

# Textile Waste Water Treatment by Advanced Oxidation Processes

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**Abstract**— Textile effluent are abundant source of colored pollutant that present an enhancing the environmental danger. So the color present in textile effluent is that major concern of researcher today. Dyestuff present in textile effluent is mainly xenobiotic in nature and not easily self-biodegradable. Intensive treatment is necessary to degrade the dyestuff and reduces the COD and turbidity of textile effluent. The present work is an attempt to review the all possible treatment methods for remove dyestuff from textile effluent by Advanced Oxidation Processes (AOPs). The proposed studies in this paper summarize the capability and potential of conventional treatment for degradation of dyestuff from textile effluent. Conventional method for treatment of textile effluent has own certain limitations that can be well overcome by advance oxidation processes (AOPs).

**Keywords**— Advanced oxidation processes, Dyestuff, Photolysis, membranes, nanoparticles, ozonation, photo-Fenton, TiO<sub>2</sub>, UV/hydrogen peroxide, supported photocatalysts, zerovalent iron.

## I. INTRODUCTION

Nowadays, dye effluents are responsible for major environment concern in wastewater treatment. Textile industries consume huge amount of water and it create remarkable amount of wastewater which contain unconsumed dyes and its constituents [1]. Textile industry generates highly polluting wastewater which contains dyes and their decomposition is creating very serious problem to wastewater treatment plant. High color, TDS, toxic metals are present in textile effluents which have been responsible for decrease the capacity of self-degradation of pollutants in wastewater [2]. Historically, different methods have been used for treatment of industrial and domestic wastewaters, drinking water purification and disinfection, ultrapurification of water for especial uses (pharmaceutics or microelectronics), etc.

In most cases, anthropogenically polluted water can be effectively treated by conventional methods, such as biological processes, adsorption on activated carbon or other materials, thermal oxidation, chlorination, ozonation, flocculation precipitation, reverse osmosis (RO), etc.

Biological process is not suitable for decolorization of dyes because of most of the dye is in inorganic and toxic in nature to microorganism used in process. Coagulation technique is more suitable for insoluble dyes but not for soluble dyes, whereas activated carbon is only effective for soluble dyes. Most of the dyes particularly reactive dyes cause highly environment problem due to their decomposition products [3]. Degradation of dyes from textile effluent is very tricky because of complex structure and recalcitrant nature of dyes [4].

However, in some cases, conventional procedures are not adequate to reach the degree of purity required by international or local regulations or by the subsequent use of the effluent. In these cases, Advanced Oxidation Processes (AOPs) or Advanced Oxidation Technologies (AOTs) are efficient novel methods for water treatment that permit the total or partial elimination of compounds resistant to conventional treatments, reduction of toxicity or destruction of pathogen microorganisms.

Advance oxidation processes (AOPs) has great potential to degrade the dyes than conventional methods and it has proved itself as a promising alternative to biological, chemical and physical technique to remove the dyes from textile effluents. AOPs are operating at near atmospheric pressure and temperature which are based on formation of hydroxyl radicals to initiate the oxidation of organic pollutants. AOP can thoroughly oxidize the organic pollutants to CO<sub>2</sub>, H<sub>2</sub>O, salt. AOP are used for degrading the dissolved organic pollutants such as cyclic compounds, halogenated hydrocarbons, phenols, pesticides as well as more suitable for inorganic pollutants such as nitrile, sulfide and cyanide. Combine treatment of various AOPs are responsible for synergistic effect which can reduce the operating time and cost.

AOPs can often demonstrate synergistic effects are based on:

- Ozone (O<sub>3</sub>)
- Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)
- O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>
- Fenton's reaction, Photofenton reaction
- Photochemical oxidation
- UV/ H<sub>2</sub>O<sub>2</sub>
- UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>

- Photochemical catalysis
- UV/TiO<sub>2</sub>

Hydroxyl radicals are highly reactive than ozone. H<sub>2</sub>O<sub>2</sub> reduces the operating cost and size of treatment plants. Mainly all conventional technique produces the secondary pollution after degradation of dyes from wastewater. AOPs can able to remove most of the pollutant from textile effluent without formation of secondary pollutants.

*Characteristics of textile dye effluent:*

Dye effluent of textile industry is mainly generates from bleaching, washing processes. Textile dye effluents are very difficult to treat because of high fluctuation in pH, color, temperature, total dissolved solid (TDS), total suspended solid (TSS) and dissolved solid.

Classification of the dye effluents are carried out in three types according to their chemical oxidation demand (COD), color intensity; high, average and low concentration dye effluents. High concentration dye effluent has COD greater than 1500ppm and negligible light permeability. Average concentration dye effluent has COD in between 800-1500ppm whereas lower concentration dye effluent has less than 800ppm COD content. Generally wastewater treatment is work on upper and lower concentration level.

Category	BOD (ppm)	COD (ppm)	pH	Temperature (°C)
High	500	1500	10	28
Average	270	970	9	28
Low	100	460	10	31

Table 1: Characteristics of dye effluent

Main characteristics of dye effluent are discussed below:

**Color:** Conjugated double bonds in chromospheres group present in dyes are responsible for color.

Color present in dyes effluent is not only creating negative aesthetic effect but also inhibits the self-purification potential of dye effluent by reducing the photochemical synthesis of O<sub>2</sub> and disturb the aquatic ecosystem [8]. Color present in dye effluent absorbs the sunlight which is most necessary aquatic plant to sustain and reducing the aquatic plant which leads to minimise the dissolve oxygen in wastewater. 1-2 ppm concentration of dye color is tolerable limits but more than that of are resisting to oxidizing species, photochemical degradation, and biodegradation. Decolorization of dye effluent is most tricky job for most of the textile industry wastewater treatment plant [9-11].

**Dissolved solids:** Dissolved solid in dye effluents are also important characteristics of textile industry effluent.

Common salt are used in dye processes which tremendously increase total dissolve solid (TDS) in dye effluents. Conventional methods are not sufficient for treating the high TDS dye effluents. High TDS dye effluents has potential to disturb the ground and surface water quality

of water. High TDS water cannot be used as raw water for industry as well as not suitable for irrigation purpose.

**Chlorine:** Chlorine salt is used in textile industry result in residual Cl<sub>2</sub> in textile effluent.

Chlorine present in dyes effluent which reduces the dissolve oxygen (DO) in water body as well as chlorine react with other compound and form complex chlorine salt. Chlorine is very harmful for microbe which used in biodegradation processes.

**Organic materials:** Organic pollutants arise in dye effluent from organic compound are used in textile processing.

Organic dyes, acid, enzymes, tallow and sizing material etc. are contributed to Organic pollutants in dye effluents. Presence of organic pollutants in dye effluents are measured in analysis of BOD and COD. Most of the valuable oxygen is consumed to decompose the organic pollutants in dye effluent.

**Toxic metals:** Metals may act as primary or secondary pollutants and it's very toxic in nature to the aquatic life.

Dye effluent contains metals result from textile processing. That metal creates adverse impact on treatment processes. Removal of metals from dye effluent is very difficult to the conventional process<sup>12</sup>. Metals are reacts with other compound in dye effluent and form complex metal salt which is very difficult to remove from dye effluents. Most of the toxic metals in dye effluent are chromium (Cr), cadmium (Cd), nickel (Ni), zinc (Zn), copper (Cu), lead (Pb), ferrous (Fe) etc.

Metals	mg/L.
Cr	19.2
Cd	16.7
Ni	8.5
Zn	15.8
Cu	47.7
Pb	32.2
Fe	7.5

Table 2: Metals present in dye effluent from textile industry

## II. TREATMENT OF TEXTILE DYE EFFLUENT

Most of the dye effluent is generated from preparation processes rather than dyeing operation in textile industry. Dye effluent is mainly consisting of dyes, salt, sizing agent, moderant and surfactants [12].

Normal wastewater treatment plants are not suitable for removing the reactive dyes from textile effluent due to their

retardation towards the aerobic and short period anaerobic treatment [14]. Mainly 3 methods are used for treatment of textile effluent. Those methods have been detail categorized on the basis of their working principle involved. The physical removal of dye from textile effluent is used in physical treatment whereas chemical treatment involved the chemical method for removal of dyes while biodegradation of dye are involved in biological treatment.

**Physical treatment:** Physical methods likes adsorption, ion-exchange and irradiation, filtration are most applicable methods in treatment of textile wastewater plants. These methods are widely used in industry to its high dye removal potential and low operating cost [15]. Ion exchange is very specific in nature for dyes and other impurity present in wastewater which has responsible for reduces the capability of processes [22, 23]

**Chemical treatment:** Physical methods are not suitable for complete removal of dye from textile effluent, because it requires further treatment for remove the solid waste from textile effluent that add extra cost to the treatment. Chemical methods have their own drawbacks but it is commonly used for their easiness and cost benefits. Chemical methods likes flocculation and coagulation [24] technique are commonly used for remove the organic pollutants. Coagulation technique are very effective for degrade the insoluble dyes but not so well for soluble dyes in textile effluent [25, 26]. The major drawbacks of these methods are generation of mud and extra cost required for remove such mud [27]. It leads to the increase the total operating cost of the process.

**Biological treatment:** Physical and chemical methods are not much applicable for removing the dyes from textile effluent, because of the high cost, low efficiency, highly specific in nature. Biological methods are a green technique to remove dye from textile effluent with minimum cost and optimum operating time [28]. Biological method can effectively remove the chemical oxygen demand (COD) and turbidity [29] but not much effective for decolorization of textile effluent. For decolorization of textile effluent, series arrangement of anaerobic followed by an aerobic treatment is the most suitable arrangement for decolorization in biological treatment [31-32].

**Advanced Oxidation Processes (AOP's):** AOP are generating highly oxidizing species and hydroxyl radical, which can responsible for decomposition of organic pollutant present in wastewater. Oxidation potential ( $E < 2.72$  v/s NHE) of these radicals is high, which result in high reactivity with pollutants. Other reactive oxygen species (ROS) like  $HO\bullet$ ,  $O_2\bullet^-$ ,  $HO_2\bullet$ ,  $H_2O_2$  are also formed and contribute to the redox processes enabling the transformation of the target pollutant.

The reaction of these radicals with organic pollutants depends on functional group present in it. The organic components are oxidizing to formation of unstable radicals, which can easily oxidize to  $H_2O$ ,  $CO_2$  and acids.

Most common AOPs are listed in Table 3:

Non-Photochemical Processes	Photochemical Processes	
	Type of Process	Irradiation Wavelength Range ( $\lambda$ /nm)
Alkaline ozonation ( $O_3/HO\bullet$ )	Water photolysis in vacuum ultraviolet (VUV)	< 190
Ozonation with hydrogen peroxide ( $O_3/H_2O_2$ )	UV/hydrogen peroxide (UV/ $H_2O_2$ )	< 280
Fenton and related processes ( $Fe^{2+}/H_2O_2$ )	UV/ozone (UV/ $O_3$ )	280-315
Electrochemical oxidation	Photo-Fenton (PF) and related processes	UV-Vis up to 450
$\gamma$ -Radiolysis and electron-beam treatment	Zerovalent iron plus UV light	UV range
Non-thermal plasma (surface corona discharge)	Heterogeneous photocatalysis (HP) using $TiO_2$	UV: up to 380-400
Electrohydraulic discharge-ultrasound (US, cavitation)		
Wet air oxidation		
Supercritical water oxidation		
Zerovalent iron (ZVI)		
Ferrate		

Table 3: Advanced Oxidation Processes

**NON-PHOTOCHEMICAL PROCESSES:**

**Ozonation:** Ozonation processes are very effective for degradation of reactive dyes [41], reduction of COD [42], removal of toxic pollutants [43-45] from textile effluent.

Pre-oxidation processes are shows the remarkable improvement in biological degradation of organic pollutants

[46-48] and post-oxidation process enhance the treated effluent quality to meet the environmental legislation [49]. The main drawback of ozonation is its short half-life period; this can be again reduced if dyestuffs are present. Acidic condition is more favorable for ozonation, so that careful adjustment of the textile effluent pH is required [50].

**Electrochemical process:** Electrochemical process is widely used for removal of dyestuff from textile effluent in green pathway [51].

This process is very effective to remove the toxic and inorganic pollutant from textile effluent by direct or indirect oxidation. Most of the electrochemical process is widely used for degradation of dyestuff containing either mercury electrode [52], graphite rod [53], iron [54], boron doped diamond electrode [55], platinum foil [56], Al [57], titanium/platinum as anode and SS304 as cathode [58] in treatment of textile effluent. This method is very economic because of very small amount of chemical required for the process and stability of process is easily achieved by manipulating the electric current.

**Ozonation (O<sub>3</sub>) / hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>):** The combine treatment of ozone and hydrogen peroxide are very useful for degradation of dyes in textile effluent [60].

Additions of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> in textile effluent are enhancing the decomposition of O<sub>3</sub> and accelerate the generation of hydroxide radicals. At alkaline condition, slow reaction is observed in between hydrogen peroxide and ozone whereas at pH greater than the 5 a rapid acceleration has been observed [61]. At higher pH, maximum hydrogen peroxide is dissociated in to hydroxyl radicals [62].

**Fenton process:** The reaction of ferrous iron with hydrogen peroxide is known as fenton's reaction.

Fenton process is broadly used for the degradation of reactive dyes due to the coagulation and catalytic oxidation properties of fenton reagent [63]. Fenton process is very economic, easy to use and effective for the degradation of an organic pollutant [64]. The main advantage of the fenton process is that no energy required for activating the H<sub>2</sub>O<sub>2</sub>.

Fenton process is very effective process when high amount of chemical oxidation demand reduction is required [64-67].

#### PHOTOLYTIC CHEMICAL PROCESS

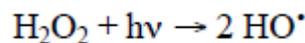
*Homogeneous Photolytic chemical process:*

**Ultraviolet lamp (UV):**

Mainly UV process is used to initiate the oxidizing agent such as hydrogen peroxide and degradation of dyestuff influenced by the pH, dye structure, dye effluent composition and intensity of UV radiation [68]. UV process can be used to dyes molecules into CO<sub>2</sub>, H<sub>2</sub>O and salt [69]. Mainly UV process operated at lower pressure with principle wavelength of 254nm. Strong oxidizing agent generate the hydroxyl radical in presence of UV light to degrade the dyestuff in textile effluent [70]. The main advantage of this process is no mud/slug formation after treatment.

**UV/H<sub>2</sub>O<sub>2</sub>**

The oxidizing power of hydrogen peroxide can be sensibly improved by HO• generation through cleavage of the O-O union with photons of high energy ( $\lambda < 280$  nm). The reaction has a low quantum yield ( $\phi_{HO\bullet} = 0.5$ ) due to rapid recombination of the radicals in solution, and produces almost quantitatively one HO• per quantum of radiation absorbed in the 200-300 nm range:

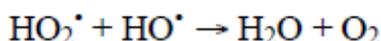
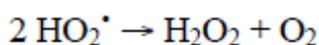
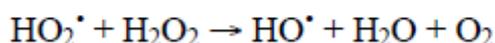


H<sub>2</sub>O<sub>2</sub> photolysis is usually performed with low- or medium- pressure mercury vapor lamps. Almost 50% of the energetic consumption is lost in the form of heat or emissions less than 185 nm, which are absorbed by the quartz jacket. Generally, cheap germicidal lamps are used; however, since H<sub>2</sub>O<sub>2</sub> absorption is maximal at 220 nm, it is more convenient to use Xe/Hg lamps that - although more expensive - emit in the 210-240 nm range.

In addition to H<sub>2</sub>O<sub>2</sub> other species can absorb photons at these short wavelengths, and they can act as light filters. However, if the contaminants can be directly photolyzed, this may improve the efficiency of the oxidative destruction process. Since the intensity of UV radiation decays exponentially towards the bulk of the solution, it is necessary to establish conditions of turbulent flow to renew continuously the solution surrounding the luminous source. The UV fluence rate [85] varies with distance from the lamp and it is a function of the absorptive characteristics of the media through which the UV radiation passes. Both the organic contaminant and H<sub>2</sub>O<sub>2</sub> may absorb UV radiation, reducing the transmitted fluence rate and changing the effectiveness of HO• production throughout the photoreactor. Reflection, refraction, shadowing, and lamp characteristics influence also the radiant power distribution within a UV reactor [86].

In the presence of oxygen and organic compounds, multiple pathways are operative in the UV/H<sub>2</sub>O<sub>2</sub> system involving the generation of hydroxyl, organic and organic peroxy radicals [87].

A high pH should be avoided because bicarbonate and carbonate ions (coming from the mineralization or present in the waters) are competitive HO• trapping species. In most degradations performed by UV/H<sub>2</sub>O<sub>2</sub>, optimum values for H<sub>2</sub>O<sub>2</sub> concentration have been found, beyond which an inhibitory effect takes place [88]. At high H<sub>2</sub>O<sub>2</sub> concentrations, competitive reactions occur in accordance with the following scheme [89]:



Hydroxyperoxyl ( $\text{HO}_2^\bullet$ ) radicals are produced through reaction but these radicals are much less reactive than  $\text{HO}^\bullet$  ( $E_0 = 1.7$  vs.  $2.8$  V).

In all cases, it is necessary to determine the optimal  $\text{H}_2\text{O}_2$  concentration, which will depend on the concentration and chemical nature of the pollutants in the effluent stream. Consequently, treatability tests are needed to determine the right amount of  $\text{H}_2\text{O}_2$  and to validate the technology. The use of UV/peroxide offers some advantages: the oxidant is commercially accessible, thermally stable, and can be stored in the site of use (with the required precautions). Since  $\text{H}_2\text{O}_2$  has an infinite solubility in water, it is an effective source of  $\text{HO}^\bullet$ . There is no mass transfer problems associated with gases, as in the case of ozone. Since the needed amounts of the reagent are relatively low, the process is rather economical. The method has a low efficiency for treating waters of high absorbance at  $\lambda < 300$  nm, or containing substances that compete with  $\text{HO}^\bullet$  generation. In these cases, a large amount of  $\text{H}_2\text{O}_2$  is needed [89].

The UV/ $\text{H}_2\text{O}_2$  technology is one of the oldest AOPs and has been successfully used in the removal of contaminants from industrial effluents, including organochlorinated aliphatics, aromatics, phenols (chlorinated and substituted) and pesticides. It allows to extend the earlier UV-C technology for disinfection for simultaneous treatment of chemical detoxification.

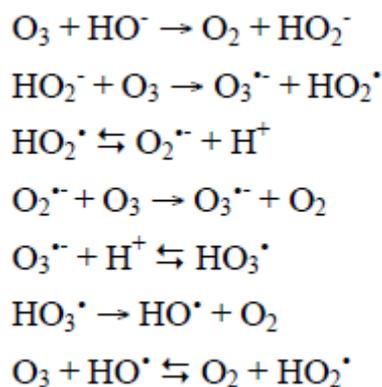
At present, UV/ $\text{H}_2\text{O}_2$  technology is totally commercialized. The method can be sensibly improved by combination with ultrasound or by pretreatment with ozone [89].

A more ambitious approach was made by Alpert et al. [86] by using numerical models for the design and optimization of UV/ $\text{H}_2\text{O}_2$  systems incorporating both reaction design (hydrodynamics, lamp orientation) and chemical kinetics (reaction mechanisms, kinetic rate constants) using computational fluid dynamics (CFD) and solving the fluid dynamics equations through space and time, including the conservation of mass, momentum, and energy. The authors concluded that effective CFD models for AOPs should incorporate rigorous turbulence and fluence rate submodels, kinetic rate equations, and proper characterization of the background water matrix. As soon as oxidation pathways for water contaminants are identified, a simulation model may become an important tool for the design and optimization of AOPs, and the model will allow evaluation of multiple design scenarios, including number of lamps, layout of reactors, and upstream hydraulic conditions. More advanced turbulence models, including those incorporating the Reynolds Stress Model and/or the Large Eddy Simulation, would enhance the modeling, together with a more rigorous method for validation of the UV fluence (dose) distribution in UV/AOP. In addition, reactors should be evaluated using multiple irradiance sensors and/or online chemical actinometers. Since the reaction mechanisms for additional emerging contaminants become available, especially quantification of specific byproduct formation, CFD should be considered as a tool for predicting the outcome of direct

photolysis and advanced oxidation on environmentally important compounds.

#### UV/ $\text{O}_3$ :

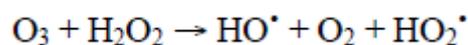
It has been demonstrated that ozone decomposition in aqueous solution forms  $\text{HO}^\bullet$ , especially when initiated by  $\text{OH}^-$



It must be highlighted that ozone final products are  $\text{O}_2$  and  $\text{H}_2\text{O}$ , making the method less toxic to other conventional treatments that use  $\text{C}_{12}$  or chromic acid. Ozonation is a good pretreatment before a biological treatment, because complex organics are transformed into aldehydes, ketones or carboxylic acids, all easily biodegradable compounds. Ozonation is also versatile to be combined with other conventional or AOPs.

However, from the operational point of view, there are limitations associated with the gas-liquid ozone mass transfer [89-92]. Consequently, the process requires efficient reactor design in order to maximize the ozone mass transfer coefficient; increasing the interfacial area of contact (the bubble size by using small size diffusers, ceramic membranes, etc. [92]), good stirring, line mixers, contact towers, etc. can favor the process. In addition, increasing the retention time in the reactor by large bubble columns, or increasing the solubility of ozone by increasing the pressure to several atmospheres, may be effective. Addition of  $\text{H}_2\text{O}_2$  to the ozonation system enhances the oxidation capacity of the process through secondary reactions.

Hydrogen peroxide initiates  $\text{O}_3$  decomposition by electron transfer. Set of reactions is initiated by  $\text{HO}^\bullet$  producing reaction [89]:

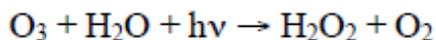


The process is expensive but fast, and can treat organic pollutants at very low concentrations (ppb), at pH between 7 and 8; the optimal  $\text{O}_3/\text{H}_2\text{O}_2$  molar ratio is  $\cong 2:1$ . It was suggested that the acceleration of ozonation is due to the increase of ozone transfer in water by  $\text{H}_2\text{O}_2$ .

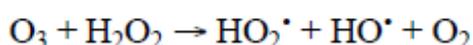
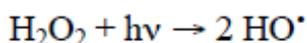
One of the principal fields of application of this treatment is in the degradation of pesticides [93]. It is also effective for

the post-treatment of water previously treated with chlorine because it can decompose trihalomethanes or related compounds.

When ozone is combined with UV irradiation, several processes take place. Irradiation of ozone in water leads to quantitative formation of H<sub>2</sub>O<sub>2</sub> [94]:



As said before, photolysis of H<sub>2</sub>O<sub>2</sub> by UV-C radiation yields two hydroxyl radicals per each molecule of hydrogen peroxide; the reagent also reacts with O<sub>3</sub>:



As well as H<sub>2</sub>O<sub>2</sub>, ozone reacts with hydroxyl radicals to form superoxide radicals:



Since ozone has a higher absorption coefficient than H<sub>2</sub>O<sub>2</sub> (ε<sub>254</sub> = 3300 M<sup>-1</sup> cm<sup>-1</sup>), this combined AOP can be used to treat water with high UV absorption background.

**O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV:** Generation of hydroxyl radicals are remarkable enhance when hydrogen peroxide is added in O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> [71]. These OH radical generation process is very effective and fast for mineralization of pollutants [72]. In treatment of textile effluent O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV processes are observed that the complete decolorisation is achieved [73].

**Photo-fenton process:** In photo-fenton process, hydroxyl radical formation is greatly enhanced by UV lamp [74-75]. Efficiency of decolorisation of textile effluent by fenton process is similar to photo-fenton process but mineralization process is highly improved in case of photo-fenton process [76].

#### Heterogeneous Photolytic chemical process:

In photo-catalytic process, photo-induced reaction enhances the efficiency of the process [79]. Absorption of photon with energy (≥ band gap energy of catalyst) is essential for carry out the photo-catalyst reaction [80]. Photo-catalyst process is widely used for degradation of dyestuff from textile effluent because of complete mineralization can achieved [81-88]. Mostly TiO<sub>2</sub> and ZnO are widely used as a photo catalyst to remove organic pollutant and dyestuff from wastewater.

AOPs are developed and commercialized to a variable degree and are undergoing constant change as technological advances take place. At present, UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>, PF and HP are totally or partially commercialized.

Semiconductor is consisting of two energy band, high energy conduction and low energy valence band. Semiconductor-sensitized photolytic chemical oxidation is used for formation OH radical in heterogeneous processes. Zinc oxide, strontium titanium trioxide and TiO<sub>2</sub> have been used for commercial application [77].

Valence and conduction band of semiconductor material separated by energy gap or band gap [78].

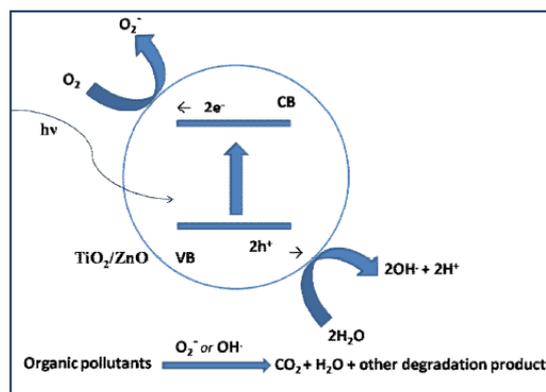
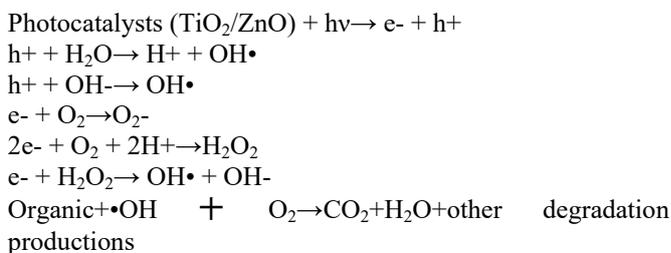


Figure 1: Schematic of the photocatalytic mechanism for TiO<sub>2</sub>/ZnO photocatalysts.

When a photocatalytic surface is exposed by a radiation of energy equal to or greater than the bandgap energy of the semi-conductor photocatalyst material, it creates a positively charged hole in the valence band and negatively charged electron in the conduction band by exciting the electrons in the valence band to the conduction band.



The conduction band electron reduces oxygen (into O<sub>2</sub><sup>-</sup>) adsorbed to photocatalyst surface (TiO<sub>2</sub>/ZnO) whereas the positively charged hole oxidizes either organic pollutants directly or indirectly by water to produce hydroxyl free radicals (HO).

### III. PRACTICAL APPLICATIONS

#### Coupling of AOPs with Biological Treatments

The use of AOPs as a single treatment stage is not economically convenient to treat large volumes of effluents due to high electrical or chemical costs compared with

biological treatments. On the contrary, although biological treatments are cheaper, they are time-consuming and several pollutants are biorecalcitrant. In last times, some studies aimed to reduce the toxicity of an effluent with an AOP up to a certain level beyond which a biological oxidation is applied to achieve total detoxification; the application of the initial AOP pretreatment decreases the total treatment time. Due to the extension of this article, these couplings will not be described here, but several references can be found in the literature [95-97].

### **Comparative Studies on AOPs**

The election of one AOP for the treatment of a wastewater must be evaluated from an economical and practical point of view. Mostly, the choice of the AOP is based on its effectiveness to achieve the target concentration, pH, COD, etc. and, once the process is shown to be adequate, the election must be economical. The criteria to compare the performance depend highly on the properties of the wastewater. From the existing literature, it can be seen that generally direct photolysis results in incomplete and slow degradation of the pollutant unless the target compound absorbs strongly at the irradiation wavelength. Addition of  $H_2O_2$  to the UV illuminated system results in a faster degradation; however, a strict control of the  $H_2O_2$  dose is needed to avoid excess of the reagent, which becomes a competitor for  $HO\cdot$ . It has been observed, when comparing different technologies, that photo-Fenton is generally the most efficient, and complete mineralization occurs in most cases only using the individual process; however, the ratio of reagents (i.e., the  $Fe/H_2O_2$  molar ratio) needs to be always optimized. Another drawback of the PF technology is that acid pH is needed and must be maintained to prevent precipitation of iron compounds. This restriction adds a previous acidification step and the further alkalization for iron elimination of the media [98]. Gogate and Pandit [92] compare five different oxidation processes: cavitation, HP, Fenton processes, ozonation and use of  $H_2O_2$ . Although US/cavitation is not treated in the present article, the reference should be consulted as the following main points highlighted by the authors are applicable to all AOPs:

- 1) The efficacy of the process depends strongly on the rate of generation of free radicals together with a good contact of these radicals and/or chemical oxidants with the pollutant molecules; the efficient design should then aim at maximizing both features.
- 2) Although a large amount of literature is available for application of HP to wastewater treatment for different model pollutants, studies with real effluents are scarce and strong efforts are required in this direction.
- 3) The development of global kinetic models to predict the reaction rates, helpful in designing large-scale reactors, are needed. The models should be function of critical parameters such as pollutant concentration, presence of radical scavengers, or presence of constituents enhancing the rates by arresting the electron-hole recombination.

4) Fenton chemistry seems to be beneficial if used as a supplement to enhance the rates of, e.g., HP and acoustic cavitation processes rather than its use as individual technology.

5) Ozone or hydrogen peroxide as individual processes is not economically favorable, and they should be used in combination with others (mainly ultrasound and UV irradiation, which lead to the formation of free radicals).

### **Combination of AOPs:**

Although most AOPs can be used individually in wastewater treatment applications with good economics and high degree of energy efficiency, hybrid methods (mostly a combination of AOPs) generally improve the global treatment.

These combinations increase the photoprocess efficiency by decreasing the reaction time in respect to the separated operations, or decrease the cost in respect of HP alone, generally in terms of light energy. The most used combinations are  $UV/O_3/H_2O_2$ , photo-Fenton processes combined with  $TiO_2$ , combinations with PAOPs with ultrasound, wet air oxidation or other non-photochemical AOP, etc. As said before, combination of AOPs with conventional methods, mainly biological oxidation is very much studied at present.

The choice of the combination will be dictated by the type of wastewater to be treated. It is always mandatory to perform a treatability study of wastewaters before real application of the technologies.

Recently, Lucas et al. [99] compared different ozonebased advanced oxidation processes ( $O_3$ ,  $O_3/UV$  and  $O_3/UV/H_2O_2$ ) for the treatment of winery wastewater in a pilot-scale bubble column reactor. It was found that at the natural pH of the studied wastewater (pH 4),  $O_3/UV/H_2O_2$  was the most effective treatment, followed by  $O_3/UV$  and  $O_3$ . The authors performed an economic analysis of the operating costs showing that the  $O_3/UV/H_2O_2$  combination was also the most economical process.

A recent review [94] analyzes combinations of HP with chemical and physical operations as tools for improving the photoprocess performance. In the specific case of HP, two categories of combinations were considered because the efficiency may be affected by different factors. In the first one, the technology influences directly (and can enhance) the photocatalytic mechanism, as this is the case of e.g. ultrasonic irradiation, photo-Fenton, ozonation or electrochemical treatments. A second category includes the coupling with methods not affecting the photocatalytic mechanism, such as biotreatments, membrane reactor, membrane photoreactor, or physical; in these cases, the combination increases the efficiency of the overall process. Thus, the application of the combined technologies should be directed to the factors affecting these two different aspects. The authors highlight that the main drawback of HP are the very low quantum efficiencies reached (< 1%), which

implies that only one over one hundred of the incident photons is able to produce an oxidation/ reduction step.

Depending on the concentration of the contaminant present and on the desired degree of oxidation, it is necessary to provide the photoreacting system with a photon flow two orders of magnitude higher than that eventually utilized. In real contaminated waters, having different pollutants, at high concentrations and in high volumes, the magnitude of the photon flow needed for the treatment would be very high, and the process would not be economic. Sun can also give photons but only ca. 5% of them (ca. 30 W m<sup>-2</sup>) can be used by TiO<sub>2</sub> (due to its bandgap), and this cannot satisfy the needs of the treatment in a realistic way. Based on these considerations, the authors propose that the use of photocatalysis for wastewater remediation would be successful if addressed only to the transformation of recalcitrant to non-recalcitrant compounds, which subsequently can be easily degraded by conventional techniques. Therefore, the coupling of HP with other chemical and physical operations seems a good strategy to achieve the remediation goal. Additionally, for each system, treatability tests in different conditions must be done to find the best technology.

#### IV. CONCLUSION:

The paper shows that various methods are available for textile effluent treatment but none of the single method is sufficient to remove all pollutants from textile effluent, because of each and every methods are suffer from certain limitation either these are very costlier, lack of efficiency, generation of secondary pollutants and some of them treatment can pose risk to human health. Whereas, advance oxidation processes (AOPs) system are emerge as promising alternative with great potential to remove all kind of pollutant from textile effluent. AOP systems are highly specific in nature and its selection are mainly depend on dyestuff which need to be remove from form textile effluent. Combined AOP systems are most effective and economic than the single AOP system. Combination of AOP system and its sequence has been decided after laboratory research. Prior to implement the AOP system, laboratory test is very essential to check the economy and performance of AOP system. Ultimately, paper concluded that AOP are arises as most promising option compared to other conventional treatment methods for textile effluent.

#### REFERENCES

- [1] S.S. Kalra, S. Mohan, A. Sinha and G. Singh, Advanced Oxidation Processes for Treatment of Textile and Dye Wastewater: A Review, 2nd International Conference on Environmental Science and Development, 2011, 4, 271-275.
- [2] R.G. Saratale, G.D. Saratale, J.S. Chang, S.P. Govindwar, Bacterial decolorization and degradation of azo dyes: A review, Journal of the Taiwan Institute of Chemical Engineers, 2011, 42 (1), 138-157.
- [3] I. Arslan-Alaton, O. Seremet, Advanced treatment of biotreated textile industry wastewater with ozone, virgin/ozonated granular activated carbon and their combination, Journal of Toxic/Hazardous Substances and Environmental Engg., 2004, 39, 1687-1700.
- [4] D. Brown, Effects of colorants in the aquatic environment, Journal of Ecotoxicology and Environmental Safety, 1987, 13, 139- 147.
- [5] S. Palit, Studies on ozone-oxidation of dye in a bubble column reactor at different pH and different oxidation-reduction potential, Journal of Environmental Science and Development, 2010, 1, 341-346.
- [6] J.H. Carey, An introduction to AOP for destruction of organics in wastewater, Water Quality Research Journal of Canada, 1992, 27 (1), 1-21.
- [7] S.H. Lin, C.F. Peng, Treatment of textile wastewater by electrochemical method, Journal of Water Research, 1994, 28 (2), 277-82.
- [8] X. Zhou, X. Xiang, Effect of different plants on azo-dye wastewater bio-decolorization, Procedia Environmental Sciences, 2013, 18, 540- 546.
- [9] K. Turhan, I. Durukan, S. A. Ozturkcan, Z. Turgut, Decolorization of textile basic dye in aqueous solution by ozone, Dyes and Pigments, 2012, 92 (3), 897-901.
- [10] K. Turhan, Z. Turgut, Decolorization of direct dye in textile wastewater by ozonization in a semibatch bubble column reactor, Desalination, 2009, 242, 256-263.
- [11] A.B. Dos Santos, F.J. Cervantes, J.B. van Lier, Review paper on current technologies for decolorisation of textile wastewaters: Perspectives for anaerobic biotechnology, Bioresource Technology, 2007, 98 (12), 2369-2385.
- [12] K. Gopalakrishnan, T. Jeyadoss, Comparative study on biosorption of Zn(II), Cu(II) and Cr(VI) from textile dye effluent using activated rice husk and activated coconut fibre, Indian journal of chemical technology, 2011, 18, 61-66.
- [13] R.S. Lokhande, P.U. Singare, D.S. Pimple, Toxicity study of heavy metals pollutants in waste water effluent samples collected from taloja industrial estate of Mumbai, India, Resources and Environment, 2011, 1, 13-19.
- [14] G.M. Shaul, T.J. Holdsworth, C.R. Dempsey, K.A. Dostal, Fate of water soluble azo dyes in activated sludge process, Chemosphere, 1991, 22 (1-2), 107-119.
- [15] M.J. Iqbal, M.N. Ashiq, Adsorption of dyes from aqueous solutions on activated charcoal, Journal of Hazardous Materials, 2007, 139 (1-2), 57-66.
- [16] M.F.R. Pereira, S.F. Soares, J.J.M. Orfao, J.L. Figueiredo, A desorption of dyes on activated carbons: influence of surface chemical groups, Carbon, 2003, 41 (4), 811-821.
- [17] G. Mckay, G. Ramprasad, P.P. Mowli, Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-cost materials, Water Air and Soil Pollution, 1986, 29 (3), 273-283.
- [18] S.K. Khare, K.K. Panday, R.M. Srivastava, V.N. Singh, Removal of victoria blue from aqueous solution by fly ash, Journal of Chemical Technology and Biotechnology, 1987, 38 (2), 99-104.
- [19] B.K. Singh, N.S. Rawat, Comparative sorption equilibrium studies of toxic phenols on fly ash and impregnated fly ash, Journal of Chemical Technology and Biotechnology, 1994, 61 (4), 307-317.
- [20] B.K.G. Theng, N. Wells, Assessing the capacity of some new zealand clays for decolorizing vegetable oil and butter, Applied Clay Science, 1995, 9, 321-326.
- [21] R.S. Juang, F.C. Wu, R.L. Tseng, The ability of activated clay for the adsorption of dyes from aqueous solutions, Environment Technology, 1997, 18 (5), 525-531.
- [22] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technology, 2001, 77 (3), 247-255.

- [23] K. Dajkaa, E. Tak!Acsa, D. Solpanb, L. Wojnarovitsa, O. Guven, High-energy irradiation treatment of aqueous solutions of C.I. reactive black 5 azo dye: pulse radiolysis experiments, *Radiation Physics And Chemistry*, 2003, 67 (3), 535–538.
- [24] S. Meric, H. Selcukb, V. Belgiorno, Acute toxicity removal in textile finishing wastewater by fenton's oxidation, ozone and coagulation–flocculation processes, *Water Research*, 2005, 39 (6), 1147–1153.
- [25] S.F. Kang, C.H. Liao, S.T. Po, Decolorization of textile wastewater by photo-fenton oxidation technology, *Chemosphere*, 2000, 41 (8), 1287-1294.
- [26] W. G. Kuo, Decolourizing Dye Wastewater with Fenton's reagent, *Water Research*, 1992, 26 (7), 881- 886.
- [27] M. Fukushima, K. Tatsumi, K. Morimoto, The fate of aniline after a photo-fenton reaction in an aqueous system containing iron(III), humic acid, and hydrogen peroxide, *Environmental Science and Technology*, 2000, 34 (10), 2006-2013.
- [28] I.M. Banat, P. Nigam, D. Singh, R. Marchant, Microbial decolorization of textile-dye containing effluents: a review, *Bioresource Technology*, 1996, 58 (3), 217-227.
- [29] S. Jun Kim, K. Ishikawa, M. Hirai, M. Shoda, Characteristics of a newly isolated fungus, *geotrichum dec 1*, which decolorizes various dyes, *Journal of Fermentation and Bioengineering*, 1995, 79 (6), 601-607.
- [30] S.H. Lin, C. C. Lo, Fenton process for treatment of desizing wastewater, *Water Research*, 1997, 31 (8), 2050-2056.
- [31] S. Ledakowicz, M. Solecka, R. Zylla, Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes, *Journal of Biotechnology*, 2001, 89 (2-3), 175-184.
- [32] S-A. Ong, E. Toorisaka, M. Hirata, T. Hano, Treatment of azo dye orange ii in aerobic and anaerobic- SBR systems, *Process Biochemistry*, 2005, 40 (8), 2907–2914.
- [33] H. Bornick, P. Eppinger, T. Grischek, E. Worch, Simulation of biological degradation of aromatic amines in river bed sediments, *Water Research*, 2001, 35 (3), 619-624.
- [34] L. Wang, S. Barrington, J-W. Kim, Treatment of azo dye orange ii in aerobic and anaerobic-SBR systems, *Process Biochemistry*, 2005, 40 (8), 2907–2914.
- [35] F. Orshansky, N. Narkis, Characteristics of organics removal by pact simultaneous adsorption and biodegradation, *War. Research*, 1997, 31 (3), 391-398.
- [36] M. Fukushima, K. Tatsumi, K. Morimoto, The fate of aniline after a photo-fenton reaction in an aqueous system containing iron(III), humic acid, and hydrogen peroxide, *Environmental Science and Technology*, 2000, 34 (10), 2006-2013.
- [37] E. Pramauro, A.B. Prevot, V. Auquqliaro, L. Palmisano, Photocatalytic treatment of laboratory wastes containing aromatic amines, *Analyst*, 1995, 120, 237-242.
- [38] H.M. Pinheiro, E. Touraud, O.Thomas, Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters, *Dyes and Pigments*, 2004, 61 (2), 121–139.
- [39] I. Oller, S. Malato, J.A. Sanchez-Perez, Combination of advanced oxidation processes and biological treatments for wastewater decontamination—A review, *science of the total Environment*, 2011, 409 (20), 4141–4166.
- [40] W. Chu, W.K. Choy, T.Y. So, The effect of solution pH and peroxide in the TiO<sub>2</sub>-induced photocatalysis of chlorinated aniline, *Journal of Hazardous Materials*, 2007, 141, 86–91.
- [41] S. Liakou, S. Pavlou, G. Lyberatos, Ozonation of dyes, *Water Science and Technology*, 1997, 141, 279-286.
- [42] O. Karahan, H. Dulkadiroglu, I. Kabdasli, S. Sozen, F.G. Babuna, D. Orhon, Effect of ozonation on the biological treatability of a textile mill effluent, *Environmental Technology*, 2002, 23 (12), 1325- 1336.
- [43] S. G.de Moraes, R. S. Freire, N. Duran, Degradation and toxicity reduction of textile effluent by combined photocatalytic and ozonation processes, *Chemosphere*, 2000, 40 (4), 369-373.
- [44] A.R. Tehrani-Bagha, N.M. Mahmoodi, F.M. Menger, Degradation of a persistent organic dye from colored textile wastewater by ozonation, *Desalination*, 2010, 260 (1-3), 34–38.
- [45] H. Selcuk, Decolourization and detoxification of textile wastewater by ozonation and coagulation processes, *Dyes and Pigments*, 2005, 64 (3), 217-222.
- [46] S. Ledakowicz, M. Solecka, R. Zylla, Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes, *Journal of Biotechnology*, 2001, 89 (2-3), 175-184.
- [47] I.A. Arslan, A.B. Isil, W.B. Detlef, Advanced oxidation of reactive dye bath effluent: comparison of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>/UV-C and TiO<sub>2</sub>/UV-A processes, *Water Research*, 2002, 36 (5), 1143-1154.
- [48] A. Baban, A. Yediler, D. Lienert, N. Kemerdere, A. Kettrup, Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant, *Dyes and Pigments*, 2003, 58 (2), 93-98.
- [49] B.R. Lim, H.Y. Hu, K.H. Ahn, K. Fujie, Oxidative treatment characteristics of biotreated textiledyeing wastewater and chemical agents used in a textile-dyeing process by advanced oxidation process, *Water Science Technology*, 2004, 49 (5-6), 137-143.
- [50] B. Ahmet, Y. Ayfer, L. Doris, N. Nese, K. Antonius, Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant, *Dyes and Pigments*, 2003, 58 (2), 93-98.
- [51] F.M. Esteves, J.D. Saliva, Electrochemical degradation of reactive blue 19 dye in textile wastewater, *Roubaix*, 2004, 4, 1-6.
- [52] M.V.B. Zanoni, A.G. Fogg, C.C.I. Guaratini, Assessment of the application of cathodic stripping voltammetry to the analysis of diazo reactive dyes and their hydrolysis products, *Dyes and Pigments*, 2001, 50 (3), 211 – 221.
- [53] E-S. Z. El-Ashtoukhy, N. K. Amin, M. H. Abdel-Aziz1, Decolorization of Acid Brown and Reactive Blue Dyes by Anodic Oxidation in a Batch Recycle Electrochemical Reactor, *International Journal of Electrochemical Science*, 2012, 7, 11137 – 11148.
- [54] I. A. Sengil, M. Ozacar, The decolorization of C.I. Reactive Black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes, *Journal of Hazardous Materials*, 2009, 161 (2-3), 1369–1376.
- [55] A. Lopes, S. Martins, A. Morao, M. Magrinho, I. Goncalves, Degradation of a Textile Dye C. I. Direct Red 80 by Electrochemical Processes, *Portugaliae Electrochimica Acta*, 2004, 22, 279-294.
- [56] D. Dogan, H. Turkdemir, Electrochemical treatment of actual textile indigo dye effluent, *Polish Journal of Environmental Studies*, 2012, 21 (5), 1185-1190.
- [57] Y. S. Yildiz, Optimization of Bomaplex Red CR-L dye removal from aqueous solution by electrocoagulation using aluminum electrodes, *Journal of Hazardous Materials*, 2008, 153 (1-2), 194– 200.
- [58] N.M. Abu Ghalwa, M.S. Abdel-Latif, Electrochemical degradation of acid green dye in aqueous wastewater dyestuff solutions using a lead oxide coated titanium electrode, *Journal of the Iranian Chemical Society*, 2005, 2 (3), 238-243.
- [59] M.N. Priya, K. Palanivelu, Electrochemical oxidation of reactive dye green HE4BD using solar energy, proceeding

- of the 10th International Conference on Environmental Science and Technology, 2007, 5, 870-876.
- [60] A. Al-Kdasi, A. Idris, K. Saed, C.T. Guan, Treatment of textile wastewater by advanced oxidation processes – A review, *Global Nest: the International Journal*, 2004, 6, 222-230.
- [61] J. Staehlin, J. Hoigne, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, *Environmental Science and Technology* (1982) 16 676-681.
- [62] I. Arslan, A.B. Isil, I.A. Tuhkanen, Advanced oxidation of synthetic dyehouse effluent by O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>/UV processes, *Environmental Technology* (1999) 20 921-931.
- [63] R. Liu, H.M. Chiu, C.S. Shiau, R.Y.L. Yeh and Y.T. Hung, Degradation and sludge production of textile dyes by Fenton and photo-Fenton processes, *Dyes and Pigments* (2007) 73 1-6.
- [64] P. Bautista, A.F. Mohedano, M.A. Gilarranz, J.A. Casas, J.J. Rodriguez, Application of Fenton oxidation to cosmetic wastewaters treatment, *Journal of Hazardous Materials* (2007) 143 128-134.
- [65] R.J. Bigda, Consider Fenton's chemistry for wastewater treatment, *Journal of Chemical Engineering Progress* (1995) 91 62-66.
- [66] H. Lee, M. Shoda, Removal of COD and color from livestock wastewater by the fenton method, *Journal of Hazardous Materials* (2008) 153 1314-1319.
- [67] T. Yonar, Treatability studies on traditional hand-printed textile industry wastewaters using fenton and fenton-like processes: plant design and cost analysis, *Fresenius Environmental Bulletin* (2010) 19 122758-122768.
- [68] H. Chun, W. Yizhong, Decolorization and biodegradability of photocatalytic treated azo dyes and wool textile wastewater, *Chemosphere* (1999) 39 2107-2115.
- [69] L. Stanisław, G. Monika, Optimization of oxidants dose for combined chemical and biological treatment of textile wastewater, *Water Research*, 1999, 33, 2511-2516.
- [70] N.H. Ince, D.T. Gonenc, Treatability of a textile azo dye by UV/H<sub>2</sub>O<sub>2</sub>, *Environmental Technology*, 1997, 18, 179-185.
- [71] S. Contreras, M. Rodriguez, E. Chamarro, S. Esplugas, J. Casado, Oxidation of Nitrobenzene by UV/O<sub>3</sub>: the Influence of H<sub>2</sub>O<sub>2</sub> and Fe(III) Experiences in a Pilot Plant, *Water Science and Technology* 2001, 44, 39-46.
- [72] A. Mokrini, D. Oussi, S. Esplugas, Oxidation of aromatic compounds with UV Radiation/Ozone/Hydrogen Peroxide, *Water Science and Technology*, 1997, 35, 95-102.
- [73] J. Perkowski, L. Kos, Decolouration of model dye house wastewater with advanced oxidation processes, *Fibres and Textiles in Eastern Europe*, 2003, 11, 67-71.
- [74] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, Discoloration and mineralization of reactive red HE-3B by heterogeneous photo- Fenton reaction, *Water Research*, 2003, 37, 3776-3784.
- [75] M. Muruganandham, M. Swaminathan, Decolourisation of reactive orange 4 by fenton and photofenton oxidation technology, *Dyes and Pigments*, 2004, 63, 315-321.
- [76] M.S. Lucas, J.A. Peres, Decolorization of the azo dye reactive black 5 by fenton and photo-fenton oxidation, *Dyes and Pigments*, 2006, 71, 236-244.
- [77] C. Kormann, D.F. Bahnemann, M.R. Hoffmann, Photolysis of chloroform and other organic molecules in aqueous TiO<sub>2</sub> suspensions, *Environmental Science and Technology*, 1991, 25, 494-500.
- [78] W.Z. Tang, H. An, Photocatalytic degradation kinetics and mechanism of acid blue 40 by TiO<sub>2</sub>/UV in aqueous solution, *Chemosphere*, 1995, 31, 4171-4183.
- [79] A. Mills, S.L. Hunte, An overview of semiconductor photocatalysis, *Journal of Photochemistry and Photobiology A: Chemistry*, 1997, 108, 1-35.
- [80] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium oxide, *Progress in Solid State Chemistry* 2004, 32(1-2), 33-177.
- [81] M. Sleiman, D. Vildozo, C. Ferronato, J.M. Chovelon, Photocatalytic degradation of azo dye metanil yellow: optimization and kinetic modeling using a chemometric approach, *Journal of Applied Catalysis B: Environment*, 2007, 77, 1-11.
- [82] S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *Journal of Hazardous Material*, 2004, 112 (3), 269-278.
- [83] C.G. Silva, W. Wang, J.L. Faria, Photocatalytic and photochemical degradation of mono-, di- and triazo dyes in aqueous solution under UV irradiation, *Journal of Photochemistry and Photobiology A: Chemistry*, 2006, 181 (2-3), 314-324.
- [84] M.P. Reddy, A. Venugopal, M. Subrahmanyam, Hydroxyapatite Photocatalytic degradation of calmagite (an azo dye) in aqueous suspension, *Journal of Applied Catalysis B: Environment*, 2007, 69 (3-4), 164-170.
- [85] Braslavsky, SE. Glossary of terms used in photochemistry. 3rd ed. *Pure Appl Chem* 2007; 79: 293-465.
- [86] 86.Alpert SM, Knappe RUD, Ducoste JJ. Modeling the UV/hydrogen peroxide advanced oxidation process using computational fluid dynamic. *Water Res* 2010; 44: 1797-808.
- [87] Legrini O, Oliveros E, Braun AM. Photochemical processes for water treatment. *Chem Rev* 1993; 93: 671-98.
- [88] Cisneros LR, Espinoza GA, Litter MI. Photodegradation of an azo dye from the textile industry. *Chemosphere* 2002; 248: 393-9.
- [89] Litter MI. Introduction to photochemical advanced oxidation processes for water treatment. In: Bahnemann D, Boule P, Eds. *The Handbook of environmental chemistry, series, Volume M, Part L: Environmental Photochemistry Part II*. Springer-Verlag: GmbH Publish 2005; pp. 325-66.
- [90] Mohey el-Dein A, Libra JA, Wiesmann U. Mechanism and kinetic model for the decolorization of the azo dye Reactive Black 5 by hydrogen peroxide and UV radiation. *Chemosphere* 2003; 53: 1069-77.
- [91] Behnajady MA, Modirshahla N, Shokri M, Vahid B. Design equation with mathematical continuous-flow photoreactor. *J Hazard Mater* 2009; 165: 168-73.
- [92] Gogate PR, Pandit AB. A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Adv Environ Res* 2004; 8: 501-51.
- [93] Pignatello JJ, Oliveros E, MacKay A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit Rev Environ Sci Technol* 2006; 36: 1-84.
- [94] Augugliaro V, Litter M, Palmisano L, Soria J. The combination of heterogeneous photocatalysis with chemical and physical operations: a tool for improving the photoprocess performance. *J Photochem Photobiol C* 2006; 7: 127-44.
- [95] Pulgarin C, Sarria V, Kenfack S, Guillod O. An innovative coupled solar-biological system at field pilot. *J Photochem Photobiol A* 2003; 159: 89-99.
- [96] Oller I, Malato S, Sanchez-Perez J, et al. A combined solar photocatalytic- biological field system for the mineralization of an industrial pollutant at pilot scale. *Catal Today* 2007; 122: 150-9.

- [97] Kitis M, Adams CD, Daigger GT. The effects of Fenton's reagent pretreatment on the biodegradability of nonionic surfactants. *Water Res* 1999; 33: 2561-8.
- [98] de la Fuente L, Acosta T, Babay P, Curutchet G, Candal R, Litter MI. Degradation of nonylphenol ethoxylate-9 (NPE-9) by photochemical advanced oxidation technologies. *Ind Eng Chem Res* 2010; 49: 6909-15.
- [99] Lucas MS, Peres JA, Li Puma G. Treatment of winery wastewater by ozone-based advanced oxidation processes (O<sub>3</sub>, O<sub>3</sub>/UV and O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>) in a pilot-scale bubble column reactor and process economics. *Separ Purif Technol* 2010; 72: 235-41.
- [100] Babay PA, Emilio CA, Ferreyra RE, Gautier EA, Gettar RT, Litter MI. Kinetics and mechanisms of EDTA photocatalytic degradation with TiO<sub>2</sub> under different experimental conditions. *Int J Photoenergy* 2001; 3:193-9.
- [101] Iojoiu, EE, Miachon S, Landrison E, Walmsley JC, Ræder H, Dalmon J-A. Wet air oxidation in a catalytic membrane reactor: Model and industrial wastewater in single tubes and multichannel contactors. *Appl Catal B* 2007; 69: 196-206.