



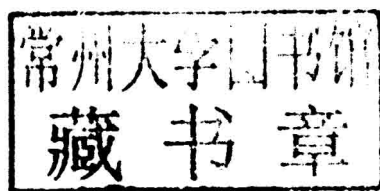
Textile Effluent Treatment

Victor Bonn



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Edited by Victor Bonn



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Preface

This book covers various aspects related to the treatment of textile effluents. The management of textile wet processing effluent to meet severe legislative regulations is a complex and constantly changing procedure. Treatment techniques that were acceptable in the past may not be applicable today or in the future. This book presents some concepts and processes to help the textile industry in meeting the demanding requirements of handling textile waste matter.

The researches compiled throughout the book are authentic and of high quality, combining several disciplines and from very diverse regions from around the world. Drawing on the contributions of many researchers from diverse countries, the book's objective is to provide the readers with the latest achievements in the area of research. This book will surely be a source of knowledge to all interested and researching the field.

In the end, I would like to express my deep sense of gratitude to all the authors for meeting the set deadlines in completing and submitting their research chapters. I would also like to thank the publisher for the support offered to us throughout the course of the book. Finally, I extend my sincere thanks to my family for being a constant source of inspiration and encouragement.

Editor

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Decolorisation of Textile Dyeing Effluents Using Advanced Oxidation Processes

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1. Introduction

Textile industry is a leading industry for most countries, such as China, Singapore, UK, Bangladesh, Italy, Turkey etc. But, environmental pollution is one of the main results of this industry. Parallel to usage of huge amounts of water and chemicals, the textile dyeing and finishing industry is one of the major polluters among industrial sectors, in the scope of volume and the chemical composition of the discharged effluent (Pagga & Brown, 1986).

Textile industry effluents can be classified as dangerous for receiving waters, which commonly contains high concentrations of recalcitrant organic and inorganic chemicals and are characterised by high chemical oxygen demand (COD) and total organic carbon (TOC), high amounts of surfactants, dissolved solids, fluctuating temperature and pH, possibly heavy metals (e.g. Cu, Cr, Ni) and strong colour (Grau, 1991, Akal Solmaz et al., 2006).

The presence of organic contaminants such as dyes, surfactants, pesticides, etc. in the hydrosphere is of particular concern for the freshwater, coastal, and marine environments because of their nonbiodegradability and potential carcinogenic nature of the majority of these compounds (Demirbas et al., 2002, Fang et al., 2004, Bulut & Aydin, 2006, Mahmoudi & Arami, 2006, Mahmoudi & Arami, 2008, Mozia et al., 2008, Li et al., 2008, Atchariyawut et al., 2009, Mahmoudi & Arami, 2009a, Mahmoudi & Arami, 2009b, Mahmoudi & Arami, 2010, Amini et al., 2011.). The major concern with colour is its aesthetic character at the point of discharge with respect to the visibility of the receiving waters (Slokar & Le Marechal, 1997).

The main reason of colour in textile industry effluent is the usage of large amounts of dyestuffs during the dyeing stages of the textile-manufacturing process (O'neil et al., 1999, Georgiou et al., 2002). Inefficient dyeing processes often result in significant dye residuals being presented in the final dyehouse effluent in hydrolysed or unfixed forms (Yonar et al., 2005). Apart from the aesthetic problems relating to coloured effluent, dyes also strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem. Stricter regulatory requirements along with an increased public demand for colour-free effluent necessitate the inclusion of a decolorisation step in wastewater treatment plants (Kuo, 1992).

Well known and widely applied treatment method for the treatment of textile industry wastewater is activated sludge process and its modifications. Combinations of activated sludge process with physical and chemical processes can be found in most applications. These traditional treatment methods require too many spaces and are affected by

wastewater flow and characteristic variations. But, either activated sludge process modifications itself or combinations of this process with physical or chemical processes are inefficient for the treatment of coloured waste streams (Venceslau et al., 1994, Willmott et al., 1998, Vendevivere et al., 1998, Uygur & Kok, 1999).

On the other hand, existing physico-chemical advanced treatment technologies such as, membrane processes, ion exchange, activated carbon adsorption etc. can only transfer pollutants from one phase the other phase rather than eliminating the pollutants from effluent body. Recovery and reuse of certain and valuable chemical compounds present in the effluent is currently under investigation of most scientists (Erswell et al., 2002). At this point, The AOPs show specific advantages over conventional treatment alternatives because they can eliminate non-biodegradable organic components and avoid the need to dispose of residual sludge. Advanced Oxidation Processes (AOPs) based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have been used with an increasing interest due to the their high oxidant power (Kestioglu et al., 2005). In this chapter, discussion and examples of colour removal from textile effluent will be focused on those of most used AOPs.

2. Advanced Oxidation Processes: Principles and definitions

Advanced Oxidation Processes (AOPs) are defined as the processes which involve generation and use of powerful but relatively non-selective hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in the effluent water (Gogate & Pandit, 2004a, EPA, 1998). Hydroxyl radicals ($\text{OH}\cdot$) has the highest oxidation potential (Oxidation potential, E_0 : 2.8 eV vs normal hydrogen electrode (NHE)) after fluorine radical. Fluorine, the strongest oxidant (Oxidation potential, E_0 : 3.06 V) cannot be used for wastewater treatment because of its high toxicity. From these reasons, generation of hydroxyl radical including AOPs have gained the attention of most scientists and technology developers.

The main and short mechanism of AOPs can be defined in two steps: (a) the generation of hydroxyl radicals, (b) oxidative reaction of these radicals with molecules (Azbar et al., 2005). AOPs can convert the dissolved organic pollutants to CO_2 and H_2O . The generation of highly effective hydroxyl radical might possibly be by the use of UV, UV/O_3 , $\text{UV}/\text{H}_2\text{O}_2$, $\text{Fe}^{+2}/\text{H}_2\text{O}_2$, $\text{TiO}_2/\text{H}_2\text{O}_2$ and a number of other processes (Mandal et al., 2004).

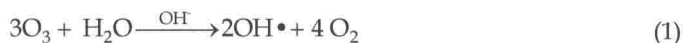
AOPs can be classified in two groups: (1) Non-photochemical AOPs, (2) Photochemical AOPs. Non-photochemical AOPs include cavitation, Fenton and Fenton-like processes, ozonation at high pH, ozone/hydrogen peroxide, wet air oxidation etc. Short description of some important AOPs are given below. Photochemical oxidation processes include homegenous (vacuum UV photolysis, $\text{UV}/\text{hydrogen peroxide}$, UV/ozone , $\text{UV}/\text{ozone}/\text{hydrogen peroxide}$, photo-Fenton etc), and heterogeneous (photocatalysis etc) processes.

2.1 Non-photochemical oxidation processes

Non-photochemical oxidation processes can be classified as (1) Ozonation, (2) Ozone/Hydrogen Peroxide, (3) Fenton Process, (4) Electrochemical Oxidation, (5) Supercritical water oxidation, (6) Cavitation, (7) Electrical discharge-based nonthermal plasma, (8) gamma-ray, (9) x-ray and (10) electron beam. Ozonation, ozone/hydrogen peroxide and Fenton-process are widely applied and examined processes for the treatment of textile effluent. From this reason, brief explanations and examples are given below.

2.1.1 Ozonation

Ozone is well known and widely applied strong oxidizing agent for the treatment of both water and wastewater, in literature and on site. Ozone has high efficiency at high pH levels. At these high pH values (>11.0), ozone reacts almost indiscriminately with all organic and inorganic compounds present in the reacting medium (Steahelin & Hoigne, 1982). Ozone reacts with wastewater compounds in two different ways namely direct molecular and indirect radical type chain reactions. Both reactions occur simultaneously and hence reaction kinetics strongly depend on the characteristics of the treated wastewater (e.g. pH, concentrations of initiators, promoters and scavengers (Arslan & Balcioglu, 2000). Simplified reaction mechanisms of ozone at high pH is given in below;



2.1.2 Ozone/hydrogen peroxide (peroxone) process ($\text{O}_3/\text{H}_2\text{O}_2$)

The combination of ozone and hydrogen peroxide is used essentially for the contaminants which oxidation is difficult and consumes large amounts of oxidant. Because of the high cost of ozone generation, this combination make the process economically feasible (Mokrini et al., 1997). The capability of ozone to oxidise various pollutants by direct attack on the different bonds (C=C bond (Stowell & Jensen, 1991), aromatic rings (Andreozzi et al. 1991) is further enhanced in the presence of H_2O_2 due to the generation of highly reactive hydroxyl radicals ($\bullet\text{OH}$). The dissociation of H_2O_2 results in the formation of hydroperoxide ion, which attacks the ozone molecule resulting in the formation of hydroxyl radicals (Forni et al., 1982, Steahelin & Hoigne, 1985, Arslan & Balcioglu, 2000). General mechanism of peroxon process is given below:



The pH of solution is also critical for the process efficiency like other AOPs. Addition of hydrogen peroxide to the aqueous O_3 solution at high pH conditions will result in higher production rates of hydroxyl radicals (Glaze & Kang, 1989). Indipendence of peroxone process from any light source or UV radiation gives a specific advantage to this process that it can be used in turbid or dark waters.

2.1.3 Fenton process

The dark reaction of ferrous iron (Fe(II)) with H_2O_2 known as Fenton's reaction (Fenton 1894), which is shown in Eq.-15, has been known for over a century (EPA, 2001).



The hydroxyl radical thus formed can react with Fe(II) to produce ferric ion (Fe(III)) as shown in Eq.-16;



Alternatively, hydroxyl radicals can react with and initiate oxidation of organic pollutants in a waste stream,



At value of pH (2.7–2.8), reactions can result into the reduction of Fe^{+3} to Fe^{+2} (Fenton-like).



proceeding at an appreciable rate. In these conditions, iron can be considered as a real catalyst (Andreozzi et al., 1991).

At pH values <4.0, ferrous ions decompose H_2O_2 catalytically yielding hydroxyl radicals most directly. However, at pH values higher than 4.0, ferrous ions easily form ferric ions, which have a tendency to produce ferric hydroxo complexes. H_2O_2 is quite unstable and easily decomposes itself at alkaline pH (Kuo, 1992).

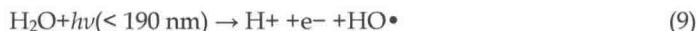
Fenton process is cost-effective, easy to apply and effective for the degradation of a wide range of organic compounds. One of the advantages of Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents (Bautista et al., 2007). The Fenton process consists of four stages. At first, pH is adjusted to low pH. Then the main oxidation reactions take place at pH values of 3–5. The wastewater is then neutralized at pH of 7–8, and, finally, precipitation occurs (Bigda, 1995, Lee & Shoda, 2008). Furthermore, it commonly requires a relatively short reaction time compared with other AOPs. Thus, Fenton's reagent is frequently used when a high reduction of COD is required (Bigda, 1995, Bautista et al., 2007, Lee & Shoda, 2008, Yonar, 2010).

2.2 Photochemical oxidation processes

2.2.1 Homogeneous photochemical oxidation processes

2.2.1.1 Vacuum UV (VUV) photolysis

The Vacuum Ultraviolet range is absorbed by almost all substances (including water and air). Thus it can only be transmitted in a vacuum. The absorption of a VUV photon causes one or more bond breaks. For example, water is dissociated according to;



Photochemistry in the vacuum-ultraviolet (VUV) spectral domain (approx. 140–200 nm) is of high applicatory interest, e.g. (i) in microelectronics, where materials with surface structures of high spatial resolution provide a basis for the fast development of high computational and electronic and optical storage capacities or (ii) in environmental techniques, in particular for the production of ultra pure water and for the oxidative treatment of waste gas and water (Bolton, 2002, Gonzaleza et al., 2004). VUV-photolysis can be achieved by the usage of either a monochromatic (Xe-eximer Xe_2^*) or polychromatic (Hg) radiation sources. These light sources have some limitations such as high price, wave length variations etc. From these reasons application of VUV photolysis are too limited.

2.2.1.2 Hydrogen peroxide/UV ($\text{H}_2\text{O}_2/\text{UV}$) process

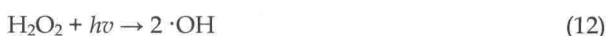
This method is based on the direct photolysis of hydrogen peroxide molecule by a radiation with a wavelength between 200–300 nm region. The main reaction of $\text{H}_2\text{O}_2/\text{UV}$ is given below:



The low, medium and high pressure mercury vapor lamps can be used for this process because it has significant emittance within 220-260 nm, which is the primary absorption band for hydrogen peroxide. Most of UV light can also be absorbed by water. Low pressure mercury vapour lamps usage can lead to usage of high concentrations of H_2O_2 for the generation of sufficient hydroxyl radical. However, high concentrations of H_2O_2 may scavenge the hydroxyl radical, making the H_2O_2 /UV process less effective. Some more variables such as temperature, pH, concentration of H_2O_2 , and presence of scavengers affect the production of hydroxyl radicals (EPA, 1998, Bolton, 2001, Mandal et al., 2004, Azbar et al., 2005).

2.2.1.3 Ozone/UV (O_3 /UV) process

Photolysis of ozone in water with UV radiation in the range of 200-280 nm can lead to yield of hydrogen peroxide. Hydroxyl radicals can be generated by these produced hydrogen peroxide under UV radiation and/or ozone as given equations below:



Starting from low pressure mercury vapour lamps all kind of UV light sources can be used for this process. Because, O_3 /UV process does not have same limitations of H_2O_2 /UV process. Low pressure mercury vapor UV lamps are the most common sources of UV irradiation used for this process. Many variables such as pH, temperature, scavengers in the influent, turbidity, UV intensity, lamp spectral characteristics and pollutant type(s) affect the efficiency of the system (EPA, 1998, Azbar, 2005). Number of laboratory, pilot and full scale applications of Ozone/UV and Hydrogen peroxide/UV processes can be found in literature. Commercial applications of these processes can also be available.

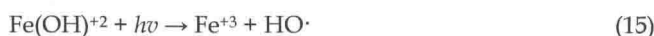
2.2.1.4 Ozone/hydrogen peroxide/UV (O_3 / H_2O_2 / UV) process

This method is considered to be the most effective and powerful method which provides a fast and complete mineralisation of pollutants (Azbar, 2005, Mokrini et al., 1997). Similar to other ozone including AOPs, increasing of pH affects the hydroxyl radical formation. Additional usage of UV radiation also affects the hydroxyl radical formation. Efficiency of ozone/hydrogen peroxide/UV process is being much more higher with addition of hydrogen peroxide (Horsch, 2000, Contreras et al., 2001). Main short mechanism of O_3 / H_2O_2 / UV process is given below:



2.2.1.5 Photo-Fenton process

The combination of Fenton process with UV light, the so-called photo-Fenton reaction, has been shown to enhance the efficiency of Fenton process. Some researchers also attributed this to the decomposition of the photo active $\text{Fe}(\text{OH})^{+2}$ which lead to the addition of the $\text{HO}\cdot$ radicals (Sun & Pignatello, 1993, He & Lei, 2004). The short mechanism of photo-Fenton reaction is given below:



With $\text{Fe}(\text{OH})^{2+}$ being the dominant $\text{Fe}(\text{III})$ species in solution at pH 2-3. High valence Fe intermediates formed through the absorption of visible light by the complex between $\text{Fe}(\text{II})$ and H_2O_2 are believed to enhance the reaction rate of oxidation production (Pignatello, 1992, Bossmann et al., 2001).

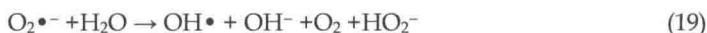
2.2.2 Heterogeneous Photochemical Oxidation processes

Widely investigated and applied Heterogeneous Photochemical Oxidation processes are semiconductor-sensitized photochemical oxidation processes.

Semiconductors are characterized by two separate energy bands: a low energy valence band (h^+_{VB}) and a high-energy conduction (e^-_{CB}) band. Each band consists of a spectrum of energy levels in which electrons can reside. The separation between energy levels within each energy band is small, and they essentially form a continuous spectrum. The energy separation between the valence and conduction bands is called the band gap and consists of energy levels in which electrons cannot reside. Light, a source of energy, can be used to excite an electron from the valence band into the conduction band. When an electron in the valence band absorbs a photon, the absorption of the photon increases the energy of the electron and enables the electron to move into one of the unoccupied energy levels of the conduction band (EPA, 1998).

Semiconductors that have been used in environmental applications include TiO_2 , strontium titanium trioxide, and zinc oxide (ZnO). TiO_2 , is generally preferred for use in commercial APO applications because of its high level of photoconductivity, ready availability, low toxicity, and low cost. TiO_2 has three crystalline forms: rutile, anatase, and brookite. Studies indicate that the anatase form provides the highest hydroxyl radical formation rates (Korrmann et al., 1991, EPA, 1998).

The photo-catalyst titanium dioxide (TiO_2) is a wide band gap semiconductor (3.2 eV) and is successfully used as a photo-catalyst for the treatment of organic pollutants (Hsiao et al., 1983, Korrmann et al., 1991, Zahhara, 1999). Briefly, for TiO_2 , the photon energy required to overcome the band gap energy and excite an electron from the valence band to the conduction band can be provided by light of a wavelength shorter than 387.5 nm. Simplified reaction mechanisms of TiO_2/UV process is given in following equations (eq. 16- eq. 19).



The overall result of this reversal is generation of photons or heat instead of $-\text{OH}$. The reversal process significantly decreases the photo-catalytic activity of a semiconductor (EPA, 1998). Main advantage of TiO_2/UV process is low energy consumption which sunlight can be used as a light source.

3. Characterisation of textile industry wastewater

Textile industry produces large amounts of liquid by-products. Volume and composition of these wastewater can vary from one source to other source. In the scope of volume and the chemical composition of the discharged effluent, the textile dyeing and finishing industry is

one of the major polluters among industrial sectors. Textile industry dyes are intentionally designed to remain photolytically, chemically and biochemically stable, and thus are usually not amenable to biodegradation (Pagga & Braun, 1986). Like many other industrial effluents, textile industry wastewater varies significantly in quantity, but additionally in composition (Correira et al., 1994).

These wastes include both organic and inorganic chemicals, such as finishing agents, carriers, surfactants, sequestering agents, leveling agents etc. From these reasons, textile effluents are characterized with high COD ($\approx 400\text{--}3.000\text{ mg/L}$), BOD₅ ($\approx 200\text{--}2.000\text{ mg/L}$), Total Solids ($\approx 1.000\text{--}10.000\text{ mg/L}$), Suspended Solids ($\approx 100\text{--}1.000\text{ mg/L}$), TKN ($\approx 10\text{--}100\text{ mg/L}$), Total Phosphorus ($\approx 5\text{--}70\text{ mg/L}$), Conductivity ($1.000\text{--}15.000\text{ mS/cm}$) and pH ($\approx 5\text{--}10$ usually basic) (Grau, 1991, Pagga and Braun, 1991, Kuo, 1992, Correira et al., 1994, Arslan and Balcioglu, 2000, Nigam et al., 2000, Azbar et al., 2005, Akal Solmaz et al., 2006, Yonar et al., 2006, Mahmoudi & Arami, 2009, Yonar, 2010).

Another important problem of textile industry wastewater is color. Without proper treatment of coloured water, these dyes may remain in the environment for a long time (Yonar et al, 2005). The problem of colored effluent has been a major challenge and an integral part of textile effluent treatment as a result of stricter environmental regulations. The presence of dyes in receiving media is easily detectable even when released in small concentrations (Little et al., 1974, Azbar et al., 2004). This is not only unsightly but dyes in the effluent may have a serious inhibitory effect on aquatic ecosystems as mentioned above (Nigam et al., 2000).

Definition and determination of colour is another important point for most water and wastewater samples. Some methods can be found in literature for the determination of colour in samples. But, selection of true method for the determination of colour is very important. According to "Standard Methods for the Examination of Water and Wastewater" (APHA- AWWA, 2000), importance of colour is defined with some sentences given below:

"Colour in water may result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and *industrial wastes*. Colour is removed to make a water suitable for general and industrial applications. Coloured industrial wastewaters may require colour removal before discharge into watercourses."

From these reasons, colour content should be determined carefully. In Standard Methods, colour content of water and wastewater samples can be determined with four different methods such as (i) Visual Comparison Method, (ii) Spectrometric Method, (iii) Tristimulus Filter Method, and (iv) ADMI Tristimulus Filter Method. Selection of true and appropriate method for samples is very important. Visual comparison method is suitable for nearly all samples of potable water. This method is also known as Platinum/Cobalt method. Pollution by ceratin industrial wastes may produce unusual colour that can not be easily matched. In this case, usage of instrumental methos are appropriate for most cases. A modification of the spectrometric and tristimulus methods allows calculation of a single colour value representing uniform cromaticity differences even when the sample exhibits colour significantly different from that of platinum cobalt standards (APHA-AWWA, 2000).

4. Colour removal from textile industry wastewater by AOPs

Most commonly applied treatment flow scheme for textile effluent in Turkey and other countries generally include either a single activated sludge type aerobic biological

treatment or combination of chemical coagulation and flocculation + activated sludge process (Yonar et al., 2006). Furthermore, it is well known that aerobic biological treatment option is ineffective removal for colour removal from textile wastewater in most cases and the chemical coagulation and flocculation is also not effective for the removal of soluble reactive dyestuffs. Therefore, dyes and chemicals using in textile industry in effluent may have a serious inhibitory effect on aquatic ecosystems and visual pollution on receiving waters, as mentioned above (Venceslau et al., 1994, Willmott et al., 1998, Vendevivere et al., 1998).

There are several alternative methods used to decolorize the textile wastewater such as various combinations of physical, chemical and biological treatment and colour removal methods, but they cannot be effectively applied for all dyes and these integrated treatment methods are not cost effective. Advanced Oxidation Processes (AOPs) for the degradation of non-biodegradable organic contaminants in industrial effluents are attractive alternatives to conventional treatment methods and are capable of reducing recalcitrant wastewater loads from textile dyeing and finishing effluents (Galindo et al., 2001, Robinson et al., 2001, Azbar et al., 2004, Neamtu et al., 2004). In this section, applied AOPs for colour removal from textile effluent are given. Technological advantages and limitations of these AOPs is also discussed.

4.1 Colour removal with non-photochemical AOPs

Ozonation at high pH, ozone/hydrogen peroxide and Fenton processes are widely applied and investigated AOPs for colour removal from textile effluents and textile dyes. As it can be clearly seen from former sections, ozone can produce hydroxyl radicals at high pH levels. According to this situation, pH is very important parameter for ozonation process. As it was described above, under conditions aiming hydroxyl free radical ($\text{HO}\bullet$) production (e.g., high pH), the more powerful hydroxyl oxidation starts to dominate (Hoigne & Bader, 1983). Since the oxidation potential of ozone reportedly decreases from 2.07mV (acidic pH) to 1.4mV (basic pH) (Muthukumanar et al., 2001), it is clear that another more powerful oxidant ($\text{HO}\bullet$) is responsible for the increase in the dye degradation, with a consequent colour absorbance decrease. The efficiency of ozonation in the removal of colour and COD from textile wastewater is important to achieve to discharge limits (Somensia et al., 2010).

Textile wastewaters are very complex due to the organic chemicals such as many different dyes, carriers, biocides, bleaching agents, complexion agents, ionic and non-ionic surfactants, sizing agents, etc. As a result, it is hard to explain the overall degradation of the organic matter by ozone in textile wastewater individually. Thus, some global textile wastewater parameters such as color, COD and dissolved organic carbon are used for the degradation kinetic of organic matter by ozonation (Sevimli & Sarikaya, 2002, Selcuk, 2005). Textile wastewaters exhibit low BOD to COD ratios (< 0.1) indicating non-biodegradable nature of dyes and Willmott et al. (1998) have claimed that aerobic biological degradation is not always effective for textile dye contaminated effluent (Sevimli & Sarikaya, 2002).

Somensia et al., (2010), tested pilot scale ozonation for the pre-treatment and colour removal of real textile effluent. Authors have mentioned that the importance of pH on the process efficiency and colour removal efficiencies were determined as 40.6% and 67.5% at pH 3.0 and 9.1, respectively. COD removal efficiencies were also determined as 18.7% (pH=3) and 25.5% (pH=9). On the other hand, toxicity can be reduced significantly compared with raw wastewater. Azbar et al., (2004) carried out a comparative study on colour and COD removal

from acetate and fiber dyeing effluent. In this study, various advanced oxidation processes (O_3 , O_3/UV , H_2O_2/UV , $O_3/H_2O_2/UV$, Fe^{+2}/H_2O_2) and chemical treatment methods using $Al_2(SO_4)_3$, $18H_2O$ $FeCl_3$ and $FeSO_4$ for the Chemical Oxygen Demand (COD) and colour removal from a polyester and acetate fiber dyeing effluent is undertaken. Ozonation showed superior performance at pH=9 and 90% COD and 92% colour can be removed. Akal Solmaz et al., 2006, applied ozonation to real textile wastewaters and found 43% COD and 97% colour removal efficiencies at pH 9 and CO_3 1.4 g/h. In the another study of Akal Solmaz et al., (2009), group has tested different AOPs on two different textile wastewater. 54-70% COD removal and 94-96 % colour removal efficiencies have been determined at pH = 9.

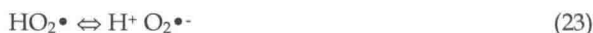
In another study, Selcuk, (2005), have tested coagulation and ozonation for color, COD and toxicity removal from textile wastewater. Author found that, ozonation was relatively effective in reducing colour absorbances and toxic effects of textile effluents compared with chemical coagulation. Almost complete colour absorbances (over 98%) were removed in 20 min ozone contact time, while COD removal (37%) was very low and almost stable in 30 min ozonation period.

Yonar et al., (2005), have been studied AOPs for the improvement of effluent quality of a textile industry wastewater treatment plant. Authors were mainly tested homogeneous photochemical oxidation processes (HPOP's) (H_2O_2/UV , O_3/UV and $H_2O_2/O_3/UV$) for colour and COD removal from an existing textile industry wastewater treatment plant effluent together with their operating costs. At pH=9, 81% COD and 97% colour removal efficiencies were reported for ozonation process.

As it can be clearly seen from literature, ozonation is very effective for the removal of colour from textile wastewater. COD and toxicity can also be removed by ozonation. But, for decision making on these processes advantages and limitations of these processes should be known. Main advantage of ozonation is no need to addition of any chemicals to water or wastewater. Because, ozone is mostly produced by cold corona discharge generators. And these generators need dry air for the production of ozone. On the other hand, sludge or similar residues is not produced during this process. At this point, specific advantage can be stated for textile effluents. Mostly, the pH value of textile wastewater are higher than 7 and in some situations higher than 9. Thus, ozonation can be applied to textile effluent without any pH adjustment and chemical addition. But, ozonation process has some disadvantages, such as, inefficient production capacities of cold corona discharge (CCD) generators (2-4%), less solubility of gas phase ozone in water, higher energy demands of CCD generators, possible emission problems of ozone etc. These disadvantages can be overcome by the production of efficient ozone generators like membrane electrochemical ozone generators.

Ozone/Hydrogen peroxide process is another efficient AOPs for the treatment of recalcitrant organics. Similar to ozonation, ozone including other processes mostly needs alkaline conditions. This argument has been extensively and successfully studied by Hoigne (1998) in the attempt of giving a chemical explanation to the short life time of ozone in alkaline solutions. Hoigné showed that the ozone decomposition in aqueous solution develops through the formation of hydroxyl radicals. In the reaction mechanism OH^- ion has the role of initiator:





It is clear therefore that the addition of hydrogen peroxide to the ozone aqueous solution will enhance the O_3 decomposition with formation of hydroxyl radicals. The influence of pH is also evident, since in the ozone decomposition mechanism the active species is the conjugate base HO_2^- whose concentration is strictly dependent upon pH. The increase of pH and the addition of H_2O_2 to the aqueous O_3 solution will thus result into higher rates of hydroxyl radicals production and the attainment of higher steady-state concentrations of hydroxyl radicals in the radical chain decomposition process (Glaze & Kang, 1989). It must be remarked that the adoption of the $\text{H}_2\text{O}_2/\text{O}_3$ process does not involve significant changes to the apparatus adopted when only O_3 is used, since it is only necessary to add an H_2O_2 dosing system (Andreozzi, 1998).

Hydrogen peroxide/ozone (peroxone) process test result for real or synthetic textile wastewater are too limited in literature but ozone and hydrogen peroxide is a very promising technique for potential industrial implementation. Kurbus et al. (2003) were conducted comparative study on different vinylsulphone reactive dyes. For all tested dyes, over 99% colour removal can be achieved at pH=12. Kos & Perkovski (2003), were tested different AOPs including peroxone process on real textile wastewater. Textile wastewater initial COD is over 5000 mg/L and authors declared that nearly 100% colour removal can be achieved with peroxone process. According to Akal Solmaz et al., (2006), addition of hydrogen peroxide to ozone is increased colour and COD removal efficiencies nearly 10%. Perkovski et al., (2003), were tested peroxone process on anthraquinone dye Acid Blue 62 and they found 60% colour removal efficiency.

Main advantage and disadvantage of peroxone process is addition of hydrogen peroxide. Addition of hydrogen peroxide is giving higher efficiencies and no need to upgrade the existing ozonation systems. But, addition of hydrogen peroxide means additional costs for the treatment of wastewater.

Finally, Fenton process is mostly applied on both textile and other industrial wastewaters. Nevertheless, the high electrical energy demand is general disadvantage of most AOPs. As it mentioned above, the greatest advantages of Fenton process is that no energy input is necessary to activate hydrogen peroxide. Most other AOPs need energy input for this activation such as UV based processes, US based processes, wet air oxidation etc.

The dark reaction of ferrous ion with hydrogen peroxide was found by Fenton (1894). During the last decades, important scientific studies were carried out on the treatment of most toxic chemicals and waste streamns with this process. Another advantage of Fenton process is the applicability of this process in full scale. Because, this process can be accepted as the modification of traditional physico-chemical treatment. Fenton process can control in different steps of mixing and settling processes. By other words this process does not need