DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

TREATMENT OF TOBACCO INDUSTRY WASTEWATERS BY ADVANCED OXIDATION PROCESSES

by

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September, 2005

İZMİR

TREATMENT OF TOBACCO INDUSTRY WASTEWATERS BY ADVANCED OXIDATION PROCESSES

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We have read the thesis entitled **"Treatment of Tobacco Industry Wastewaters by Advanced Oxidation Processes"** completed by **Çağdaş GÖNEN** under supervision of **Prof. Dr. Ayşen TÜRKMAN** 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.

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TREATMENT OF TOBACCO INDUSTRY WASTEWATERS BY ADVANCED OXIDATION PROCESSES

ABSTRACT

Tobacco is an agricultural product used for the commercial purpose. Tobacco production is an important activity for the agriculture and economy of Turkey. Tobacco is commonly used for cigarette production. There are three cigarette production factories and several tobacco factories in Izmir.

In this thesis study, the treatability of wastewater obtained from a cigarette factory in Izmir is determined by advanced oxidation process (AOPs). The wastewater of cigarette factory contains process wastewater and domestic wastewater. Average daily flowrate of the wastewater was 240 m^3/day. Treatment plant basically includes equalization tank, chemical treatment unit and biological treatment unit. Samples were collected from chemical treatment unit exit. The following advanced oxidation processes were applied; UV light and hydrogen peroxide ($UV+H_2O_2$) process and photo Fenton process ($UV+H_2O_2+Fe^{+2}$). Treatability research aimed determining optimum reaction conditions (pH value, reaction time, and oxidant and catalyst dosage), in addition to determine a treatment which is efficient and reasonable from economical point of view.

The efficiency of Photo Fenton process ($UV+H_2O_2+Fe^{+2}$) was determined to be greater than the ultraviolet hydrogen peroxide ($UV+H_2O_2$) process.

Keywords: tobacco industry wastewater, advanced oxidation, photofenton, UV light

SİGARA ENDÜSTRİSİ ATIKSULARININ İLERİ OKSİDASYON TEKNİKLERİ İLE ARITIMI

ÖZ

Tütün dünya üzerinde ticari amaçla üretilen bir tarımsal üründür. Türkiye de tütün üretimi tarımda ve ülke ekonomisinde önemli bir yer tutmaktadır ve daha çok sigara üretiminde kullanılmaktadır. İzmirde 3 adet sigara fabrikası ve çok sayıda tütün işleme tesisi bulunmaktadır.

Bu çalışmada İzmir'deki bir sigara fabrikasından alınan atıksuyun ileri oksidasyon teknikleriyle arıtılabilirliği araştırılmıştır. Fabrikanın atıksuyu üretimden gelen atıksu ile evsel nitelikli atıksuyun karışımından oluşmaktadır. Günlük ortalama debisi 240 m^3/gün olup arıtma tesisi temel olarak dengeleme ünitesi, kimyasal arıtım ve biyolojik arıtım ünitelerinden oluşmaktadır. Numuneler kimyasal arıtma ünitesi çıkışından alınmıştır. Atıksuda yapılan arıtılabilirlik çalışmalarında çeşitli proseslerden oluşan ileri oksidasyon prosesleri uygulanmıştır. İleri oksidasyon prosesleri olarak; ultraviyole ışığı+hidrojen peroksit ($UV+H_2O_2$) ve Foto-Fenton ($UV+H_2O_2+Fe^{+2}$) prosesleri çalışmalarda kullanılmıştır. İleri oksidasyon prosesleri ile atıksuyun arıtılması denemelerinde; her proses için optimum reaksiyon koşullarının (pH, reaksiyon süresi, oksidant ve katalizör dozu) belirlenebilmesi için çalışmalar yapılmıştır. Bu çalışmalarda en uygun reaksiyon koşullarının bulunması ve bulunan en uygun koşullarda ekonomik olarak optimum kirletici giderimi hedeflenmektedir.

Yapılan denemelerin sonucunda her proses için ayrı ayrı optimum reaksiyon koşulları bulunmuş ve Foto-Fenton ($UV+H_2O_2+Fe^{+2}$) prosesinin ultraviyole ışığı+hidrojen peroksit ($UV+H_2O_2$) prosesinden daha etkin olduğu görülmüştür.

Anahtar sözcükler: sigara endüstrisi atıksuyu, ileri oksidasyon, fotofenton, UV ışığı

CONTENTS

Page

CHAPTER ONE
INTRODUCTION

1.1 Introduction

The economical value of tobacco and cigarette production industry is bigger than thousands of billion dollars per year and it is the one of the most powerful and larger industries in the world. The process used in this industry is confidential because of economical and rivalry reasons. The companies have to keep their product contents and their production technologies secret for several reasons. Also many researches and statistics were made and published about the effect of tobacco smoking and its economical influences. The number of the published research is very limited about cigarette production wastewater and its treatment. That's why; finding scientific research data about this industry was very difficult. Therefore, under this restricted conditions, cigarette production wastewater treatment with various advanced oxidation processes were studied in this thesis.

In this study, some advanced oxidation technologies which contains UV light and hydrogen peroxide (UV/H_2O_2) process and also photo Fenton process ($UV/H_2O_2/Fe^{+2}$) optimum conditions were determined for the cigarette industry wastewater.

1.2 Objective and Scope

The major objectives of this thesis can be summarized as follow:

1. To investigate effectiveness of various advanced oxidation technologies for the treatment of wastewater from a cigarette production factory.

2. To determine most effective advanced oxidation process for the treatment of cigarette production wastewater.

3. To evaluate the effects of reaction conditions such as oxidant concentration, pH value, reaction time, and the combinations of the oxidants and other conditions on wastewater treatment performance.

4. To decide the most appropriate oxidant concentration and irradiation time for TOC and color removal.

5. To evaluate the effects of operation conditions for the selected oxidation methods.

6. To determine the optimum chemical dosages for each advanced oxidation method to reach better efficiency.

7. To determine optimum pH value and significant reaction time for the advanced oxidation process.

In general, different oxidation methods were applied for the treatment of the cigarette production wastewater. Total organic carbon (TOC) and color parameters were used in order to evaluate and compare the treatment performance of different oxidation methods. Because cigarette production includes numerous patented chemicals and additives (about 599 additives see appendix). Total organic carbon parameter is used as general pollution parameter.

The limit of color parameter is not presented in the environmental Regulations of Turkey. On the other hand, generally people decide the pollution level according to color of the wastewater; also color parameter was examined in this thesis.

Advanced oxidation processes were applied to samples which were collected from the chemical treatment unit exit of the treatment plant of cigarette production factory. Ultraviolet light and hydrogen peroxide (UV/H_2O_2) and light assisted photo Fenton ($UV/H_2O_2/Fe^{+2}$) processes were used in order to obtain most effective TOC and color removal.

CHAPTER TWO
ADVANCED OXIDATION PROCESSES (AOPs)

2.1 Introduction

Over the past twenty years, environmental regulation requirements have become more and more stringent by the governments, due to the risk on human health and the ecology by environmental pollutants.

Contaminants and toxic organic substances originating from industrial wastewaters enter the ecological system by contaminating soil, water and air. In addition, these compounds may be incorporated into human life by food chain or water.

Advanced oxidation processes is the generation and the use of the hydroxyl radical (OH*) as a powerful oxidant to destroy compounds that cannot be oxidized by conventional oxidants such as oxygen, ozone and chlorine. The efficiency of the system is shown as the rate constant for the reaction of hydroxyl radicals with most organic pollutants are much higher. The hydroxyl radical typically reacts one million to one billion times faster then chemical oxidants like ozone and hydrogen peroxide (Çokay, 2002).

Many of the conventional treatment processes are quite sufficient for the treatment of wastewater excluding toxic organics. Commonly, these are biological treatment systems. Toxic and inhibitory organic compounds affect the treatment efficiency of these conventional treatment processes in a negative way. These contaminants limit the treatment yield. Moreover, when the industrial wastewater is treated, conventional biological system generates sludge which may include toxic or heavy metal materials that may require for further treatment and disposal. So, these processes are not cost effective. In addition, microorganisms probably die on a large scale because of these toxic and inhibitory organic compounds in the course of the treatment process.

For these reasons, new treatment technologies are researched and investigated. Most of the limitations given can be eliminated by advanced oxidation technologies.

These oxidation processes have shown tremendous potential for the treatment of wastewaters containing hazardous chemicals that has toxic and inhibitory characteristics, compared to conventional biological treatment methods.

In oxidation processes organic compounds could be oxidized to carbon dioxide, water, and inorganic salts. Chemical oxidation methods include various oxidants, such as ozone, hydrogen peroxide, potassium permanganate, sodium hypochlorite, ultraviolet light and Fenton's Reagent. However, advanced oxidation processes (AOPs) may either completely mineralize organic compounds (i.e. to carbon dioxide and water), or convert complex organic compounds into simpler molecules that can be treated by conventional methods. AOPs produce highly reactive hydroxyl radicals through a variety of techniques including ultraviolet radiation/hydrogen peroxide, ozone/hydrogen peroxide, ultraviolet radiation/ozone, Fenton's reagent, and titanium dioxide/ultraviolet radiation. The hydroxyl radicals produced by any of these methods are indiscriminant oxidants and can react with a myriad of organic compounds in water (Bergendahl et al., 2002).

Many organic and inorganic chemicals in the environment absorb sunlight and cause transformation to new molecular species. Thus, most of the photochemical processes initiate the breakdown of organic molecules into simpler molecules and ultimately to carbon dioxide and other mineral products (Çokay, 2002).

Advanced Oxidation Processes has gained popularity during the past two decades for the treatment of industrial effluents (Chidambara et al., 2004).

Advanced oxidation processes, which involve an in-situ generation of highly potent chemical oxidants such as hydroxyl radicals, have emerged as an important class of technologies to accelerate the non-selective oxidation. These technologies, such as hydrogen peroxide oxidation (H_2O_2), hydrogen peroxide assisted UV photochemical oxidation (UV/H_2O_2), TiO_2 photocatalytic oxidation (PCO), are

widely used for the destruction of a wide range of recalcitrant organic contaminants in wastewater which cannot be eliminated biologically. As can be seen from Table 2.1, hydroxyl radicals are powerful oxidizing agents with an oxidation potential of 2.33 V and can react with most organic and any inorganic solutes with high rate constants (Zhihui et al., 2005).

Table 2.1 Oxidants potentials of different oxidants

Oxidant	**Oxidant Potential, V**
Fluorine	3,00
Hydroxyl Radical	2,33
Ozone	2,10
Hydrogen peroxide	1,80
Potassium Permanganate	1,70
Chlorine Dioxide	1,50
Chlorine	1,40

AOPs have common principles in terms of the production of hydroxyl radicals that are assumed to be operative during the reaction. Although it is claimed that there are other species involved, the active species responsible for the destruction of contaminants in most cases seems to be the hydroxyl radical (OH*) which is unstable and quite reactive. Due to the instability of OH* radical, it must be generated continuously ‘‘in situ’’ through chemical or photochemical reactions described in the literature. Hydroxyl radicals produced in either way of described above may attack organic molecules by abstracting a hydrogen atom from the molecule. A common pathway for the degradation of organics by the hydroxyl radicals is as follow (Azbar et al., 2004),

$OH^* + RH \rightarrow H_2O + R^*$

$R^* + H_2O_2 \rightarrow ROH + OH^*$

$R^* + O_2 \rightarrow ROO^*$

$ROO^* + RH \rightarrow ROOH + R^*$

Treatment with advanced oxidation process is used not only for industrial wastewater treatment but also is used for advanced treatment of sewage. However, concerns arise from the fact that trace organic substances in the reacted water may still have potential hazard for human health. Advanced oxidation technologies have merged as one of the main environmental friendly technologies in the remediation of wastewater and or general water treatment. The combined usage of UV, ozone (O_3) and hydrogen peroxide to facilitate the complete degradation of contaminants are receiving increasing interest due to their advantages (Yang et al., 2005).

2.2 Advanced Oxidation Process Using Ozone

Ozone is one of the reactants used in advanced oxidation processes. As an oxidant, ozone rarely could be mixed with the reaction directly but nowadays, could be used with other kinds of oxidants like UV, H_2O_2 and TiO_2. Ozone is powerful oxidant for contaminants originating from industrial wastewaters. The rate of treatment efficiency could reach to 99% with ozone oxidation in optimal conditions. Ozone and its combination with other oxidants could be used successfully in industrial wastewater treatment.

In board paper industry; the effect of pH on the ozonization process is very important. Ozone is much more effective in basic media, most probably due to the involvement of hydroxyl radical, which is a better oxidizing agent than molecular ozone (Amat et al., 2005).

The standard oxidation-reduction potential for ozone is high (+2.07 V) in acid solutions. Ozone is a powerful oxidizing agent yet it offers the advantage that little or no secondary products are formed upon treatment of the wastewater containing cyanide. Ozone consumption data obtained in the experiments confirm that one mole of cyanide is oxidized by one mole of ozone to produce one mole of cyanate, according to literature (Parga et al., 2003). As a result of this case study cyanide removal was reached 99,9% about in 20 minutes.

In another case study which was performed with olive mill wastewater, ozonation technique was applied. Recent studies have shown that the ozonation process is effective in removing a wide variety of organic contaminants. Thus, chemical oxidation using ozone is a way to reduce polyphenol content and, in addition, improve the biodegradability of these types of waste waters, and hence the efficiency of the biological step. Ozone oxidation rate increases by pH value or the addition of Fenton reagent and/or UV radiation due to generation of hydroxyl radicals, OH*. The UV/Fenton/O_3 treatment yields the highest p-Coumaric acid degradation rate among all the treatment methods applied (Monteagudo et al., 2005).

2.3 Advanced Oxidation Process Using Ultraviolet Light

UV is part of electromagnetic waves. Ultraviolet light electromagnetic radiation ranges between 400 and 10 nm, and is subdivided into several regions. The range of invisible UV light is established downward from 400-nm wavelengths (Masschelein, 2003).

Table 2.2 Classification of UV range

Type	Range	Comment
UV-A	From 400 to 315 nm	Between 400 and 300 nm, sometimes called near UV
UV-B	From 315 to 280 nm	Sometimes called medium UV
UV-C	From 280 to 200 nm	Range to be considered in more detail in water disinfection

The effect of UV light on toxic materials and organic compounds in various systems has been thoroughly studied during the past decades. Photochemical oxidation process is a recent development in wastewater treatment and related to the required elimination of pollutants that are resistant to the more conventional treatment methods. UV oxidation is the process by which chemical bound of the contaminants in the aqueous form are degraded under the influence of UV light. The varieties of photo oxidation products are according to the matrix in which the process

occurs, but the complete reaction product of an organic contaminant is CO_2, H_2O and inorganic salts.

Photo oxidation method using UV light and addition of H_2O_2 is a branch of advanced oxidation technologies and it has proven to be very efficient for the removal of toxic organic pollutants found in aquatic environment (Çokay, 2002).

2.4 Advanced Oxidation Process Using UV and H_2O_2

Photochemical synergism of advanced oxidation processes is a recent development in water and wastewater treatment. UV and H_2O_2 oxidation is widely used for wastewater treatment and these are still important aspects for investigating subjects related to photochemical oxidation.

There is tremendous number of studies about UV and H_2O_2 photochemical oxidation. Most of them belong to textile industry. The oxidation process produces free radicals (OH*) which attack and degrade the refractory organic compounds in wastewater unselectively. UV irradiation together with hydrogen peroxide (UV/H_2O_2), efficiently decolorize the dye containing wastewater. In the UV/H_2O_2 photoreactor, the reaction rates were predominantly influenced by the UV light intensity, volume and pH of treated wastewater, dosage of hydrogen peroxide, and initial dye concentration. Theoretically, the higher the UV power, the faster is the formation of OH* free radicals. The results showed that the thin gap plug flow UV/H_2O_2 process can almost completely decolorize the synthesized azo dye wastewater under various operating conditions. The decolorization rates of acid orange 10 (AO10) were affected significantly by the hydrogen peroxide concentration, UV intensity, and initial dye concentrations (Hung-Yee & Ming-Chin, 2005). The color removal treatment efficiency of this research was between 90% and 99%.

The UV light primarily serves as a source of UV photons that facilitate the decomposition of conventional oxidants (hydrogen peroxide/ozone) to form hydroxyl radicals, which then initiate chain oxidation reactions. Many refractory organics can be destroyed rapidly by these processes and have been well documented elsewhere. There are numerous studies involving phenol degradation, either by direct UV photolysis or by AOP techniques. The phenol molecules disappear within 50 min under UV/ H_2O_2 oxidation, whereas the COD is reduced to fairly low level (~2 mg/l – 1 mg/l) within about 2 h. The main reactions are aromatic ring oxidation (producing hydroquinone, catechol and benzoquinone) and then carboxylic acid formation (muconic, fumaric, oxalic and formic acids). Ethylene glycol is degraded into oxalic and formic acids under UV/ H_2O_2 (Horng, 2003).

The hydroxyl radical, a powerful oxidant second only to fluorine in oxidation power, is approximately two times more reactive than chlorine. It can react at near diffusion rates, and has the ability to oxidize a wide range of organic chemicals. AOPs that generate hydroxyl radicals have been found to be very effective for treating drinking water, groundwater, and contaminated soils (Bergendahl et al., 2002).

2.5 Advanced Oxidation Process Using UV and Fenton's Reagent

Fenton's reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s. Although Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water, the main advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts. The Fenton reaction causes the dissociation of the oxidant and favors the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants. Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals according to the reaction. The ferrous iron (Fe^{2+}) initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of the radicals involves a complex reaction

sequence in an aqueous solution: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^-$, $k_1 \approx 70M^{-1}\ s^{-1}$ (Neyens & Baeyens, 2003).

Fenton's reaction could be described as the catalytic producing of hydroxyl radicals from a chain reaction between ferrous iron and hydrogen peroxide. The basic mechanism of Fenton treatment process includes the chemical oxidation and chemical coagulation of organic compounds. Fenton's reagent yields a solution with powerful oxidizing capability. The mixture of hydrogen peroxide with iron salts is effective only in acidic pH ranges of about 2-5. This pH limitation usually makes the process application difficult.

Photo-Fenton process was especially used for wastewater containing non biodegradable or toxic compounds. Wastewater arises from different chemical industries like resin manufacturing, petrochemical, oil-refineries, paper making, coking and iron-smelting has high concentration of phenol and their derivatives which are extremely toxic and refractory in nature. The maximum mineralizing efficiency of phenol with Fenton, solar and UV-Fenton processes are given as 41%, 96% and 97%, respectively. In Fenton process, carboxylic acids like acetic acid and oxalic acid preformed as end products during the degradation of phenol while in photo-Fenton processes, both these ions were identified during the early stages of phenol degradation and were oxidized almost completely at 120 min of the reaction time (Kavitha & Palanivelu, 2004).

Reaction rates with Fenton's Reagent are generally limited by the rate of OH generation (i.e., concentration of iron catalyst) and decreases by the specific wastewater being treated. Fenton's Reagent is most effective as a pretreatment tool, where COD's are > 500 mg/L. This is due to the loss in selectivity of pollutant levels which decrease. Iron dose may also be expressed as a ratio to H_2O_2 dose. It is also possible to recycle the iron after the reaction. This can be done by increasing the pH, separating the iron floc, and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse. The optimal pH occurs between pH 3 and pH 6. The decrease in efficiency on the

basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. (www.h2o2.com, 2005)

The advantage of the Photo Fenton process, as an oxidative pretreatment step over other photochemical oxidation process is its being cost effective. It has high oxidation efficiency especially, if aromatic compounds are destroyed. Because no specific technical equipment is necessary, the method can be considered as practical. (Çokay, 2002).

CHAPTER THREE
TOBACCO AND CIGARETTE INDUSTRY

3.1 General Review of Industry

Cigarette industry is one of the biggest industries in the world. The economical value of tobacco and cigarette production industry was more than 3 quadrillion dollars. Big amount of cigarette is being produced in the world. The order of production from biggest amount to smaller ones is; China, USA, Russian, Japanese, Indonesia, Germany, Turkey, Korea, Netherlands, UK, Brazil and India (www.yapraktutun.gov.tr, 2005).

The story of tobacco and cigarette use goes back to 6000 BC and its history is given in appendix (www.tobacco.org, 2005).

Tobacco and cigarette production industry is one of the most powerful industry on the world. The process used in this industry is confidential because of economical and rivalry reasons. The companies have to keep their product contents and their production technologies secret for several reasons.

Today's tobacco products manufacturing is quite different from the ancient methods since it includes many chemical additions, to provide a better taste. Since every brand has its own secret flavor, it is almost impossible to know exact composition of these products. Non-tobacco smoking materials and denicotinization are other unknowns about tobacco manufacturing.

Today, 17 million cigarette smokers are present in Turkey and these buyers pay 17 million dollar in one day. Turkey spends about 2 billion dollar for a year with additional cost of disease originated smoking expenses. Developing countries consume 70% of produced cigarette on the world (www.rshm.saglik.gov.tr, 2005).

Table 3.1 Cigarette consumption in the world

Region	% Consumption
North America	4,7
Latin America	8,9
West Europe	9,3
Middle and East Europe	10,8
Africa and Middle East	11,8
Asia	54,5

Cigarette production amount of the world according to primary producer country as years shown on the Table 3.2 (www.yapraktutun.gov.tr, 2005)

Table 3.2 Amount of cigarette production of the major countries as years

Country	2000		2001		2002		2003	
	Ton	%	Ton	%	Ton	%	Ton	%
China	1.698.500	30,28	1.701.000	30,14	1.733.540	30,94	1.793.423	31,67
US	594.700	10,60	580.000	10,28	532.000	9,50	500.000	8,83
Russian	341.000	6,23	374.000	6,63	390.000	6,96	385.000	6,80
Japan	257.965	4,60	256.200	4,54	229.000	4,09	219.000	3,87
Indonesia	232.724	4,15	221.293	3,92	200.358	3,58	186.000	3,28
Germany	206.770	5,16	213.793	5,32	212.500	5,34	205.200	5,20
Turkey	127.800	3,19	128.350	3,20	130.830	3,29	126.000	3,19
W. Korea	98.286	2,45	97.700	2,43	93.750	2,36	122.341	3,10
Netherlands	123.071	3,07	122.753	3,06	126.292	3,17	115.561	2,93
UK	126.105	3,15	126.141	3,14	133.014	3,34	107.922	2,73
Brazil	104.900	2,62	109.435	2,72	106.685	2,68	96.705	2,45
India	97.000	1,73	86.300	1,53	90.500	1,62	92.000	1,62
Total	4.008.821	71,47	4.016.965	71,19	3.978.469	71,01	3.949.152	69,75
Others	1.600.326	28,53	1.625.866	28,81	1.624.018	28,99	1.713.119	30,25
Worlds Total	5.609.147	100,0	5.642.831	100,0	5.602.487	100,0	5.662.271	100,0

Note: 1 ton = 1 million cigarettes

As it is very well known smoking is very harmful for the human health and also non-smokers are affected by cigarette smoking of others. So the harmful effects of smoking are proven by numerous scientific researches at past and present. According to WHO, about 4 million people dies every year due to smoking related causes on the world (www.sigara.gen.tr, 2005).

Tobacco manufacturing can be considered as a two step process. First stage is production of tobacco which mainly consists of physical operations such as drying and cutting which do not contribute to wastewater production. In later stages, nicotine, synthetic flavoring agents and residues of pesticides reach to the wastewater.

The tobacco manufacturing process produces liquid, solid, and airborne wastes. Liquid wastes include tobacco slurries, solvents, oils, and greases that originate from the manufacturing processes, building services, and facilities that may need special treatment or disposal. Solid wastes include paper, wood, plastics, unusable tobacco, packaging materials and dirt that originate in the manufacturing process. These waste products are resold, recirculated, compacted, or put in landfills. Airborne wastes include non-toxic odors of manufacturing, in-plant dust, tobacco volatiles and particles, and other emissions. Abatement programmes for airborne wastes include use of filters, dust collectors and scrubbers, low-sulphur fuels, and other controls (Novotny & Zhao, 1999).

Tobacco industry wastewater contains some toxic contaminants which inhibit the microbial consortium in biological treatment plants. Sources of these toxic contaminants are nicotine, flavoring chemicals containing glycogen and alcohol, adsorbable organic halogens (AOX), and pesticides from tobacco leaves (Sponza, 2001).

The tobacco manufacturing process produces liquid, solid, and airborne waste. Among those wastes, some materials, including nicotine, are designated by the EPA as Toxics Release Inventory (TRI) chemicals. These are possible environmental health hazards. In the United States in 1992, the Toxics Release Inventory reported in the Statistical record of the environment that tobacco manufacturing generated more than 27 million kilograms of production-related chemical waste, of which 2.2 million kilograms were treated or released into the environment. Overall, the tobacco industry ranked 18th among all industries in total chemical waste production (Novotny et al., 1999).

Effluents containing non-biodegradable compounds pose a challenge to biological treatment schemes. Biological processes do not normally remove non-biodegradable chemicals and in some cases, high concentration of such chemicals may inhibit the biological processes resulting in poor performance. Non-biodegradable compounds can be recalcitrant and/or toxic to microorganisms. The presence of such compounds requires non-biological processes for effective elimination and AOPs have such a capability (Chidambara & Han, 2004).

3.2 Cigarette Production

Tobacco is a crop that can be grown in a wide range of soils and climatic conditions. Then the tobacco is prepared for processing and cigarette production. The tobacco can be stored temporarily in hoppers.

Immediately after harvesting, tobacco is cured to remove all of the natural sap from the leaves so that it can be further processed. There are three primary methods of curing cigarette tobaccos, air curing, flue curing and sun curing, but all curing focuses on regulating the rate at which moisture is removed from the tobacco.

In primary process; after the tobacco is stored and aged, it goes through a final processing phase according to blend formulas used for making various types of cigarettes. This process includes blending, conditioning, casing, cutting, drying and top flavoring. A number of other ingredients may be added to the tobacco, including processing aids, humectants (which keep the tobacco moist and pliable), preservatives and brand-specific flavors. Once this is done, the raw material is finally ready to be made into cigarettes.

After the tobacco has been treated and processed, the tobacco is made into cigarettes in a machine typically called the "Maker". The paper is wrapped around the tobacco and sealed to form continuous rods. These are then cut to proper length for cigarettes. Packer machines insert cigarettes into packs, packs into cartons and cartons into cases. The cases are then conveyed to the Finished Goods Department for temporary storage. From there they are shipped to warehouses to be sold to wholesale distributors.

3.3 Wastewater Characteristics of Tobacco Industry

Flavorings are added to the blend by spraying, soaking or dripping in the process. During flavoring process, the waste flavorings come out in the form of moisture when spraying process is applied to the blend. This form of waste flavorings is dissolved in the water so it is mixed to the water called wastewater.

Cigarette production wastewater has varying characteristics. Range of some of the parameters is given in Table 3.3. Because of fluctuating characteristic of wastewater generally equalization is required. Wastewater is treated using biological methods (sometimes with supplementary use of chemicals).

Table 3.3 Cigarette production wastewater characteristics range

Parameter	Value
COD	3000 – 8000 mg/l
BOD	500 – 2000 mg/l
pH	5,5 – 7,5
Total nitrogen	70 – 150 mg/l
Total phosphate	5 – 15 mg/l

Apart from above information; large quantities of tobacco wastewater are generated during processing and cigarette making and these wastes would be toxic due to the presence of alkaloids, nicotine and tannins. (Sponza, 2001)

3.4 Discharge Standards

In Turkey according to water pollution control Regulation (official gazette, 2004) the industries have different discharge standards. Cigarette industry has to obey the discharge standards given for plant processing and similar industries discharge standards (Table 5.10: Sector: Food industry). According to this Regulation, cigarette industry has to discharge according to the limit values given in Table 3.4.

Table 3.4 Cigarette industry wastewater discharge standard (Water Pollution Control Regulation, 2004) .

Parameters	Composite sample 2 hours	Composite sample 24 hours
Chemical oxygen demand (COD)	200 mg/l	150 mg/l
Fish bioassay (toxicity dilution factor)	4	3
pH	6-9	6-9

CHAPTER FOUR
MATERIALS AND METHODS

4.1 Tobacco Process and Cigarette Production Factory

4.1.1 Production Process of the Cigarette Factory

In this study wastewater samples are brought from a cigarette factory near the Izmir. After harvesting and cutting, tobacco leaf is transported to manufacturing factory. Different blends of cigarettes are produced in the cigarette factory. Turkish tobacco and American tobacco are mixed in different ratios so that variant blend can be produced.

Tobacco is the major ingredient of the cigarette; the other ingredients, such as additives are added to the tobacco during the processing and they aid tobacco having specific flavor, preservatives, and humectants which keep the tobacco moist and pliable.

Tobacco coming to the factory is prepared for processing and cigarette production. Turkish tobacco leaves are brought to the factory. Since dried tobacco leaf is very brittle, tobacco leaves are humidified in order to make it easier to work. Tobaccos are carried by transporters to other production steps. In the course of this transportation rotating rakes eliminate the unwanted materials. In order to separate different colored tobaccos, optic scanner is used in the factory and then simultaneously splitted colored tobaccos can be mixed with their counterparts of American tobaccos. The blend is mixed in the closed tank and humidified and applied some ingredients. The rest of the processes are applied to this mixture. The proportions in this mixture designate the type and the taste of cigarette.

The tobacco mixture is passed through the cutters where rotating blades cut the tobacco leaves. The blended tobacco is chopped into piece of appropriate size in this unit process. Final product is stored in silos before flavoring and manufacturing process.

The tobacco which has been chopped comes to a batch reactor, flavorings and ingredient additives are blended with the processed tobacco in this reactor. The patented flavoring agents are sprayed to the blend. Mixture is kept in the reactor in the course of adequate time so that blend absorbs the flavorings. The waste flavorings blend with moisture is collected aiming at reuse with the next blend process.

The blend of tobacco which is called half product cut into small parts again before directed to the second flavoring unit. Several different kinds of flavoring which are patented are sprayed again onto tobacco blend.

The cutting tobacco mixture is transferred to the cigarette making machine, tobacco blend is supplied into a paper tube to from cigarette. The material of the cigarette paper is mostly flax, paper that provides uniformity. Cigarette paper must be perfectly air permeable in order to allow cigarettes to burn properly. The special cigarette paper has two important functions; one of them is that blended and cut tobacco is held together by the special paper as a cylindrical form. Secondly when the cigarette has been smoked, cigarette paper ash takes a thick form around the hot tobacco ash. Thus cigarette paper has to contain very special characteristic.

Filters are inserted to the chopping cigarettes by a special instrument. Cellulose acetate fiber filter called tow, eliminates particular substances from tobacco smoke. Carbon is also applied in cigarette filters, in order to remove defined gasses from inhaled tobacco smoke.

4.1.2 Wastewater Source

Moisture is added to the tobacco during the whole process. Patented chemicals and flavorings are added to the blend by spraying, soaking or dripping. During this flavoring process, the waste flavorings come out in the form of moisture when spraying process is applied to the blend. This form of waste flavorings is dissolved in the water so it is mixed to the water called wastewater. Flavoring agents are sprayed in the reactor in liquid solution form. Wastewater comes from this flavoring process is conveyed to the treatment plant of factory. Wastewater which has the same characteristics also comes from other favoring unit by the same production process. Generally, the first flavoring agent includes glycogenic matter and other flavoring agent contains alcoholic component, generally ethanol.

Pesticide is used by the tobacco farmers. Particularly, Triazines, Cabamoyls, Organophosphates and Carbamates are used during the agricultural activities of tobacco production. Frequently Organophosphates are used more than the other chemicals. Therefore, tobacco leaves include pesticide and this pesticide is humidified during the different steps of the cigarette production process. Thus, existing moisture is condensed and transported to treatment plant as wastewater content.

The sources of the domestic wastewater of the factory are restaurants, toilets, showers, washing machines and dishwashers. The number of the workers in the factory is about 1000. Domestic wastewater is pumped to treatment plant to be mixed with process wastewater.

4.1.3 Wastewater Treatment Plant of the Factory

The main principles of the wastewater treatment plant are physical pretreatment, chemical, biological treatment and sludge stabilization and dewatering units. Wastewater treatment plant are inspected and controlled with using PLC (programmable logic control) system.

The wastewater which comes from process sources and domestic sources are collected in the septic collection tank and pumped to the wastewater treatment plant. The wastewater first, passes through the bar screen unit by gravity, cleaning of this unit is made with automatic mechanical instruments; the space of between the bars is 2 cm, so this unit eliminate large solid particle. Then wastewater is collected in equalization tank (volume of tank is 350 m^3), which is continuously mixed to prevent the sedimentation. Next step is chemical treatment which includes coagulation and flocculation unit, ferric chloride and lime are added to rapidly mixed coagulation tank, anionic polymer is directly added into flocculation unit. The purpose of the lime addition is pH adjustment of the wastewater. Wastewater reaches to the two settling tanks. These tanks are one of the sludge sources. The sludge settles down in the wastewater and is pumped out of the tanks for further sludge process (Figure 4.1).

The partially treated wastewater then flows to the biological unit. Biological unit principle is sequencing batch reactor process, aeration and sedimentation which are both in same tank. The numbers of aeration tanks are two and each biologic pond works for about eight hours, surface aerators are used for producing dissolved oxygen. The shape of the ponds is square (10 x 10 m), urea and diamonium phosphate (DAP) solutions are added into the entrance of the tanks because of the lack of nitrogen and phosphate. The depth of the pond rises from beginning to end of the pond. At the beginning tank depth is 2 m, on the other end; the tank depth is 4 m. Second sludge source is this biologic unit. Treated wastewater flows to the chlorination basin and effluent wastewater is used for irrigation of recreation areas. The plant has one emergency storage tank; all the units are connected to this 200 m^3 storage tank for emergency situation.

Sludge stabilization and dewatering unit of treatment plant has two sludge sources: chemical settling tank and biological unit. Sludge which comes from these two units is mixed and collected into the sludge thickener, and followed by sludge stabilization and filter press. Gravity sludge thickener is cylindrical and with circle shape. Cationic polymer is added into the sludge stabilization tank. Stabilized sludge

reach the filter press, this unit designed 2,5% dry solid ratio influent and 25-30% dry solid ratio on the effluent sludge. Dewatered sludge collected into barrels and send to incinerator plant which is placed in Izmit, Turkey. Since the sludge carries the characteristic of hazardous wastes according to the Hazardous Waste Control Regulation (1995).

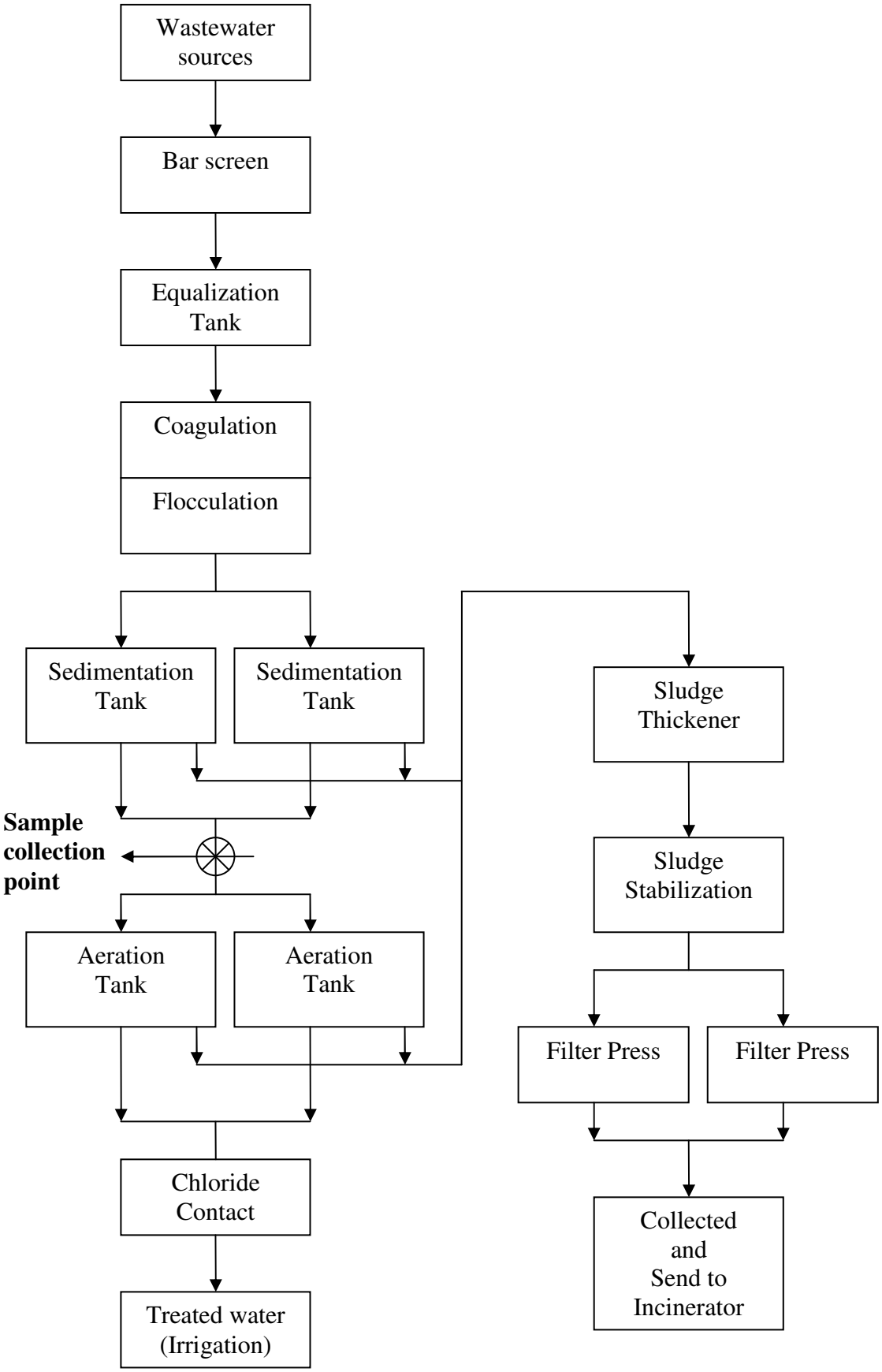

Figure 4.1 Flow scheme of the treatment plant from where wastewater samples taken.

4.2 Experimental Setup UV Photoreactor

Photoreactor is used for all photochemical experiments, during the reactions reactor temperature is constant and aqueous solution in the reactor is continuously stirred. Photoreactor is made of Pyrex-glass and has cylindrical shape, it has no metal parts, total volume of the photoreactor is 2,2 L (Figure 4.2). Ultraviolet radiation is provided by an UV lamp which is installed center axis of the reactor. The UV lamp is 16 watt low pressure monochromatic mercury lamp, and can emit short wave ultraviolet radiation at 254 nm and encased in a quartz tube due to the transmission of light. Since a constant temperature is required, the UV lamp is surrounded with a water-cooling jacket, due to the heating. Water-cooling jacket material is also glass.

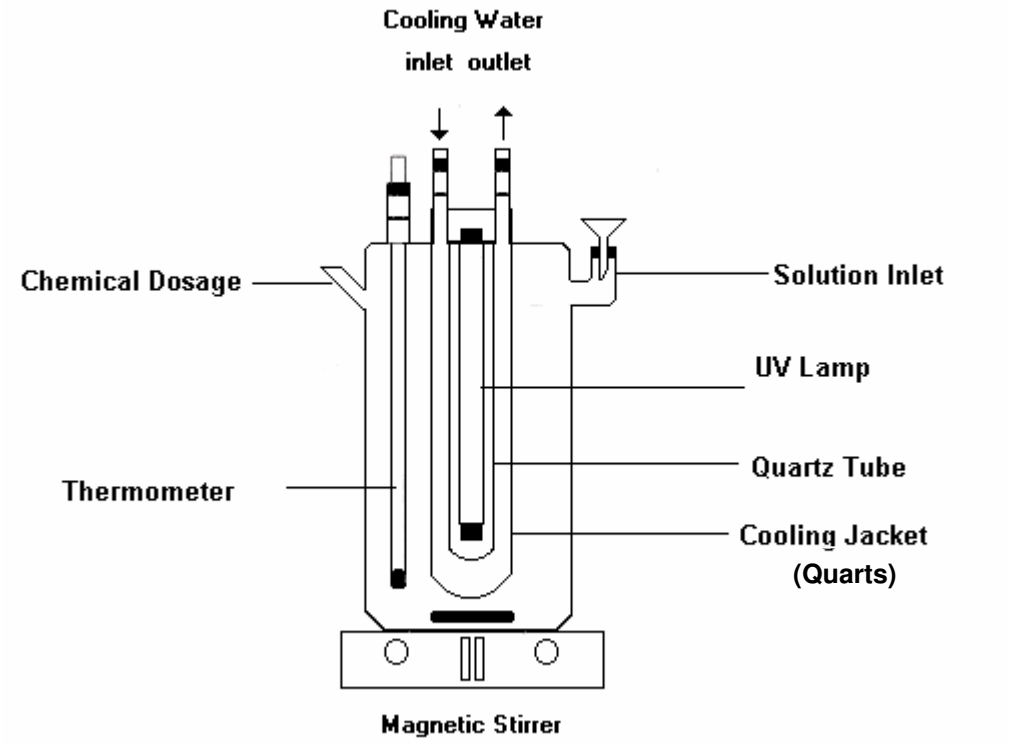

Figure 4.2 The schematic diagram of photochemical reactor used in the experimental study.

At the top of the reactor, ports are located; solutions, chemical reactants and also samples can be fed by these ports. Two of the ports are used for cooling water inlet and outlet. Third port is used for measuring the temperature and the last one is used for withdrawing sample. Temperature value is observed from an Omega digital

thermometer. Magnetic stirrer placed at the bottom of the reactor to mix the aqueous solution. The entire reactor surface is covered with aluminum sheet.

4.3 Sample Collection and Storage

Samples were taken from the chemical treatment exit called biological aeration tank entrance, located at the wastewater treatment plant of the cigarette factory. Collected wastewater was kept in the refrigerator at 4°C and let the warm up to the room temperature (25 °C) before the experimental study is performed.

4.4 Analytical Methods

TOC, COD, color, pH and electric conductivity measurements were made during the experiments. TOC and COD analyses of all samples were done according to Standard Methods (1992). Omega digital thermometer was used for temperature monitoring.

4.4.1 Solutions and Preparation of Stock Solutions

In experimental studies, hydrogen peroxide (35% w/w solution M = 34,01 g/mol) used supplied from Merck. Fe^{2+} solutions were prepared using iron II sulphate heptahydrate ($FeSO_4.7H_2O$ 99,5%) from Merck, as oxidants. Fe^{2+} solution is surrounded with the aluminum sheet and stored in a dark place. In the course of the experimental studies sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) from Merck were used for maintaining the pH value. Before using, all glass equipments were rinsed with tap water and then with distilled water.

4.4.2 Total Organic Carbon (TOC) Analysis

DOHRMAN DC-190 High Temperature TOC Analyzer was used to analyze the total organic carbon concentration of collected samples.

4.4.3 Chemical Oxygen Demand (COD) Analysis

COD values were analyzed with Dichromat Reflux Method described in Standard Methods. According to analysis requirements, wastewater samples were diluted (1/100) before measurements. Firstly 5 ml H_2SO_4 was poured into the COD bottle to diluted sample, then 0,5 g mercury sulphate was added to the solution after 10 ml potassium dichromate and 25 ml sulfuric acid were added. COD bottles were heated for two hours and than cooled to the room temperature (25 °C). Afterwards 80 ml distilled water was added into vessel and 2 or 3 drops of ferroin indicator was added, to change color from yellow to green. The solution was titrated with ferrous ammonium sulphate (FAS). Color of the aqueous solution has changed from green to blue and later sharp color change has occurred from blue to reddish brown in the course of the titration with FAS. The COD concentration was calculated by using the equation given below;

$$COD(mg/L) = \frac{(X-Y)x8000xdilutionfactor}{(ml)sample}$$

X: ml FAS used for blank, Y: ml FAS used for sample

4.4.4 Color Measurements

The measurements of color in raw wastewater and effluent wastewater from the photoreactor were measured with Pharmacia LKB-Novaspec II spectrometer.

4.4.5 pH Measurements

Jenway 3010 pH meter is used for all of the solutions and samples.

4.4.6 Electrical Conductivity Measurements

Electrical conductivity of samples was measured with to AGB-1001 μP Conductivity and Temperature Meter.

4.5 Advanced Oxidation Processes Experiments Summary

After the collection of wastewater samples from the chemical treatment unit exit of the cigarette factory wastewater treatment plant, the experimental studies have been performed by following the order given in Table 4.1.

Table 4.1 Summary of experimental study

Step	Study	Work
1	Determination of wastewater characteristics	COD analyze
		BOD analyze
		Total N analyze
		Total P analyze
2	UV / H_2O_2 oxidation experiment	pH value optimization
		H_2O_2 dosage optimization
3	Photo Fenton oxidation experiment	pH value optimization
		Fe^{+2} dosage optimization
		H_2O_2 dosage optimization

CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 Introduction

Tobacco industry and cigarette production has a great deal of additives, patented chemicals and toxic substances used during the cigarette production as compositions which are protected by the cigarette companies' secret. Therefore finding data about tobacco and cigarette production and their wastewater was difficult. Cigarette production includes numerous patented chemicals and additives with a total number reaching to 599, (shown in appendix), these chemicals specifications and their contents are not known. So that total organic carbon parameters were used as general pollution parameter, for the experiments.

The aim of this study was the treatment of the tobacco industry wastewaters with advanced oxidation processes. As advanced oxidation processes, ultraviolet light and hydrogen peroxide ($UV+H_2O_2$) and Photo-Fenton ($UV+H_2O_2+Fe^{+2}$) process are used in this study. All the samples were taken from chemical unit effluent wastewater in the cigarette production factory treatment plant. Studies were done in order to find out optimum reaction time, optimum pH value, optimum oxidant and catalyst dose for each process. So the intention of this study was to find an optimum treatment of the cigarette production factory wastewater regarding the economical parameters and reaction conditions.

5.2 Wastewater Characterization

The raw wastewater coming to the treatment plant includes cigarette factory production wastewater and domestic wastewater. COD concentration and pH value of the wastewater arrived to treatment plant at variable intervals. Therefore, loadings of wastewater entering to the chemical and biological unit were varying in time. This fluctuation was reduced by the equalization tank so that stationary loading was

allowed to the chemical and biological unit. Average flowrate of the wastewater was 240 m^3/day

Wastewater from the factory firstly collected in the equalization tank. At the exit of the equalization tank, COD concentration can be 1000 - 4000 mg/L, pH value was between 5,5 to 7,5 and BOD_5 concentration was 1000 - 1500 mg/L. In addition these total nitrogen concentration was 30 – 70 mg/L.

After the chemical treatment unit; effluent wastewater COD concentration was about 1500 mg/L, pH value range was not changed and total nitrogen concentration was between 15 to 35 mg/L and total phosphate concentration was in between 1 to 2,5 mg/L. Urea and DAP solution were added into the entrance of the aeration tanks because of the lack of nitrogen and phosphate.

According the analyzing of the samples collected from the chemical unit exit of the treatment plant, various contaminant parameters is shown on the Table 5.1

Table 5.1 Sample characteristics of collected wastewater from chemical unit exit.

Parameter	**Raw Wastewater (in equalization tank)**	**Chemical Unit Exit**
COD	3910 mg/l	1484 mg/l
BOD_5	2900 mg/l	750 mg/l
Total N	74,2 mg/l	15,63 mg/l
Total P	-	2,27 mg/l
pH	6,01	6,4

5.3 Experimental Procedure for Advanced Oxidation Process

The photoreactor was loaded with 2 L of cigarette wastewater taken from chemical treatment unit outlet of the treatment plant of the factory. When required, wastewater pH adjustment was made prior to loading the reactor by adding sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH). The temperature of the aqueous solution

was held constant at 25 °C during the studies. After loading the photo reactor, determined dose of hydrogen peroxide and/or ferrous salt were added to the solution. At the same time the UV light was switched on and during all the reactions photoreactor was continuously mixed. Samples were collected periodically from the photoreactor in order to perform TOC analyses and color measurements. The results of TOC and color analyses were used to improve efficiency.

The reaction time of the ultraviolet and hydrogen peroxide (UV and H_2O_2) oxidation experiment is determined as 120 minute. According to TOC and color removal results the optimum pH value was chosen between 3 to 11. Decided pH value was set constant and hydrogen peroxide (H_2O_2) dose changed between 5 mM (170 mg/L H_2O_2) and 100 mM (3400 mg/L H_2O_2) in a series of experiments. The samples taken from the photoreactor were analyzed for TOC and color.

Photo Fenton (UV, H_2O_2 and Fe^{+2}) oxidation experiment reaction time is determined as 90 minute. To optimize pH value, 3, 4 and 5 were applied. First, optimum pH value and hydrogen peroxide concentration were set constant and ferrous salt (Fe^{+2}) dose concentration was varied between 0,5 mM (28 mg/L Fe^{+2}) and 7,5 mM (420 mg/L Fe^{+2}). According to TOC and color removal rate, Fe^{+2} concentration was chosen and set as constant for determining hydrogen peroxide concentration for Photo Fenton experiments. Hydrogen peroxide (H_2O_2) dose changed between 5 mM (170 mg/L H_2O_2) to 100 mM (3400 mg/L H_2O_2) and pH value was kept constant. The results of TOC and color removal were used for improving the treatment efficiency.

Zero point sample which is the first sample collected from the photoreactor was taken after pH adjustment and hydrogen peroxide and/or ferrous salt were added to the aqueous solution in the photoreactor. Thus, chemical characteristics of raw wastewater from treatment plant differ from first sample.

5.4 Advanced Oxidation Experiments Using UV and H_2O_2

In order to evaluate the effectiveness of UV and H_2O_2 oxidation process on the treatment of cigarette wastewater, firstly, optimum pH value determination and then H_2O_2 concentration optimization were done.

5.4.1 pH Optimization Study

pH optimization experiment was done at cigarette production plant wastewater received from chemical treatment unit exit point. H_2O_2 concentration set 50 mM (1700 mg/L H_2O_2) for this pH optimization study. Predetermined pH values were 3, 7 and 11. At the end of the 120 minute reaction time, by applying UV/H_2O_2, the best TOC removal was seen at pH = 3. At pH = 3 (25 °C); TOC concentrations were 507,0 mg/L and 381,3 mg/L before and after UV/H_2O_2 oxidation respectively, resulting 25% removal efficiency. For pH = 7 TOC removal efficiency was 16% and for pH = 11 efficiency of TOC removal was 8%. C/Co ratio graphics of this study is shown in the Figure 5.1. Co is the initial concentration; C is effluent concentration of samples which collected different time of during the reaction time of 120 min.

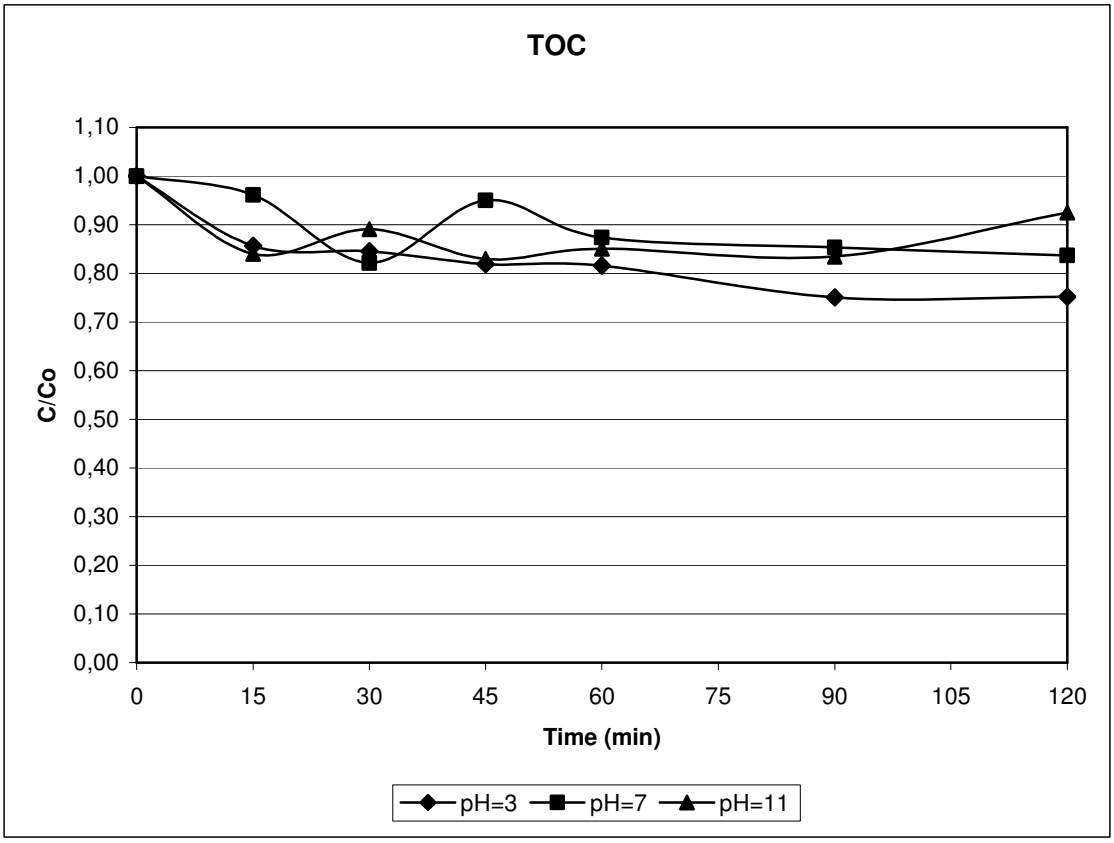

Figure 5.1 C/Co ratios for TOC in pH optimization of UV/H_2O_2 oxidation.

Color removal efficiency results were 60% at pH=11, 30% at pH=7 and 10% for pH=3 observed (25 °C). Turkish wastewater discharge standards do not include color parameter. Therefore in the study TOC parameter is considered to be more important than color parameter. On the other hand, when public impression is considered as to the polluting industries, they observe color values and sometimes consider colorful wastewater as more polluted.

Considering the pH optimization study experimental results pH value = 3 was chosen and this pH was adjusted for following UV and H_2O_2 oxidation experiments.

5.4.2 Optimization of Hydrogen Peroxide (H_2O_2) Dosage

Second part of this study was hydrogen peroxide concentration optimization at constant pH value. Running hydrogen peroxide concentration dosages were 5 mM (170 mg/L H_2O_2), 10 mM (340 mg/L H_2O_2), 25 mM (850 mg/L H_2O_2), 50 mM (1700

mg/L H_2O_2), 75 mM (2550 mg/L H_2O_2) and 100 mM (3400 mg/L H_2O_2). All dosages were applied in 2 L aqueous solution that pH value was adjusted to 3. Reaction time was determined as 120 minutes.

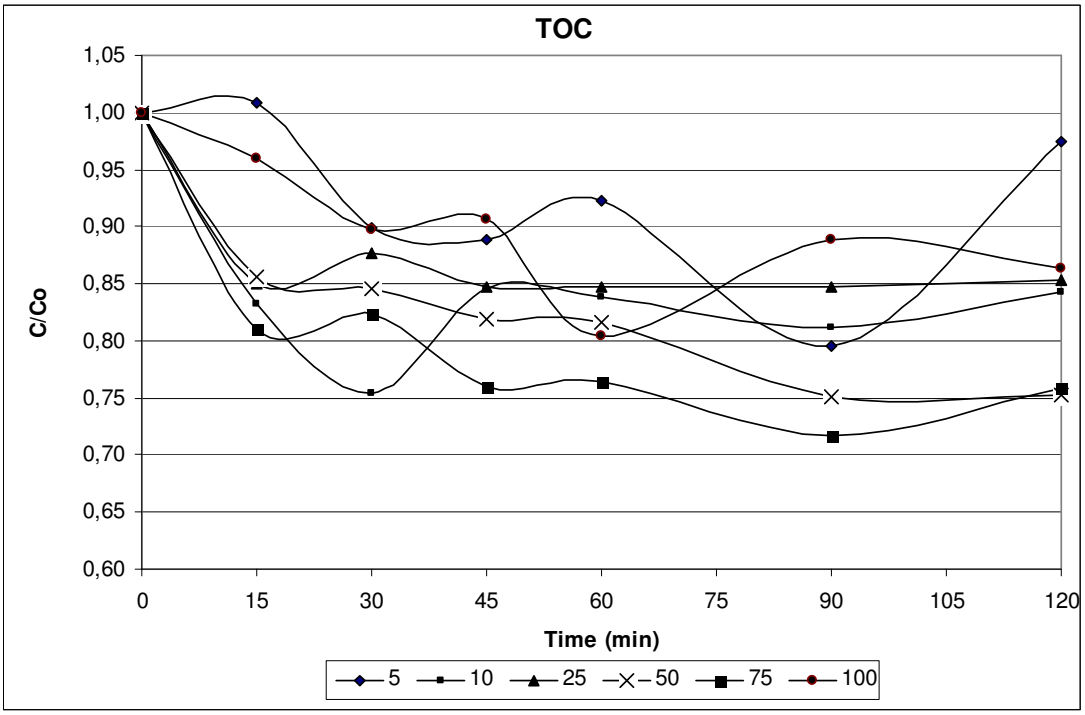

Figure 5.2 C/Co ratios for TOC in H_2O_2 optimization of UV/H_2O_2 oxidation

At the end of the reaction time, 75 mM H_2O_2 (2550 mg/L) concentration showed highest TOC removal efficiency (24%). Initial TOC concentration was 521,80 mg/L and effluent concentration was 395,4 mg/L. C/Co ratio graphics of this experimental series is given in Figure 5.2, Co is initial concentration.

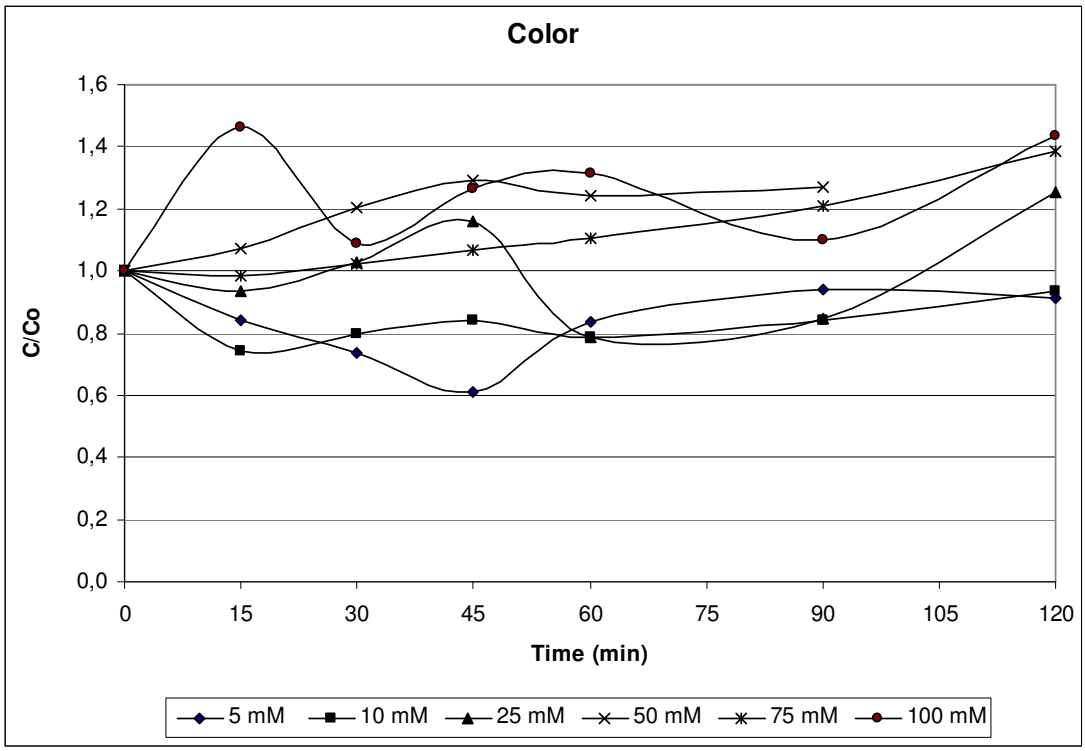

Figure 5.3 C/Co ratios for color in H_2O_2 optimization of UV/H_2O_2 oxidation

Experimental results of H_2O_2 dosage on color removal is given in Figure 5.3. As can be seen from Figure 5.3, effect of the hydrogen peroxide on the color removal efficiency is not significant; in fact, color removal rate was affected in a negative way. Therefore, decreasing hydrogen peroxide concentration increases the color removal of the aqueous solution. Maximum efficiency of the color removal was achieved with 5 mM (170 mg/L H_2O_2) concentration, the ratio of efficiency was 8,5% at pH = 3. Only 5 mM and 10 mM H_2O_2 dose concentration caused the color removal, while other doses strengthen the color. This may be due to the formation of new chemicals during the oxidation.

The first sample from the photoreactor was taken after the pH adjustment and hydrogen peroxide and/or ferrous salt addition to wastewater in the photoreactor. Thus, chemical characteristics of collected wastewater sample from treatment plant differ from first sample taken from the photoreactor. According to raw wastewater absorbance (abs) value which was measured by spectrometer, treatment efficiency values are given in Table 5.2.

Table 5.2 Color removal efficiency H_2O_2 dose optimization study in UV/H_2O_2 oxidation

Dose of H_2O_2 mM	pH	Raw wastewater abs value	After 120 minute wastewater abs value	Treatment efficiency %
5	3	0,478	0,388	19
10	3	0,478	0,215	55
25	3	0,478	0,326	32
50	3	0,478	0,410	14
75	3	0,478	0,401	16
100	3	0,478	0,367	23

Color removal results were shown Table 5.2 differs from color removal results given Figure 5.3. 10 mM (340 mg/L) H_2O_2 dose has showed maximum color removal (55%). In addition, 75 mM (2550 mg/L) H_2O_2 dose which gave maximum TOC efficiency gave color removal efficiency of 16 %.

As a result of this UV and hydrogen peroxide oxidation experiment, 75 mM (2550 mg/L) H_2O_2 concentration at pH=3 was chosen as optimum dose for 120 minute reaction time (25 °C).

5.5 Advanced Oxidation Experiments with Photo Fenton (UV, H_2O_2 and Fe^{+2})

Apart from UV and hydrogen peroxide oxidation process, Photo-Fenton oxidation process was applied to cigarette wastewater samples. In this part of case study the effect of UV light, H_2O_2 dose and ferrous salt on the tobacco wastewater was examined. Firstly, H_2O_2 and Fe^{+2} doses were set as constant and pH value was optimized. At optimum pH value, H_2O_2 dose was adjusted, later optimum Fe^{+2} dose was determined. According to optimum pH and optimum Fe^{+2} doses, H_2O_2 dose was optimized.

5.5.1 pH Optimization

During the pH optimization study, H_2O_2 and Fe^{+2} doses were set constant. H_2O_2 concentration and Fe^{+2} concentration were chosen as 50 mM H_2O_2 (1700 mg/L) and 5 mM Fe^{+2} (280 mg/L) respectively. Because Photo-Fenton processes run in acidic condition, pH values were chosen as 3, 4 and 5. Maximum TOC removal occur with pH = 4 (25 °C). At this pH value, initial TOC concentration was 401,30 mg/L and at the end of the 90 min reaction time TOC concentration was reduced to 200,20 mg/L so that TOC removal performance ratio was 50%. TOC concentration changes according to time were shown in the Figure 5.4.

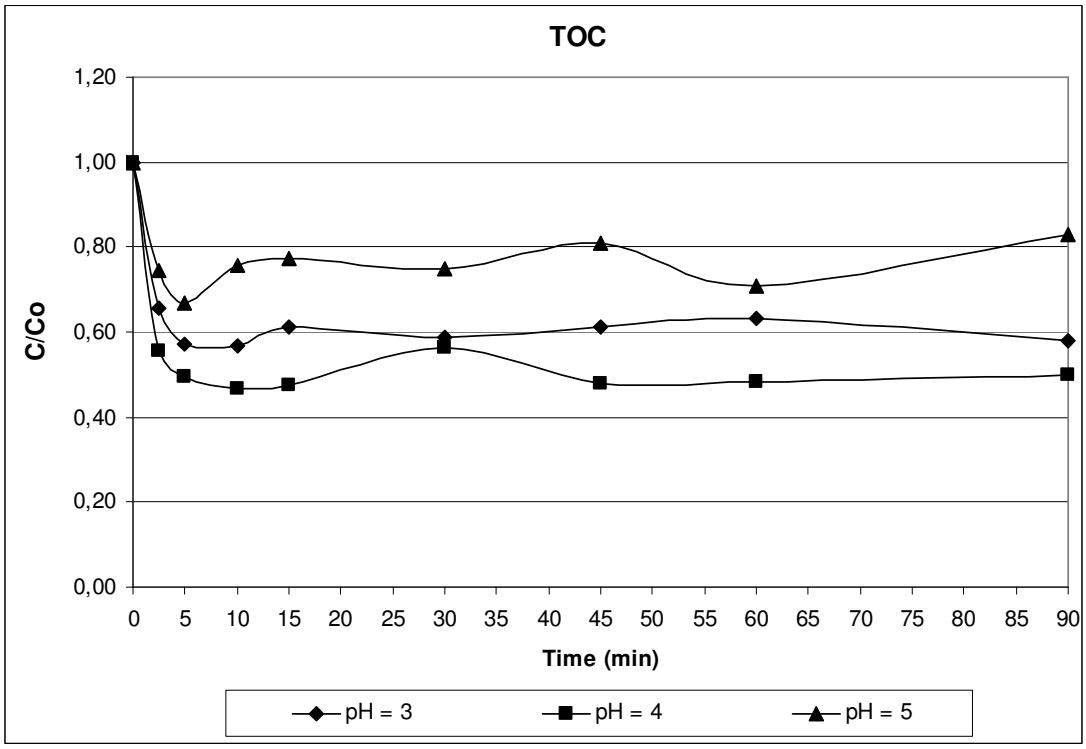

Figure 5.4 C/Co ratios for TOC in pH optimization of Photo-Fenton oxidation

According to these results, constant pH is chosen as 4 and this pH value was used for following UV, H_2O_2 and Fe^{+2} oxidation experiments. Reactor was run for 240 minute in the first experiment, and calculated TOC removal efficiency change was not significant after 90 minutes; this is why in the following experiments reaction time was set to 90 minutes. Maximum TOC removal was achieved in first 10 minute as shown in Figure 5.4.

When photo Fenton process is applied at pH = 3, 4 and 5 values, color parameter shows on increase at the first 15 minutes of the reactions (Figure 5.5). On the other hand, as time passes, color was decreased. At the end of 45 minutes reactions, there was no significant color removal. Changing the dose of H_2O_2 and Fe^{+2} in the other experiments affected color removal efficiency on the positive way. H_2O_2 and Fe^{+2} doses were chosen 50 mM H_2O_2 (1700 mg/L) and 5 mM Fe^{+2} (280 mg/L) in this pH optimization study.

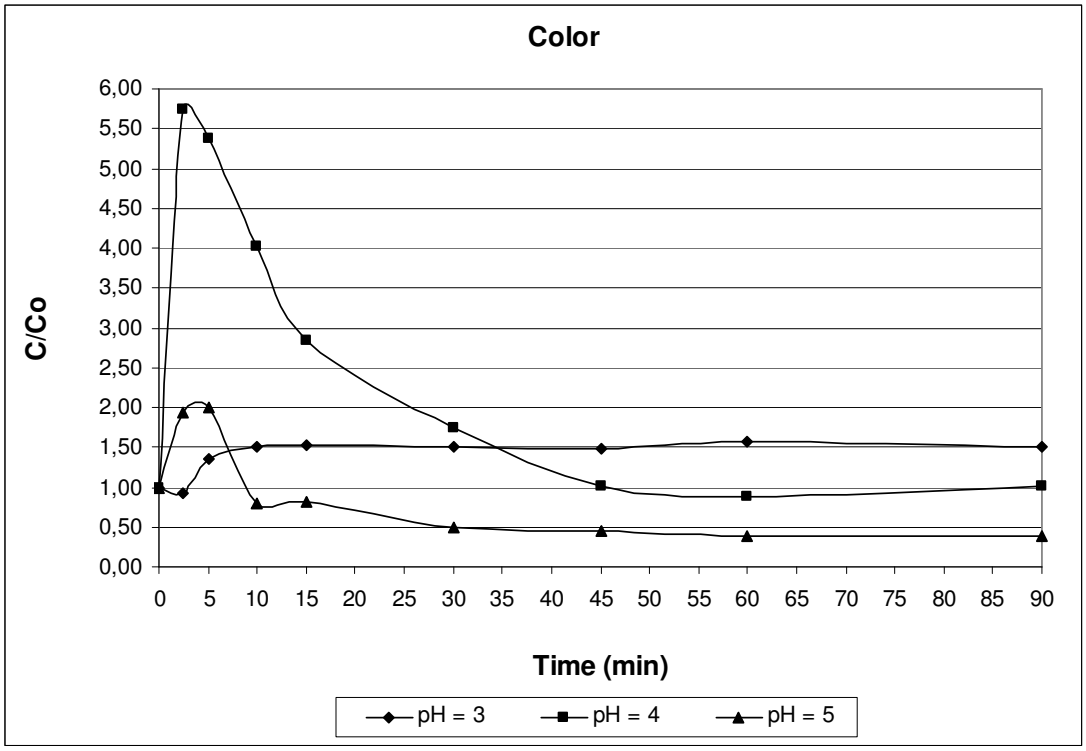

Figure 5.5 C/Co ratios for color in pH optimization of Photo-Fenton oxidation

As a result, pH value was chosen as 4 (25 °C) and this pH value used for the following UV, H_2O_2 and Fe^{+2} oxidation process experiments.

5.5.2 Optimization of Fe^{+2} Dosage

Second step of Photo-Fenton study was the determination of optimum Fe^{+2} concentrations. In this series of experiments pH value and H_2O_2 concentration were fixed as 4 and 50 mM H_2O_2 (1700 mg/L) respectively. Applied Fe^{+2} concentrations were 0,5 mM (28 mg/L Fe^{+2}), 1 mM (56 mg/L Fe^{+2}), 2,5 mM (140 mg/L Fe^{+2}), 5 mM (280 mg/L Fe^{+2}) and 7,5 mM (420 mg/L Fe^{+2}). All dosages were applied into 2 L aqueous solution at pH 4. Each reaction was 90 minutes (25 °C) and samples were collected at different times.

As can be seen in Figure 5.6; at the end of the 90 minutes reaction time, maximum TOC removal efficiency of 50% was achieved in 5 mM (280 mg/L) Fe^{+2} concentration at pH = 4 and 50 mM H_2O_2 at 25 °C.

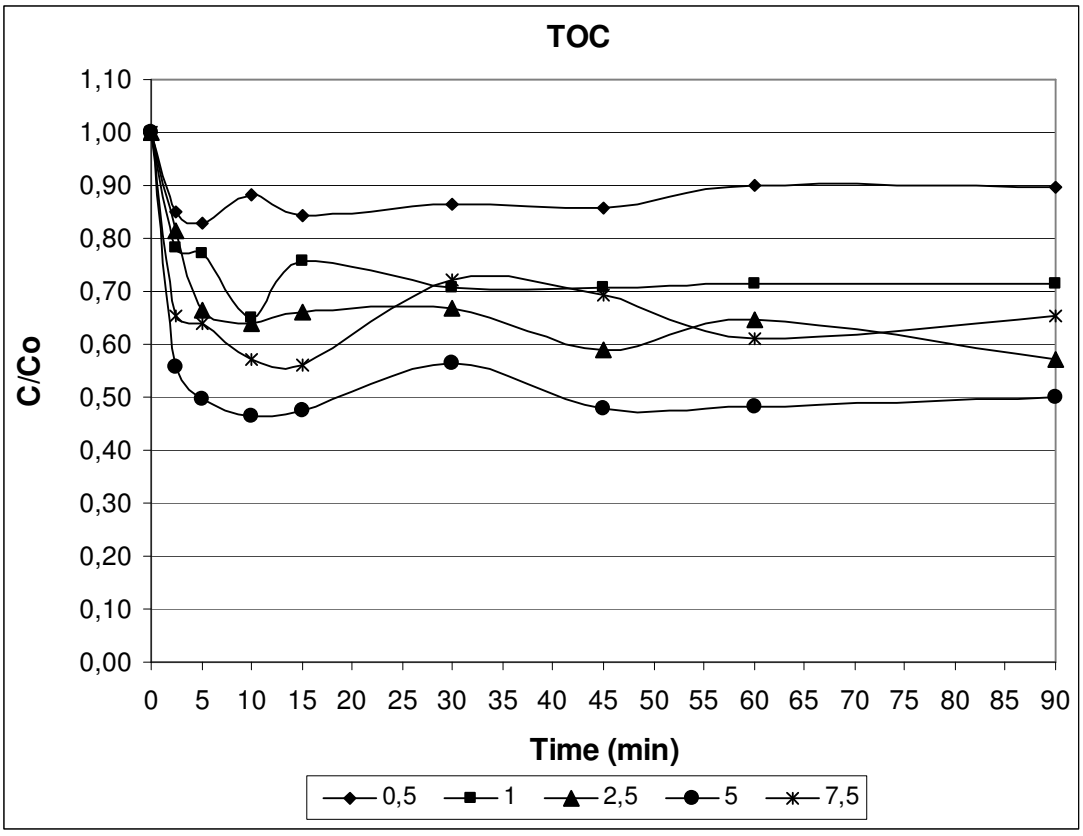

Figure 5.6 C/Co ratios for TOC in Fe^{+2} optimization of Photo-Fenton oxidation

The experimental results of color removal study are descripting in Figure 5.7. In terms of color removal efficiency, maximum color removal (75%) was obtained at 0,5 (28 mg/L) mM Fe^{+2} concentration. Same dose of Fe^{+2} was not significant for TOC removal, and only 10% TOC removal was observed with 0,5 mM Fe^{+2} concentration. Thus, optimum TOC removal and optimum color removal conditions do not match.

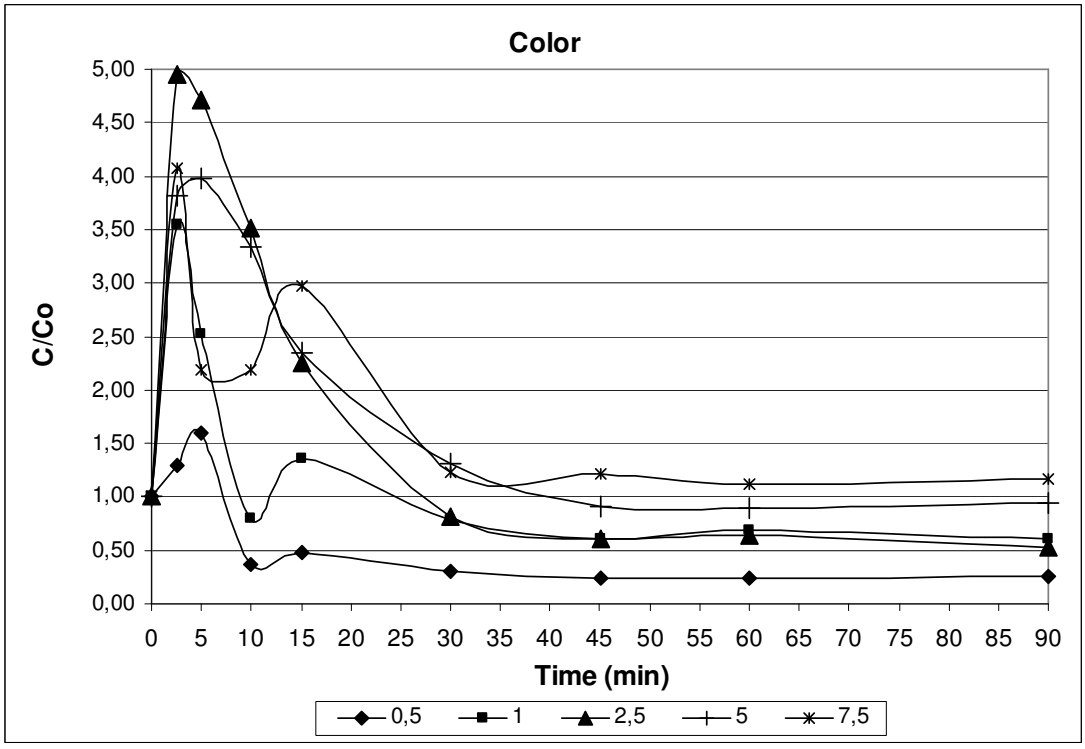

Figure 5.7 C/Co ratios for color in Fe^{+2} optimization of Photo-Fenton oxidation

When TOC and color removal efficiency results were compared, it was clear that 2,5 mM Fe^{+2} concentration was optimum for Photo-Fenton process at pH = 4 and 50 mM H_2O_2, since it supplied considerable TOC and color removal rate at the same time. 43% of TOC removal and 48% of color removal was obtained by 50 mM H_2O_2.

5.5.3 Optimization of H_2O_2 Dosage Study

Last part of the study was to find out the optimum hydrogen peroxide concentration after setting the pH value to 4 and Fe^{+2} concentration to 2,5 mM. Applied hydrogen peroxide concentration dosages were 5 mM (170 mg/L H_2O_2), 10

mM (340 mg/L H_2O_2), 25 mM (850 mg/L H_2O_2), 50 mM (1700 mg/L H_2O_2), 75 mM (2550 mg/L H_2O_2) and 100 mM (3400 mg/L H_2O_2). All dosages were applied into 2 L aqueous solution at pH value of 4 and 2,5 mM (140 mg/L) Fe^{+2} concentration. Each reaction was carried 90 minutes (25 °C) and samples were collected at predetermined intervals during the reaction for advanced oxidation process.

Maximum TOC removal ratio was observed at 100 mM H_2O_2 (3400 mg/L H_2O_2), when Fe^{+2} concentration was 2,5 mM and pH value 4. Initial TOC concentration was 158,00 mg/L and at the end of the 90 min TOC concentration was reduced to 60,12 mg/L. Therefore TOC removal performance ratio was 62%. All TOC concentrations variations according to time were given in Figure 5.8.

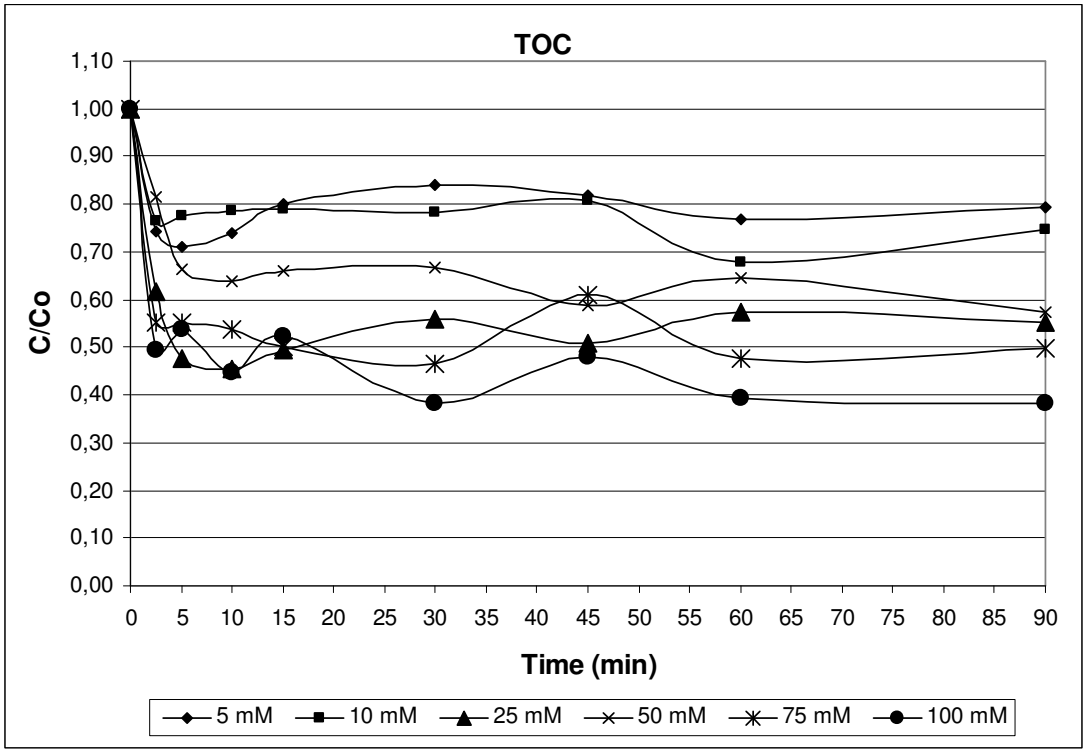

Figure 5.8 C/Co ratios for TOC in H_2O_2 optimization of Photo-Fenton oxidation

Color treatment of wastewater at different H_2O_2 concentrations is presented in Figure 5.9. When the experimental results were examined in terms of color removal efficiency, maximum color removal (75%) was realized at the 5 mM (170 mg/L) H_2O_2 (25 °C). The same dose of H_2O_2 was not significant for TOC removal. Only

21% TOC removal was observed with 5 mM (170 mg/L) H_2O_2 concentration, where color removal was maximal as can be seen in Figure 5.8.

Data on H_2O_2 dose optimization for the color removal by Photo-Fenton experiments is given in Table 5.3.

Table 5.3 After 90 min color removal efficiency for H_2O_2 optimization in Photo-Fenton oxidation

H_2O_2 Dose mM	5	10	25	50	75	100
Efficiency %	75	63	43	48	56	63

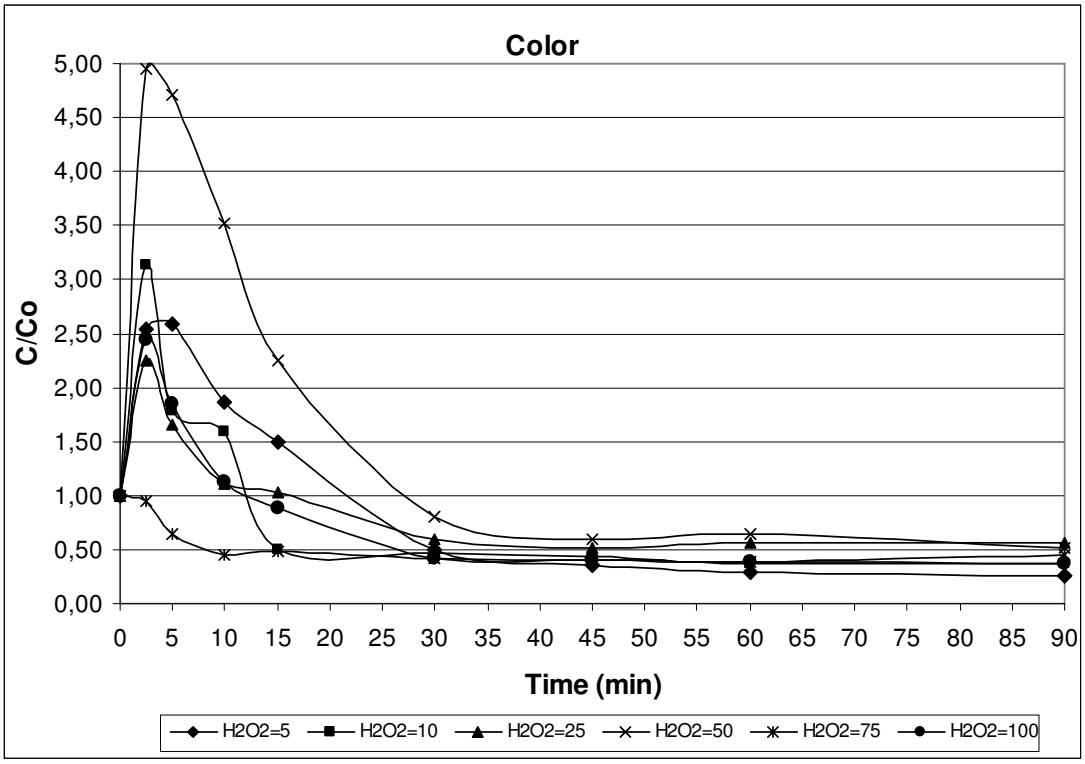

Figure 5.9 C/Co ratios for color in H_2O_2 optimization of Photo-Fenton oxidation

If TOC and color removal efficiency results are compared, it can be seen that 100 mM H_2O_2 concentration (where Fe^{+2} concentration is 2,5 mM and pH value 4) was optimum for Photo-Fenton process. Since it has given considerable TOC and color removal rate at the same time, 62% of TOC removal and 63% of color removal were optimal at 100 mM (3400 mg/L) H_2O_2 at 25 °C.

CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The results of advanced oxidation experiments which include UV and hydrogen peroxide (UV+H_2O_2) application and photo Fenton process (UV+H_2O_2+Fe^{+2}) can be summarized as follows;

- Advanced oxidation using Photo-Fenton process was found to be more efficient than the UV light and hydrogen peroxide process according to TOC and color removal efficiency.

- 2,5 mM (140 mg/L) Fe^{+2} and 100 mM (3400 mg/L) H_2O_2 concentration was optimal dosages at 25 °C for the advanced oxidation using with photo Fenton process for TOC and color removal at the same time.

- At the optimum conditions TOC removal was found as 62% and color removal was found 63% with photo Fenton process.

- Although considerable TOC and color removal was observed in first 10 minute, there was no significant removal after 90 minute reaction time in the application of photo Fenton process.

- Optimum pH value for photo Fenton process was determined as pH = 4 at 25 °C.

- In terms of color removal, most economical chemical dosages were 2,5 mM (140 mg/L) Fe^{+2} and 5 mM (170 mg/L) H_2O_2 for photo Fenton process and efficiency of color removal was 75% at 25 °C.

- In terms of TOC removal in photo Fenton process, 2,5 mM (140 mg/L) Fe^{+2} concentration and 100 mM (3400 mg/L) H_2O_2 concentration was optimum chemical dosages and TOC removal rate was 62% under these conditions.

- Optimal oxidant concentration for UV and hydrogen peroxide process was 75 mM (2550 mg/L) H_2O_2 concentration and it gave maximum TOC removal efficiency.

- Optimum reaction time was 120 minute in H_2O_2 process. After 120 minutes, no significant TOC and color removal was observed.

- 10 mM (340 mg/L) H_2O_2 was the dosage which gave maximum color removal (55%) for hydrogen peroxide process at 25 °C.

- 75 mM (2550 mg/L) H_2O_2 concentration which gives maximum TOC removal for UV and hydrogen peroxide process, gave only 16% color removal.

- Optimum pH value for UV and hydrogen peroxide was pH = 3 at 25 °C.

- The efficiency of photofenton processes application is high enough to meet discharge standards valid in Turkey (Table 3.4).

- The efficiency of UV/H_2O_2 application was insufficient to meet discharge standards, but application of this process may give acceptable results after biological treatment.

In conclusion, cigarette production factory wastewater can be oxidized and mineralized with advanced oxidation process very effectively. Degradation time, in other words effective reaction time of the photo Fenton process was shorter than the UV hydrogen peroxide process. Significant TOC removal was observed to a large extent with photo Fenton process and UV hydrogen peroxide process.

6.2 Recommendations

Advanced oxidation process can be used in combination with other treatment technologies in tobacco and cigarette production wastewater. They can also be used as pre-treatment for degradation of toxic or non-biodegradable compounds in tobacco and cigarette production wastewater.

Before real scale advanced oxidation process application has been started in wastewater treatment plant; suitable advanced oxidation method, optimal oxidant dosage, optimal reaction time and optimal reaction conditions such as pH value, UV lamp power have to be determined for any kind wastewater.

This study shows the applicability of AOPs in cigarette industry wastewater. However additional experiments are needed before application oxidation.

Oxidation and mineralization of wastewater could be raised up with increasing UV lamp power up to 1000 - 2000 watt. Wastewater which has high non-degradable organic or toxic compound might be conveniently degraded to CO_2, H_2O and inorganic salts with shorter reaction time and lower oxidant dosages.

UV/hydrogen peroxide and photo Fenton process may be combined with other advanced treatment technologies like ozone, sonolys etc. in order to improve degradation of contaminants.

Addition of other catalyzes like TiO_2 may improve removal efficiency of contaminants in the wastewater.

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APPENDICES

1. History Line of Tobacco

Although small amounts of nicotine may be found in some Old World plants, including belladonna and *Nicotiana africana*, and nicotine metabolites have been found in human remains and pipes in the Near East and Africa, there is no indication of habitual tobacco use in the Ancient world.

6000 BC : Experts believe the tobacco plant, as we know it today, begins growing in the Americas.

1 BC : Experts believe American inhabitants have begun finding ways to use tobacco, including smoking (in a number of variations), chewing and in probably hallucinogenic enemas.

1 AD: Tobacco was "nearly everywhere" in the Americas.

600-1000 AD: UAXACTUN, GUATEMALA. First pictorial record of smoking: A pottery vessel found here dates from before the 11th century. On it a Maya is depicted smoking a roll of tobacco leaves tied with a string. The Mayan term for smoking was *sik'ar*.

From Columbus' Journal

1492-10-12: Columbus Discovers Tobacco; "Certain Dried Leaves" are received as gifts, and thrown away.

On this bright morning Columbus and his men set foot on the New World for the first time, landing on the beach of San Salvador Island or Samana Cay in the Bahamas, or Gran Turk Island. The indigenous Arawaks, possibly thinking the strange visitors divine, offer gifts.

Columbus wrote in his journal, “The natives brought fruit, wooden spears, and certain dried leaves which gave off a distinct fragrance.” As each item seemed much-prized by the natives; Columbus accepted the gifts and ordered them brought back to the ship. The fruit was eaten; the pungent "dried leaves" were thrown away.

1492-10-15: Columbus Mentions Tobacco. "We found a man in a canoe going from Santa Maria to Fernandia. He had with him some dried leaves which are in high value among them, for a quantity of it was brought to me at San Salvador"

First European Smokers

1492-11: Rodrigo de Jerez and Luis de Torres discover smoking; Jerez becomes first european smoker.

They reported that the natives wrapped dried tobacco leaves in palm.After lighting one end; they commenced "drinking" the smoke through the other. Jerez became a confirmed smoker, and is thought to be the first outside of the Americas. He brought the habit back to his hometown, but the smoke billowing from his mouth and nose so frightened his neighbors he was imprisoned by the holy inquisitors for 7 years. By the time he was released, smoking was a Spanish craze.

1497: Robert Pane, who accompanied Christopher Columbus on his second voyage in 1493, writes the first report of native tobacco use to appear in Europe.

Sailors Spread the Seeds

In mid 16th century tobacco was introduced in many countries throughout the world. Many researches on tobacco’s medical use were carried out; many books were written on it. Storyline continues;

1530: MEXICO: BERNARDINO DE SAHAGUN, missionary in Mexico, distinguishes between sweet commercial tobacco (Nicotiana tabacum) and coarse Nicotiana rustica.

1554: ANTWERP: 'Cruydeboeck' presents first illustration of tobacco.

1560: PORTUGAL, FRANCE: Jean Nicot de Villemain, France's ambassador to Portugal, writes of tobacco's medicinal properties, describing it as a panacea. Nicot sends *rustica* plants to French court.

1561: FRANCE: Nicot sends snuff to Catherine de Medici, Queen of France, to treat her son Francis II's migraine headaches. She later decrees tobacco be termed *Herba Regina* (There is confusion in sources: some claim it cured Catherine's own headaches (by making her sneeze))

1571: GERMANY: MEDICINE: Dr. Michael Bernhard Valentini's *Polychresta Exotica (Exotic Remedies)* describes numerous different types of clysters, or enemas. The tobacco smoke clyster was said to be good for the treatment of colic, nephritis, hysteria, hernia, and dysentery.

1571: SPAIN: MEDICINE: Monardes, a doctor in Seville, reports on the latest craze among Spanish doctors--the wonders of the tobacco plant, which herbalists are growing all over Spain.Monardes lists 36 maladies tobacco cures.

1577: ENGLAND: MEDICINE: Frampton translates Monardes into English. European doctors look for new cures--tobacco is recommended for toothache, falling fingernails, worms, halitosis, lockjaw & cancer.

1580: TURKEY: Tobacco arrives

1587: ANTWERP: First published work totally on tobacco, 'De herbe panacea', with numerous recipies and claims of cures.

1601: TURKEY: Smoking is introduced, and rapidly takes hold while clerics denounce it. "Puffing in each other's faces, they made the streets and markets stink," writes historian Ibrahim Pecevi.

1602: ENGLAND: Publication of *Worke of Chimney Sweepers* by anonymous author identified as 'Philaretes' states that illness of chimney sweepers is caused by soot and that tobacco may have similar effects.

1602: ENGLAND: Roger Markecke writes *A Defense of Tobacco*, in response to *Chimneysweeps.*

1604: ENGLAND: King James I write “A Counterblaste to tobacco”.

1604: ENGLAND: TAXES: King James I increases import tax on tobacco 4000%.

1606: SPAIN: King Philip III decrees that tobacco may only be grown in specific locations including Cuba, Santo Domingo, Venezuela and Puerto Rico. Sale of tobacco to foreigners is punishable by death.

1610: ENGLAND: Sir Francis Bacon writes that tobacco use is increasing and that it is a custom hard to quit.

1610: ENGLAND: Edmond Gardiner publishes William Barclay's *The Trial of Tobacco* and provides a text of recipies and medicinal preparations. BArclay defends tobacco as a medicine but condemns casual use.

1612: CHINA: Imperial edict forbidding the planting and use tobacco.

1613-89: RUSSIA: Tobacco prohibition

1614: ENGLAND: King James I make the import of tobacco a royal monopoly.

1617: MONGOLIA: Emperor places dealth penalty on using tobacco.

1619: ECONOMY: Tobacco is being used as currency. It will continue to be so used for 200 years in Virginia, for 150 years in Maryland, adjusting to the vagaries of shifting values and varying qualities.

1620 (about): JAPAN: Prohibition in Japan.

1624: ENGLAND establishes a royal tobacco monopoly.

1633: REGULATION: TURKEY: Sultan Murad IV orders tobacco users executed as infidels. As many as 18 a day were executed.

1634: REGULATION: EUROPE: Greek Church claims that it was tobacco smoke that intoxicated Noah and so bans tobacco use.

1636: BUSINESS: SPAIN: Tabacalera, the oldest tobacco company in the world, is created.

1665-66: HEALTH: EUROPE: THE GREAT PLAGUE: Smoking tobacco is thought to have a protective effect. Smoking is made compulsory at Eton to ward off infection.

1665: HEALTH: ENGLAND: Samuel Pepys describes a Royal Society experiment in which a cat quickly dies when fed "a drop of distilled oil of tobacco."

1674: RUSSIA: Smoking Can Carry the Death Penalty.

1674: FRANCE: LOUIS XIV establishes a tobacco monopoly.

1689-1725: RUSSIA: PETER THE GREAT advocates smoking, repeals bans.

1698: RUSSIA: PETER THE GREAT establishes a trade monopoly with the English, against Church wishes.

1699: LOUIS XIV and his physician, FAGON, oppose smoking.

1730: VIRGINIA: BUSINESS: First American tobacco factories begun in Virginia--small snuff mills

1750: RHODE ISLAND BUSINESS: Gilbert Stuart builds snuff mill in Rhode Island, ships his products in dried animal bladders

1753: SWEDEN: Swedish Botanist Carolus Linnaeus names the plant genus, *nicotiana*. And describes two species, *nicotiana rustica*. And *nicotiana tabacum.*

1760: BUSINESS: Pierre Lorillard establishes a "manufactory" in New York City for processing pipe tobacco, cigars, and snuff. P. Lorillard is the oldest tobacco company in the US.

1761: HEALTH: ENGLAND: Physician John Hill publishes "Cautions against the Immoderate Use of Snuff" -- perhaps the first clinical study of tobacco effects. Hill warns snuff users they are vulnerable to cancers of the nose.

1762: General Israel Putnam introduces cigar-smoking to the US. After a British campaign in Cuba, "Old Put" returns with three donkey-loads of Havana cigars; introduces the customers of his Connecticut brewery and tavern to cigar smoking.

1776: AMERICAN REVOLUTION Along "Tobacco Coast" (the Chesapeake), the Revolutionary War was variously known as "The Tobacco War." Growers had found themselves perpetually in debt to British merchants; by 1776, growers owed the mercantile houses millions of pounds. British tobacco taxes are a further grievance. Tobacco helps finance the Revolution by serving as collateral for the loan

Benjamin Franklin won from France--the security was 5 million pounds of Virginia tobacco.

1779: Pope Benedict XII opens a tobacco factory

1795: HEALTH: Sammuel Thomas von Soemmering of Maine reports on cancers of the lip in pipe smokers.

1822: Hermbstdt isolates nicotine and calls the *causa efficiens* of nicotianas Nicotianin.

1827: ENGLAND: First friction match invented. Chemist John Walker calls his invention "Congreves," after the rocket maker. Later they became known as "lucifers", then "matches".

1832: TURKEY: Invention of the paper-rolled cigarette? While Southwest Indians, Aztecs and Mayans had used hollow reeds, cane or maize to fashion cylindrical tobacco-holders, and Sevillians had rolled cigar-scraps in thrown-away paper (papeletes), an Egyptian artilleryman [in the Turk/Egyptian war] is credited with the invention of the cigarette as we know it. In the siege of Acre, the Egyptian's cannon crew had improved their rate of fire by rolling the gunpowder in paper tubes. For this, he and his crew were rewarded with a pound of tobacco. Their sole pipe was broken, however, so they took to rolling the pipe tobacco in the paper. The invention spread among both Egyptian and Turkish soldiers.

1839: AGRICULTURE: NORTH CAROLINA: SLADE "yallercure" presages flue-cured Bright tobacco. Charcoal used in flue-curing for the first time in North Carolina. Not only cheaper, its intense heat turns the thinner, low-nicotine Piedmont leaf a brilliant golden color. This results in the classic American "Bright leaf" variety, which is so mild it virtually invites a smoker to inhale it.

1843: FRANCE: SEITA monopoly begins manufacture of cigarettes.

1843: MEDICINE: The correct molecular formula of nicotine is established.

1846-1848: MEXICAN WAR: US soldiers bring back from the Southwest a taste for the darker, richer tobacco favored in Latin countries--cigarros and cigareillos--leading to an explosive increase in the use of the cigar.

1847: ENGLAND: Philip Morris opens shop; sells hand-rolled Turkish cigarettes.

1848: GERMANY: REGULATION: Abolition of the last restrictions in Berlin

1849: BUSINESS: J.E. Liggett and Brother is established in St. Louis, Mo., by John Edmund Liggett

1853-1856: EUROPE: CRIMEAN WAR British soldiers learn how cheap and convenient the cigarettes ("Papirossi") used by their Turkish allies are, and bring the practise back to England.

1854: ENGLAND: BUSINESS: London tobacconist Philip Morris begins making his own cigarettes. Old Bond Street soon becomes the center of the retail tobacco trade.

1855: J.E. Lundstrom invents the safety match, which requires a special striking surface.

1863: SUMATRA: Nienhuys creates Indonesian tobacco industry Dutch businessman Jacobus Nienhuys travels to Sumatra seeking to buy tobacco, but finds poor growing and production facilities; his efforts to rectify the situation are credited with establishing the Indonesian tobacco industry.

1864: AGRICULTURE: WHITE BURLEY first cultivated in Ohio Valley; highly absorbent, chlorophyll-deficient new leaf proves ideal for sweetened chewing tobacco.

1865-70: NEW YORK CITY: Demand for exotic Turkish cigarettes grows in New York City; skilled European rollers imported by New York tobacco shops.

1868: BUSINESS: Allen & Gintner's Sweet Caporals brand is introduced.

1871: BUSINESS: R.A. Patterson founds the "Lucky Strike" company, named for the 1849 California Gold Rush.

1875: BUSINESS: R. J. Reynolds founds R.J. Reynolds Tobacco Company to produce chewing tobacco, soon producing brands like Brown's Mule, Golden Rain, Dixie's Delight, Yellow Rose, and Purity.

1878: BUSINESS: J.E. Liggett & Brother incorporates as Liggett & Myers Company. By 1885 Liggett is world's largest plug tobacco manufacturer; doesn't make cigarettes until the 1890's.

1880: BUSINESS Bonsack machine granted first cigarette machine patent.

1885: ENGLAND: BUSINESS: Leopold Morris joins with Joseph Grunebaum to establish Philip Morris & Company and Grunebaum, Ltd.

1883: BUSINESS: Oscar Hammerstien receives patent on cigar rolling machine.

1886: BUSINESS: Tampa, FL: Don Vicente Martinez Ybor opens his first cigar factory. Others follow. Within a few years, Ybor city will become the cigar capital of the US.

1887: ENGLAND: BUSINESS: Leopold Morris and Grunebaum dissolve their partnership. Company becomes Philip Morris & Co., Ltd.

1889-04-23: BUSINESS: The five leading cigarette firms, including W. Duke Sons & Company, unite. James Buchanan "Buck" Duke emerges as the president of the new American Tobacco Company.

1890: "Tobacco" appears in the *US Pharmacopoeia,* an official government listing of drugs.

1893: SCIENCE: Pure nicotine is first synthesized by Pictet and Crepieux.

1906-06-30: Federal Food and Drugs Acts prohibits sale of adulterated foods and drugs, and mandates honest statement of contents on labels. Food and Drug Administration begins. Originally, nicotine is on the list of drugs; after tobacco industry lobbying efforts, nicotine is removed from the list. Definition of a drug includes medicines and preparations listed in U.S. Pharmacoepia or National Formulary.

1911: Tobacco growing is allowed in England for the first time in more than 250 years.

1912: BUSINESS: Newly freed Liggett & Myers introduces "Chesterfield" brand cigarettes.

1912: USA: Reprint of report of the perfection of a nicotine oil spray. This makes it easier to apply the nicotine extract as an insecticide to plants.

1912: HEALTH: First strong link made between lung cancer and smoking. In a monograph, Dr. Isaac Adler is the first to strongly suggest that lung cancer is related to smoking.

1912: USA: Article on substitutes for tobacco, such as ground coffee, coffee bean, hemp, leaves of the tomato or potato or holly or camphor, or "the egg plant, and the colt's foot".

1913: BUSINESS: Birth of the "modern" cigarette: R.J. Reynolds introduces CAMEL.

1924: CONSUMPTION: 73 billion cigarettes sold in US.

1924: BUSINESS: Philip Morris introduces Marlboro, a women's cigarette that is "Mild as May"

1928: HEALTH: Lombard & Doering examine 217 cancer victims, comparing age, gender, economic status, diet, smoking and drinking. Their New England Journal of Medicine report finds overall cancer rates only slightly less for nonsmokers, but finds 34 of 35 site-specific (lung, lips, cheek, jaw) cancer sufferers are heavy smokers.

1936: American Journal of Obstetrics and Bynecology publishes an article raising concerns about the effect of smoking on unborn children

1936: GERMANY: Fritz Lickint first uses the term *"Passivrauchen"* (passive smoking) in *Tabakgenuss und Gesunheit.*

1936: BUSINESS: B&W introduces *Viceroy,* the first serious brand to feature a filter of cellulose acetate.

1952: BUSINESS: P. Lorillard introduces Kent cigarettes, with the "Micronite" filter. At the press conference at the Waldorf-Astoria Hotel, Lorillard boasted that the "Micronite" filter offered "the greatest health protection in cigarette history." Its secret: asbestos.

1956: BUSINESS: P. Lorillard discontinues use of "Micronite" filter in its Kent cigarettes.

1957: REGULATION: Pope Pius XII suggests that the Jesuit order give up smoking.

1957-07: REGULATION: Sen. Bennett (R-UT) introduces bill requiring cigarette packs carry label, "Warning: Prolonged use of this product may result in cancer, in lung, heart and circulatory ailments, and in other diseases."

1987: BUSINESS: Introduction of "Go to Hell" cigarettes. Each pack comes with two messages, first, "I like'em and I'm going to smoke'em", second, "Cheaper than psychiatry, better than a nervous breakdown".

1989-05-31: World No-Tobacco Day.

1992: Nicotine patch is introduced.

1992-07-22: "Marlboro Man" Wayne McLaren, 51, dies of lung cancer.

1994-04-13: Tobacco Industry releases "The List" of 599 cigarette additives.

2000: JAPAN: Emperor Arkihito ends the tradition (begun by Hirohito in 1964) of giving out cigarettes to his staff on his birthday.

2001-11-15: BUSINESS: Philip Morris proposes changing its corporate name to Altria, which would consist of Miller Beer, Kraft Foods, and the two cigarette branches, Philip Morris USA and Philip Morris International.

(http://www.tobacco.org)

2. List of Additives

- Acetanisole
- Acetic Acid
- Acetoin
- Acetophenone
- 6-Acetoxydihydrotheaspirane
- 2-Acetyl-3- Ethylpyrazine
- 2-Acetyl-5-Methylfuran
- Acetylpyrazine
- 2-Acetylpyridine
- 3-Acetylpyridine
- 2-Acetylthiazole
- Aconitic Acid
- dl-Alanine
- Alfalfa Extract
- Allspice Extract,Oleoresin, and Oil
- Allyl Hexanoate
- Allyl Ionone
- Almond Bitter Oil
- Ambergris Tincture
- Ammonia
- Ammonium Bicarbonate
- Ammonium Hydroxide
- Ammonium Phosphate Dibasic
- Ammonium Sulfide
- Amyl Alcohol
- Amyl Butyrate
- Amyl Formate
- Amyl Octanoate
- alpha-Amylcinnamaldehyde
- Amyris Oil
- trans-Anethole
- Angelica Root Extract, Oil and Seed Oil
- Anise
- Anise Star, Extract and Oils
- Anisyl Acetate
- Anisyl Alcohol
- Anisyl Formate
- Anisyl Phenylacetate
- Apple Juice Concentrate, Extract, and Skins
- Apricot Extract and Juice Concentrate
- 1-Arginine
- Asafetida Fluid Extract And Oil
- Ascorbic Acid
- 1-Asparagine Monohydrate
- 1-Aspartic Acid
- Balsam Peru and Oil
- Basil Oil
- Bay Leaf, Oil and Sweet Oil
- Beeswax White
- Beet Juice Concentrate
- Benzaldehyde
- Benzaldehyde Glyceryl Acetal
- Benzoic Acid, Benzoin
- Benzoin Resin
- Benzophenone
- Benzyl Alcohol
- Benzyl Benzoate
- Benzyl Butyrate
- Benzyl Cinnamate
- Benzyl Propionate
- Benzyl Salicylate
- Bergamot Oil
- Bisabolene
- Black Currant Buds Absolute
- Borneol
- Bornyl Acetate
- Buchu Leaf Oil
- 1,3-Butanediol
- 2,3-Butanedione
- 1-Butanol
- 2-Butanone
- 4(2-Butenylidene)-3,5,5-Trimethyl-2-Cyclohexen-1-One
- Butter, Butter Esters, and Butter Oil
- Butyl Acetate
- Butyl Butyrate
- Butyl Butyryl Lactate
- Butyl Isovalerate
- Butyl Phenylacetate
- Butyl Undecylenate
- 3-Butylidenephthalide
- Butyric Acid]
- Cadinene
- Caffeine

- Calcium Carbonate
- Camphene
- Cananga Oil
- Capsicum Oleoresin
- Caramel Color
- Caraway Oil
- Carbon Dioxide
- Cardamom Oleoresin, Extract, Seed Oil, and Powder
- Carob Bean and Extract
- beta-Carotene
- Carrot Oil
- Carvacrol
- 4-Carvomenthenol
- 1-Carvone
- beta-Caryophyllene
- beta-Caryophyllene Oxide
- Cascarilla Oil and Bark Extract
- Cassia Bark Oil
- Cassie Absolute and Oil
- Castoreum Extract, Tincture and Absolute
- Cedar Leaf Oil
- Cedarwood Oil Terpenes and Virginiana
- Cedrol
- Celery Seed Extract, Solid, Oil, And Oleoresin
- Cellulose Fiber
- Chamomile Flower Oil And Extract
- Chicory Extract
- Chocolate
- Cinnamaldehyde
- Cinnamic Acid
- Cinnamon Leaf Oil, Bark Oil, and Extract
- Cinnamyl Acetate
- Cinnamyl Alcohol
- Cinnamyl Cinnamate
- Cinnamyl Isovalerate
- Cinnamyl Propionate
- Citral
- Citric Acid
- Citronella Oil
- dl-Citronellol
- Citronellyl Butyrate
- itronellyl Isobutyrate
- Civet Absolute
- Clary Oil
- Clover Tops, Red Solid Extract
- Cocoa
- Cocoa Shells, Extract, Distillate And Powder
- Coconut Oil
- Coffee
- Cognac White and Green Oil
- Copaiba Oil
- Coriander Extract and Oil
- Corn Oil
- Corn Silk
- Costus Root Oil
- Cubeb Oil
- Cuminaldehyde
- para-Cymene
- 1-Cysteine
- Dandelion Root Solid Extract
- Davana Oil
- 2-trans, 4-trans-Decadienal
- delta-Decalactone
- gamma-Decalactone
- Decanal
- Decanoic Acid
- 1-Decanol
- 2-Decenal
- Dehydromenthofurolactone
- Diethyl Malonate
- Diethyl Sebacate
- 2,3-Diethylpyrazine
- Dihydro Anethole
- 5,7-Dihydro-2-Methylthieno(3,4-D) Pyrimidine
- Dill Seed Oil and Extract
- meta-Dimethoxybenzene
- para-Dimethoxybenzene
- 2,6-Dimethoxyphenol
- Dimethyl Succinate
- 3,4-Dimethyl-1,2 Cyclopentanedione
- 3,5- Dimethyl-1,2-Cyclopentanedione
- 3,7-Dimethyl-1,3,6-Octatriene
- 4,5-Dimethyl-3-Hydroxy-2,5-Dihydrofuran-2-One

- 6,10-Dimethyl-5,9-Undecadien-2-One
- 3,7-Dimethyl-6-Octenoic Acid
- 2,4 Dimethylacetophenone
- alpha,para-Dimethylbenzyl Alcohol
- alpha,alpha-Dimethylphenethyl Acetate
- alpha,alpha Dimethylphenethyl Butyrate
- 2,3-Dimethylpyrazine
- 2,5-Dimethylpyrazine
- 2,6-Dimethylpyrazine
- Dimethyltetrahydrobenzofuranone
- delta-Dodecalactone
- gamma-Dodecalactone
- para-Ethoxybenzaldehyde
- Ethyl 10-Undecenoate
- Ethyl 2-Methylbutyrate
- Ethyl Acetate
- Ethyl Acetoacetate
- Ethyl Alcohol
- Ethyl Benzoate
- Ethyl Butyrate
- Ethyl Cinnamate
- Ethyl Decanoate
- Ethyl Fenchol
- Ethyl Furoate
- Ethyl Heptanoate
- Ethyl Hexanoate
- Ethyl Isovalerate
- Ethyl Lactate
- Ethyl Laurate
- Ethyl Levulinate
- Ethyl Maltol
- Ethyl Methyl Phenylglycidate
- Ethyl Myristate
- Ethyl Nonanoate
- Ethyl Octadecanoate
- Ethyl Octanoate
- Ethyl Oleate
- Ethyl Palmitate
- Ethyl Phenylacetate
- Ethyl Propionate
- Ethyl Salicylate
- Ethyl trans-2-Butenoate
- Ethyl Valerate
- Ethyl Vanillin
- 2-Ethyl (or Methyl)-(3,5 and 6)-Methoxypyrazine
- 2-Ethyl-1-Hexanol, 3-Ethyl -2 -Hydroxy-2-Cyclopenten-1-One
- 2-Ethyl-3, (5 or 6)-Dimethylpyrazine
- 5-Ethyl-3-Hydroxy-4-Methyl-2(5H)-Furanone
- 2-Ethyl-3-Methylpyrazine
- 4-Ethylbenzaldehyde
- 4-Ethylguaiacol
- para-Ethylphenol
- 3-Ethylpyridine
- Eucalyptol
- Farnesol
- D-Fenchone
- Fennel Sweet Oil
- Fenugreek, Extract, Resin, and Absolute
- Fig Juice Concentrate
- Food Starch Modified
- Furfuryl Mercaptan
- 4-(2-Furyl)-3-Buten-2-One
- Galbanum Oil
- Genet Absolute
- Gentian Root Extract
- Geraniol
- Geranium Rose Oil
- Geranyl Acetate
- Geranyl Butyrate
- Geranyl Formate
- Geranyl Isovalerate
- Geranyl Phenylacetate
- Ginger Oil and Oleoresin
- 1-Glutamic Acid
- 1-Glutamine
- Glycerol
- Glycyrrhizin Ammoniated
- Grape Juice Concentrate
- Guaiac Wood Oil
- Guaiacol
- Guar Gum
- 2,4-Heptadienal
- gamma-Heptalactone
- Heptanoic Acid
- 2-Heptanone

- 3-Hepten-2-One
- 2-Hepten-4-One
- 4-Heptenal
- trans -2-Heptenal
- Heptyl Acetate
- omega-6-Hexadecenlactone
- gamma-Hexalactone
- Hexanal
- Hexanoic Acid
- 2-Hexen-1-Ol
- 3-Hexen-1-Ol
- cis-3-Hexen-1-Yl Acetate
- 2-Hexenal
- 3-Hexenoic Acid
- trans-2-Hexenoic Acid
- cis-3-Hexenyl Formate
- Hexyl 2-Methylbutyrate
- Hexyl Acetate
- Hexyl Alcohol
- Hexyl Phenylacetate
- 1-Histidine
- Honey
- Hops Oil
- Hydrolyzed Milk Solids
- Hydrolyzed Plant Proteins
- 5-Hydroxy-2,4-Decadienoic Acid delta- Lactone
- 4-Hydroxy-2,5-Dimethyl-3(2H)-Furanone
- 2-Hydroxy-3,5,5-Trimethyl-2-Cyclohexen-1-One
- 4-Hydroxy -3-Pentenoic Acid Lactone
- 2-Hydroxy-4-Methylbenzaldehyde
- 4-Hydroxybutanoic Acid Lactone
- Hydroxycitronellal
- 6-Hydroxydihydrotheaspirane
- 4-(para-Hydroxyphenyl)-2-Butanone
- Hyssop Oil
- Immortelle Absolute and Extract
- alpha-Ionone
- beta-Ionone
- alpha-Irone
- Isoamyl Acetate
- Isoamyl Benzoate
- Isoamyl Butyrate
- Isoamyl Cinnamate
- Isoamyl Formate, Isoamyl Hexanoate
- Isoamyl Isovalerate
- Isoamyl Octanoate
- Isoamyl Phenylacetate
- Isobornyl Acetate
- Isobutyl Acetate
- Isobutyl Alcohol
- Isobutyl Cinnamate
- Isobutyl Phenylacetate
- Isobutyl Salicylate
- 2-Isobutyl-3-Methoxypyrazine
- alpha-Isobutylphenethyl Alcohol
- Isobutyraldehyde
- Isobutyric Acid
- d,l-Isoleucine
- alpha-Isomethylionone
- 2-Isopropylphenol
- Isovaleric Acid
- Jasmine Absolute, Concrete and Oil
- Kola Nut Extract
- Labdanum Absolute and Oleoresin
- Lactic Acid
- Lauric Acid
- Lauric Aldehyde
- Lavandin Oil
- Lavender Oil
- Lemon Oil and Extract
- Lemongrass Oil
- 1-Leucine
- Levulinic Acid
- Licorice Root, Fluid, Extract and Powder
- Lime Oil
- Linalool
- Linalool Oxide
- Linalyl Acetate
- Linden Flowers
- Lovage Oil And Extract
- 1-Lysine]
- Mace Powder, Extract and Oil
- Magnesium Carbonate

- Malic Acid
- Malt and Malt Extract
- Maltodextrin
- Maltol
- Maltyl Isobutyrate
- Mandarin Oil
- Maple Syrup and Concentrate
- Mate Leaf, Absolute and Oil
- para-Mentha-8-Thiol-3-One
- Menthol
- Menthone
- Menthyl Acetate
- dl-Methionine
- Methoprene
- 2-Methoxy-4-Methylphenol
- 2-Methoxy-4-Vinylphenol
- para-Methoxybenzaldehyde
- 1-(para-Methoxyphenyl)-1-Penten-3-One
- 4-(para-Methoxyphenyl)-2-Butanone
- 1-(para-Methoxyphenyl)-2-Propanone
- Methoxypyrazine
- Methyl 2-Furoate
- Methyl 2-Octynoate
- Methyl 2-Pyrrolyl Ketone
- Methyl Anisate
- Methyl Anthranilate
- Methyl Benzoate
- Methyl Cinnamate
- Methyl Dihydrojasmonate
- Methyl Ester of Rosin, Partially Hydrogenated
- Methyl Isovalerate
- Methyl Linoleate (48%)
- Methyl Linolenate (52%) Mixture
- Methyl Naphthyl Ketone
- Methyl Nicotinate
- Methyl Phenylacetate
- Methyl Salicylate
- Methyl Sulfide
- 3-Methyl-1-Cyclopentadecanone
- 4-Methyl-1-Phenyl-2-Pentanone
- 5-Methyl-2-Phenyl-2-Hexenal
- 5-Methyl-2-Thiophenecarboxaldehyde
- 6-Methyl-3,-5-Heptadien-2-One
- 2-Methyl-3-(para-Isopropylphenyl) Propionaldehyde
- 5-Methyl-3-Hexen-2-One
- 1-Methyl-3Methoxy-4-Isopropylbenzene
- 4-Methyl-3-Pentene-2-One
- 2-Methyl-4-Phenylbutyraldehyde
- 6-Methyl-5-Hepten-2-One
- 4-Methyl-5-Thiazoleethanol
- 4-Methyl-5-Vinylthiazole
- Methyl-alpha-Ionone
- Methyl-trans-2-Butenoic Acid
- 4-Methylacetophenone
- para-Methylanisole
- alpha-Methylbenzyl Acetate
- alpha-Methylbenzyl Alcohol
- 2-Methylbutyraldehyde
- 3-Methylbutyraldehyde
- 2-Methylbutyric Acid
- alpha-Methylcinnamaldehyde
- Methylcyclopentenolone
- 2-Methylheptanoic Acid
- 2-Methylhexanoic Acid
- 3-Methylpentanoic Acid
- 4-Methylpentanoic Acid
- 2-Methylpyrazine
- 5-Methylquinoxaline
- 2-Methyltetrahydrofuran-3-One
- (Methylthio)Methylpyrazine (Mixture Of Isomers)
- 3-Methylthiopropionaldehyde
- Methyl 3-Methylthiopropionate
- 2-Methylvaleric Acid
- Mimosa Absolute and Extract
- Molasses Extract and Tincture
- Mountain Maple Solid Extract
- Mullein Flowers
- Myristaldehyde
- Myristic Acid
- Myrrh Oil

- beta-Napthyl Ethyl Ether
- Nerol
- Neroli Bigarde Oil
- Nerolidol
- Nona-2-trans,6-cis-Dienal
- 2,6-Nonadien-1-Ol
- gamma-Nonalactone
- Nonanal
- Nonanoic Acid
- Nonanone
- trans-2-Nonen-1-Ol
- 2-Nonenal
- Nonyl Acetate
- Nutmeg Powder and Oil
- Oak Chips Extract and Oil
- Oak Moss Absolute
- 9,12-Octadecadienoic Acid (48%) And 9,12,15-Octadecatrienoic Acid (52%)
- delta-Octalactone
- gamma-Octalactone
- Octanal
- Octanoic Acid
- 1-Octanol
- 2-Octanone
- 3-Octen-2-One
- 1-Octen-3-Ol
- 1-Octen-3-Yl Acetate
- 2-Octenal
- Octyl Isobutyrate
- Oleic Acid
- Olibanum Oil
- Opoponax Oil And Gum
- Orange Blossoms Water, Absolute, and Leaf Absolute
- Orange Oil and Extract
- Origanum Oil
- Orris Concrete Oil and Root Extract
- Palmarosa Oil
- Palmitic Acid
- Parsley Seed Oil
- Patchouli Oil
- omega-Pentadecalactone
- 2,3-Pentanedione
- 2-Pentanone
- 4-Pentenoic Acid
- 2-Pentylpyridine
- Pepper Oil, Black And White
- Peppermint Oil
- Peruvian (Bois De Rose) Oil
- Petitgrain Absolute, Mandarin Oil and Terpeneless Oil
- alpha-Phellandrene
- 2-Phenenthyl Acetate
- Phenenthyl Alcohol
- Phenethyl Butyrate
- Phenethyl Cinnamate
- Phenethyl Isobutyrate
- Phenethyl Isovalerate
- Phenethyl Phenylacetate
- Phenethyl Salicylate
- 1-Phenyl-1-Propanol
- 3-Phenyl-1-Propanol
- 2-Phenyl-2-Butenal
- 4-Phenyl-3-Buten-2-Ol
- 4-Phenyl-3-Buten-2-One
- Phenylacetaldehyde
- Phenylacetic Acid
- 1-Phenylalanine
- 3-Phenylpropionaldehyde
- 3-Phenylpropionic Acid
- 3-Phenylpropyl Acetate
- 3-Phenylpropyl Cinnamate
- 2-(3-Phenylpropyl)Tetrahydrofuran
- Phosphoric Acid
- Pimenta Leaf Oil
- Pine Needle Oil, Pine Oil, Scotch
- Pineapple Juice Concentrate
- alpha-Pinene, beta-Pinene
- D-Piperitone
- Piperonal
- Pipsissewa Leaf Extract
- Plum Juice
- Potassium Sorbate
- 1-Proline
- Propenylguaethol
- Propionic Acid
- Propyl Acetate
- Propyl para-Hydroxybenzoate
- Propylene Glycol
- 3-Propylidenephthalide
- Prune Juice and Concentrate
- Pyridine

- Pyroligneous Acid And Extract
- Pyrrole
- Pyruvic Acid
- Raisin Juice Concentrate
- Rhodinol
- Rose Absolute and Oil
- Rosemary Oil
- Rum
- Rum Ether
- Rye Extract
- Sage, Sage Oil, and Sage Oleoresin
- Salicylaldehyde
- Sandalwood Oil, Yellow
- Sclareolide
- Skatole
- Smoke Flavor
- Snakeroot Oil
- Sodium Acetate
- Sodium Benzoate
- Sodium Bicarbonate
- Sodium Carbonate
- Sodium Chloride
- Sodium Citrate
- Sodium Hydroxide
- Solanone
- Spearmint Oil
- Styrax Extract, Gum and Oil
- Sucrose Octaacetate
- Sugar Alcohols
- Sugars
- Tagetes Oil
- Tannic Acid
- Tartaric Acid
- Tea Leaf and Absolute
- alpha-Terpineol
- Terpinolene
- Terpinyl Acetate
- 5,6,7,8-Tetrahydroquinoxaline
- 1,5,5,9-Tetramethyl-13-Oxatricyclo(8.3.0.0(4,9))Tridecane
- 2,3,4,5, and 3,4,5,6-Tetramethylethyl-Cyclohexanone
- 2,3,5,6-Tetramethylpyrazine
- Thiamine Hydrochloride
- Thiazole
- 1-Threonine
- Thyme Oil, White and Red
- Thymol
- Tobacco Extracts
- Tochopherols (mixed)
- Tolu Balsam Gum and Extract
- Tolualdehydes
- para-Tolyl 3-Methylbutyrate
- para-Tolyl Acetaldehyde
- para-Tolyl Acetate
- para-Tolyl Isobutyrate
- para-Tolyl Phenylacetate
- Triacetin
- 2-Tridecanone
- 2-Tridecenal
- Triethyl Citrate
- 3,5,5-Trimethyl -1-Hexanol
- para,alpha,alpha-Trimethylbenzyl Alcohol
- 4-(2,6,6-Trimethylcyclohex-1-Enyl)But-2-En-4-One
- 2,6,6-Trimethylcyclohex-2-Ene-1,4-Dione
- 2,6,6-Trimethylcyclohexa-1,3-Dienyl Methan
- 4-(2,6,6-Trimethylcyclohexa-1,3-Dienyl)But-2-En-4-One
- 2,2,6-Trimethylcyclohexanone
- 2,3,5-Trimethylpyrazine
- 1-Tyrosine
- delta-Undercalactone
- gamma-Undecalactone
- Undecanal
- 2-Undecanone, 1
- 0-Undecenal
- Urea
- Valencene
- Valeraldehyde
- Valerian Root Extract, Oil and Powder
- Valeric Acid
- gamma-Valerolactone
- Valine
- Vanilla Extract And Oleoresin
- Vanillin
- Veratraldehyde
- Vetiver Oil
- Vinegar

- Violet Leaf Absolute
- Walnut Hull Extract
- Water
- Wheat Extract And Flour
- Wild Cherry Bark Extract
- Wine and Wine Sherry
- Xanthan Gum
- 3,4-Xylenol
- Yeast

(http://quitsmoking.about.com, 2005)

3. pH and Electric Conductivity Values Tables

Time was showed like minute and electric conductivity was showed like micro siemens (µS) on each table for each experiments. Oxidants dosages and pH value were shown on the table.

Table A.1 pH=3, 50 mM H_2O_2, 5mM Fe^{+2}

Time	pH	EC
0	3,00	8597,97
2,5	0,95	9580,84
5	1,40	3933,64
10	1,39	3782,76
15	1,35	3955,20
30	1,41	3750,43
45	1,40	2511,06
60	1,34	2737,38
90	1,42	3502,56

Table A.2 pH=4, 50 mM H_2O_2, 5mM Fe^{+2}

Time	pH	EC
0	4,00	2403,29
2,5	1,56	3222,35
5	1,56	3017,59
10	1,52	3028,36
15	1,48	3157,69
30	1,45	3351,68
45	1,45	3222,35
60	1,48	3254,68
90	1,40	3524,11

Table A.3 pH=5, 50 mM H_2O_2, 5mM Fe^{+2}

Time	pH	EC
0	5,00	2209,31
2,5	1,75	2640,39
5	1,85	2532,62
10	1,77	2694,27
15	1,83	2532,62
30	1,88	2629,61
45	1,76	2758,94
60	1,76	2672,72
90	1,71	2737,38

Table A.4 pH=4, 50 mM H_2O_2, 0,5mM Fe^{+2}

Time	pH	EC
0	4,00	2360,18
2,5	3,35	2306,30
5	3,34	2284,75
10	3,35	2317,08
15	3,33	2241,64
30	3,31	2381,74
45	3,34	2295,52
60	3,30	2392,52
90	3,35	2457,18

Table A.5 pH=4, 50 mM H_2O_2, 1 mM Fe^{+2}

Time	pH	EC
0	4,00	2356,71
2,5	3,25	2467,87
5	3,18	2445,64
10	3,10	2590,15
15	3,19	2523,45
30	3,18	2512,34
45	3,18	2467,87
60	3,17	2534,57
90	3,09	2667,97

Table A.6 pH=4, 50 mM H_2O_2, 2,5 mM Fe^{+2}

Time	pH	EC
0	4,00	2423,40
2,5	2,65	4635,60
5	3,07	2684,64
10	3,06	2634,62
15	3,05	2601,27
30	3,09	2612,39
45	3,08	2612,39
60	3,09	2712,43
90	3,05	2679,09

Table A.7 pH=4, 50 mM H_2O_2, 5 mM Fe^{+2}

Time	pH	EC
0	4,00	2403,29
2,5	1,56	3222,35
5	1,56	3017,59
10	1,52	3028,36
15	1,48	3157,69
30	1,45	3351,68
45	1,45	3222,35
60	1,48	3254,68
90	1,40	3524,11

Table A.8 pH=4, 50 mM H_2O_2, 7,5 mM Fe^{+2}

Time	pH	EC
0	4,00	2434,52
2,5	2,90	3123,75
5	2,90	3179,33
10	2,89	3145,98
15	2,93	2856,95
30	2,89	3201,56
45	2,90	3123,75
60	2,95	3257,14
90	2,91	3212,68

Table A.9 pH=4, 5 mM H_2O_2, 2,5 mM Fe^{+2}

Time	pH	EC
0	4,00	2360,18
2,5	3,11	2532,62
5	3,08	2564,95
10	3,09	2586,50
15	3,08	2629,61
30	3,09	2640,39
45	3,07	2694,27
60	3,08	2618,84
90	3,07	2672,72

Table A.10 pH=4, 10 mM H_2O_2, 2,5 mM Fe^{+2}

Time	pH	EC
0	4,00	2200,75
2,5	3,13	2449,89
5	3,15	2397,98
10	3,14	2460,27
15	3,12	2512,17
30	3,04	2678,27
45	3,09	2626,36
60	3,12	2449,89
90	3,11	2501,79

Table A.11 pH=4, 25 mM H_2O_2, 2,5 mM Fe^{+2}

Time	pH	EC
0	4,00	2215,60
2,5	2,93	3050,31
5	2,97	2751,46
10	2,99	2555,67
15	2,97	2586,58
30	2,98	2792,68
45	3,04	2524,75
60	2,93	2947,26
90	3,00	2730,85

Table A.12 pH=4, 50 mM H_2O_2, 2,5 mM Fe^{+2}

Time	pH	EC
0	4,00	2423,40
2,5	2,65	4635,60
5	3,07	2684,64
10	3,06	2634,62
15	3,05	2601,27
30	3,09	2612,39
45	3,08	2612,39
60	3,09	2712,43
90	3,05	2679,09

Table A.13 pH=4, 75 mM H_2O_2, 2,5 mM Fe^{+2}

Time	pH	EC
0	4,00	2133,16
2,5	1,54	2710,24
5	1,53	2669,02
10	1,52	2617,50
15	1,53	2545,36
30	1,49	2627,80
45	1,47	2627,80
60	1,49	2565,97
90	1,48	2710,24

Table A.14 pH=4, 100 mM H_2O_2, 2,5 mM Fe^{+2}

Time	pH	EC
0	4,00	2236,21
2,5	3,04	2638,11
5	2,99	2658,72
10	2,91	2854,52
15	2,99	2669,02
30	3,00	2607,19
45	2,99	2658,72
60	2,98	2658,72
90	2,99	2669,02