 | Ozone Oxidation | 350 | 96 |

As indicated in Table 4.13, selected method, which is ozone oxidation, reduced the outlet concentrations to less than 1000 OU/m$^3$, which is the limit indicated in Turkish Odor Regulation. In addition to outlet concentrations, efficiency values are in the range of 95-96% for all applications. These values are compatible with Kerc and Olmez' s study (2010) that found the efficiency as approximately 99%. Although yeast industry has one of the highest average odor concentrations, ozone oxidation method removed most of the odorous compounds successfully. In this four of the samples which can be seen in the Table 4.13, outlet concentration was reduced till 350 OU/m$^3$ with the highest efficiency value which is 97%.

All of the measurement results and their details are given in Table 4.14:

Table 4.14 Measurement results for all industries and control methods

| Sector | Measurement Point | Facility No | Inlet Odor Concentration (OU/m$^3$) | Odor Control Method | Outlet Odor Concentration (OU/m$^3$) | Removal Efficiency (%) |
|---|---|---|---|---|---|---|
| Vegetable Oil Production | Oil Deodorization | 1 | 4669 | Wet Scrubbing | 603 | 87 |
| | | | 5050 | Wet Scrubbing | 640 | 87 |
| | | 2 | 3180 | Wet Scrubbing + Ozone Oxidation | 605 | 81 |
| | | | 2580 | Wet Scrubbing + Ozone Oxidation | 550 | 79 |
| Rendering | Cooker | 1 | 33410 | Wet Scrubbing | 986 | 97 |
| | | | 24328 | Wet Scrubbing | 515 | 98 |
| | | 2 | 9583 | Wet Scrubbing | 371 | 96 |
| | | 3 | 14000 | Wet Scrubbing | 417 | 97 |
| | | | 14280 | Wet Scrubbing | 360 | 97 |
| Livestock Operations | Animal House | 1 | 3600 | Wet Scrubbing | 305 | 92 |
| Wastewater Treatment | Lift Station | 1 | 3795 | Wet Scrubbing | 1400 | 90 |
| | | 2 | 11385 | Wet Scrubbing | 370 | 88 |

Table 4.14 Continue

| | | | | | | |
|---|---|---|---|---|---|---|
| Wastewater Treatment | Wastewater Treatment and Sludge Disposal | 1 | 3795 | Wet Scrubbing | 400 | 89 |
| | | | 8385 | Wet Scrubbing | 380 | 95 |
| | | | 13325 | Wet Scrubbing | 330 | 98 |
| | | 2 | 11921 | Biofiltration | 425 | 96 |
| | | | 11075 | Biofiltration | 170 | 98 |
| | | | 7247 | Biofiltration | 285 | 96 |
| | | | 13658 | Biofiltration | 196 | 99 |
| | | | 2754 | Biofiltration | 110 | 96 |
| Brewery | Boiler | 1 | 30000 | Wet Scrubbing | 580 | 76 |
| | | | 13976 | Wet Scrubbing | 7070 | 96 |
| | | 2 | 31880 | Wet Scrubbing | 627 | 98 |
| | | | 48031 | Wet Scrubbing | 590 | 99 |
| | | | 55360 | Wet Scrubbing | 560 | 99 |
| Yeast | Fermantor | 1 | 15305 | Ozone Oxidation | 640 | 96 |
| | | | 12000 | Ozone Oxidation | 481 | 96 |
| | | | 13000 | Ozone Oxidation | 460 | 96 |
| | | | 13000 | Ozone Oxidation | 592 | 95 |
| | | | 9095 | Ozone Oxidation | 350 | 96 |

# CHAPTER FIVE
# CONCLUSIONS

In this thesis, odor concentration for industries and application of odor control methods were investigated. Industries were selected as vegetable oil production, rendering, wastewater treatment, poultry operations, brewery and yeast production, which cause odor problem. Besides, odor control methods were investigated, such as bio-filtration, wet scrubbing, adsorption and ozone oxidation.

As a result of detailed review of literature and applications, odor sources were determined for all selected sectors and samples were collected from different facilities. During the study, three rendering, two vegetable oil production, wastewater treatment and brewery, one livestock and yeast production facilities were investigated. They were measured with olfactometric method in the Air Pollution Laboratory of Dokuz Eylül University. Concentrations ranges were calculated as 2580-5050 OU/$m^3$ for vegetable oil production, 9583-33410 OU/$m^3$ for rendering, 3795-11385 OU/$m^3$ in the lift stations and 2754-13658 OU/$m^3$ wastewater treatment and sludge disposal units for wastewater treatment, 3600 OU/$m^3$ for livestock operation, 13976-55360 OU/$m^3$ for brewery production and 9095-15305 OU/$m^3$ for yeast production. According to the results, brewery production has the highest odor concentration among all of these sectors.

In the second part of this thesis, other samples were collected from outlet of odor control units and measured with olfactometric method in the Air Pollution Laboratory of Dokuz Eylül University. Most of the odor control applications reduced outlet concentration to less than 1000 OU/$m^3$, which is the limit stated in Turkish Odor Regulation. Wet scrubbing reduced the most amount of outlet concentration in vegetable oil production, rendering, lift stations, livestock and brewery industries. In the wastewater treatment and sludge disposal sources, the best result was given by the bio-filtration. Lastly, ozone oxidation was the most preferable method in the yeast industry due to the high efficiencies.

Also, it is aimed in this thesis that the results can be used as a guide for determination of sectorial average odor concentrations and choosing the best odor control method. Besides, this thesis is the first step to prepare proper odor management system in industrial base. This thesis may yield better results if more sectors and odor control methods can be investigated in further studies in order to develop a successful odor management system in our country.

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