
Integrated coupled systems as biodegradability enhancement of textile wastewater by photo-fenton process

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Sistemas acoplados integrados para la mejora de la biodegradabilidad de aguas residuales textiles mediante el proceso Foto-Fenton

Sistemes acoblats integrats per a la millora de la biodegradabilitat d'aigües residuals tèxtils mitjançant el procés Foto-Fenton

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RESUMEN

Se explora el proceso Foto-Fenton como pretratamiento fotoquímico para aumentar y mejorar la biodegradabilidad, y la completa mineralización, de las aguas residuales que provienen de una industria textil localizada al este de Alemania con colorantes reactivos y caracterizadas como biorecalcitrantes, no biodegradables y con compuestos orgánicos refractarios. El tratamiento de las aguas residuales se realiza mediante una serie de experimentos a escala laboratorio, a fin de identificar las condiciones de operación óptimas para el tratamiento de las aguas residuales textiles a la salida del conducto de efluentes. Se estudia el efecto de los parámetros de operación, como el pH, el tiempo de irradiación y las concentraciones iniciales de H₂O₂ y Fe²⁺, sobre los procesos de fotomineralización como etapa de pretratamiento y se encuentran las condiciones óptimas. La demanda química de oxígeno (DQO), el carbono orgánico total (COT) y la eliminación de color son los parámetros empleados para seguir el curso de los experimentos.

La eliminación de color de las aguas residuales textiles alcanza el 100% en 30 minutos de tratamiento fotocatalítico. Las aguas residuales son completamente degradadas por un tratamiento Foto-Fenton después de un tiempo de irradiación de 60 minutos al usar una concentración de catalizador de 50 mg/L de Fe²⁺, una concentración de H₂O₂ de 1000 mg/L y un pH=3 a 25°C. En estas condiciones óptimas de operación de la fotomineralización, el porcentaje de disminución de COT y DQO y de eliminación del color son del 89, 95 y 100%, respectivamente. Los resultados experimentales muestran que la proporción BOD₅/COD de las aguas residuales aumenta desde el valor inicial de 0,09 hasta 0,7 a los 60 minutos. Este resultado implica que la oxidación fotocatalítica mejora la biodegradabilidad de las aguas residuales que contienen colorantes y que por tanto existe relación entre decoloración y biodegradabilidad. Cuando el color desaparece completamente, las aguas residuales se biodegradan normalmente y se pueden verter para su tratamiento subsiguiente. Las prue-

bas de biodegradabilidad también demuestran que los efluentes tratados fotoquímicamente al poco de empezar el proceso Foto-Fenton son biodegradables, con una proporción DBO₅/DQO de 0,4 a los 30 minutos de irradiación. Los resultados experimentales demuestran que es posible combinar la fotocatalisis con el tratamiento biológico convencional para depurar las aguas residuales que contienen los generalmente no biodegradables colorantes azo. Los resultados del presente estudio muestran que los efluentes tratados con el proceso Foto-Fenton cumplen con las regulaciones medioambientales para el vertido de aguas textiles en Alemania.

Palabras clave: Proceso Foto-Fenton, aguas residuales textiles, compuestos recalcitrantes o inhibidores, fase de pretratamiento, biodegradabilidad.

SUMMARY

Photo-Fenton process was explored as photochemical pre-treatment to enhance and improve the biodegradability and complete mineralization of a wastewater coming from a textile industry located in the east of Germany containing reactive dyes which was characterized as biorecalcitrant, non-biodegradable and refractory organic compounds. Wastewater treatment was carried out including a series of bench scale experiments, to identify optimum operating conditions for the treatment of textile wastewater at the end of the pipe effluent. The effect of operating parameters as: pH, irradiation time and initial concentrations of both H₂O₂ and Fe²⁺ on the photomineralization processes as a pretreatment step have been studied and the optimal conditions were found. Chemical oxygen demand (COD), total organic carbon (TOC) and colour removal are the parameters used to trace the experiments course.

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The color removal of the textile wastewater reached to above 100% within 30 min of photocatalytic treatment. The wastewater was completely degraded by a photo-Fenton treatment after 60 min irradiation time by using a 50 mg/L of Fe^{2+} catalyst concentration and the H_2O_2 concentration was 1000 mg/L and $\text{pH}=3$ at 25°C . At these optimum operating conditions % removal of TOC, COD and colour removal were 89, 95 and 100 respectively of photo-mineralization. The experimental results show that the ratio of BOD_5/COD of the wastewater increased from original 0.09 up to 0.7 after 60 min. The result implies that photocatalytic oxidation enhanced the biodegradability of the dye-containing wastewater and therefore relationship between decolorization and biodegradability exists. When the color disappeared completely, the wastewater biodegraded normally and could be discharged for further treatment. The biodegradability tests also demonstrated that photo-treated effluents within a short time of starting the photo-Fenton process were biodegradable with a BOD_5/COD ratio of 0.4 after 30 min of irradiation time. The experimental results demonstrate that it is possible to combine photocatalysis with conventional biological treatment for the remedy of wastewater containing generally non-biodegradable azo dyes. The results of the present study revealed that the treated effluent by photo-Fenton process is complying with the environmental regulations for discharge of textile wastewater in Germany.

Key words: Photo-Fenton process, textile wastewater, recalcitrant or inhibitory compounds, pretreatment step, biodegradability.

RESUM

S'explora el procés Foto-Fenton com a pretractament fotoquímic per augmentar i millorar la biodegradabilitat, i la completa mineralització, de les aigües residuals provinents d'una indústria tèxtil localitzada a l'est d'Alemanya amb colorants reactius i caracteritzades com a biorecalcitrants, no biodegradables i amb compostos orgànics refractaris. El tractament de les aigües residuals es realitza mitjançant una sèrie d'experiments a escala laboratori, per tal d'identificar les condicions d'operació òptimes per al tractament de les aigües residuals tèxtils a la sortida de la conducció d'efluents. S'estudia l'efecte dels paràmetres d'operació com el pH, el temps d'irradiació i les concentracions inicials de H_2O_2 i Fe^{2+} sobre els processos de fotomineralització com a etapa de pretractament i es troben les condicions òptimes. La demanda química d'oxigen (DQO), el carboni orgànic total (COT) i l'eliminació de color són els paràmetres emprats per seguir el curs dels experiments. L'eliminació de color de les aigües residuals tèxtils assoleix el 100% en 30 minuts de tractament fotocatalític. Les aigües residuals són completament degradades per un tractament Foto-Fenton després d'un temps d'irradiació de 60 minuts en emprar una concentració de catalitzador de 50 mg/L de Fe^{2+} , una concentració de H_2O_2 de 1000 mg/L i un $\text{pH}=3$ a 25°C . A aquestes condicions òptimes d'operació de la fotomineralització, el percentatge de disminució de COT i DQO i d'eliminació del color són del 89, 95 i 100%, respectivament. Els resultats experimentals mostren que la proporció BOD_5/COD de les aigües residuals augmenta des del valor inicial de 0,09 fins a 0,7 als 60 minuts. Aquest resultat implica que l'oxidació fotocatalítica millora la biodegradabilitat de les aigües residuals

que contenen colorants i que per tant existeix relació entre decoloració i biodegradabilitat. Quan el color desapareix completament, les aigües residuals es biodegraden normalment i es poden abocar per a subsegüent tractament. Les proves de biodegradabilitat també demostren que els efluents tractats fotoquímicament al poc de començar el procés Foto-Fenton són biodegradables, amb una proporció DQO/DBO_5 de 0,4 als 30 minuts d'irradiació. Els resultats experimentals demostren que és possible combinar la fotocatalisi amb el tractament biològic convencional per depurar les aigües residuals que contenen els generalment no biodegradables colorants azo. Els resultats del present estudi mostren que els efluents tractats amb el procés Foto-Fenton compleixen amb les regulacions mediambientals per a l'abocament d'aigües tèxtils a Alemanya.

Mots clau: Procés Foto-Fenton, aigües residuals tèxtils, compostos recalcitrants o inhibidors, fase de pretractament, biodegradabilitat.

1. INTRODUCTION

The elimination of toxic chemicals from wastewater is presently one of the most important subjects in pollution control. Various industrial sectors such as (petroleum refining, textile processing, pharmaceutical, etc.) or from household and personal care areas (pesticides and fertilizers, detergents, etc.); employ these chemicals. These pollutants are either resistant to conventional chemical treatment methods, recalcitrant or inhibitory to microorganisms found in conventional biological treatments. The search for effective means of removing these compounds is of interest to regulating authorities everywhere.

Like many other industrial effluents, textile industry wastewater varies significantly in quantity, but additionally in composition [1]. The textile dyeing industry is one of the major pollutants among the industrial sector, since modern dyes are characterized by great stability and by a large degree of aromatics in their structure. Textile wastewater is strongly colored which creates an environmental as well as aesthetic problem. Colour removal from textile wastewater has been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but often due to their visibility in receiving waters. Recent studies indicated that approximately 12% of synthetic dyes are lost annually during manufacturing and processing operations and that 20% of the resultant color enter the environment through effluents from industrial wastewater treatment plants. Colour in dye-house effluents has often been associated with the application of reactive dyestuffs, during which up to 50% of the dyes may be lost to the effluent [2]. Reactive dyes are present in a hydrolyzed state in the exhausted dye-bath or wash-water, a form that can not be reused in the dyeing process. Moreover, their photolytic/chemical stability and extremely low physical affinity [3] for various adsorbents make conventional treatment a rather difficult task. Most of these dyes are resistant to aerobic biotreatment [4]. As regulations are becoming ever more stringent, the need for technically and economically more efficient means of decolorization and mineralization is obvious.

Although biological treatment is often the most cost-effective alternative it is often not effective for treatment of textile wastewater containing biorecalcitrant organic substances. There are two strategies are employed for the removal of such recalcitrant organic compounds: phase

transfer and oxidation [5, 6]. Currently, there are no economically attractive technologies to achieve color removal. Existing physicochemical technologies such as membrane filtration or activated carbon adsorption are expensive and commercially unattractive. Furthermore, these processes just transfer pollutants from one phase to another rather than eliminating them from the water matrix.

The nonbiodegradability of textile wastewater is due to their high content of dyestuffs, surfactants and other additives. Due to the stability of modern dyes, conventional biological treatment methods for industrial wastewater are ineffective, frequently resulting in an intense coloured discharge from the treatment facilities. Additionally, they are readily reduced under anaerobic conditions to potentially hazardous aromatics. Thus, there is a need for developing more effective treatment methods in eliminating dyes from a waste stream at its source. The incapability of conventional wastewater treatment methods to effectively remove many biorecalcitrant pollutants evidences that new efficient treatment systems are needed. Therefore, to enhance the efficiency of conventional processes for industrial wastewater treatment, an effective pretreatment process is always needed to destroy the toxic pollutants. Besides biological processes, several oxidation systems are currently used or in different stages of development. For the last 25 years the water purification research has been extensively growing. Rigorous pollution control and legislation in many countries have resulted in an intensive search for new and more efficient water treatment technologies.

Oxidation processes are an alternative for the destructive removal of color from textile wastewater. Chemical oxidation treatment methods known as Advanced Oxidation Processes (AOPs) are an attractive alternative for the treatment of contaminated ground, surface, and waste waters containing hardly-biodegradable anthropogenic substances as well as for the purification and disinfection of drinking waters [7-9].

The high potential and effectiveness of AOPs for the total oxidation of hazardous organic compounds is widely recognized. Recent experimental investigations have revealed that complex dyes can be decolorised by (AOPs) [10]. AOPs are ambient temperature process and are characterized by the production of hydroxyl radicals (OH), that aggressively second strongest known oxidant after fluorine. This hydroxyl radical almost indiscriminately attacks all types of refractory and recalcitrant inorganic and organic pollutants found in groundwater, surface water and industrial wastewater [11], yielding carbon dioxide, inorganic ions and water. The advantage of AOPs is enhanced by the fact that OH radicals may be produced in different ways, so they can be adapted to specific treatment requirements.

Most of the AOPs comprise combinations of UV-light with powerful oxidizing agents such as O₃ and H₂O₂ [12, 13]. In this regard, ozonation has been viewed as an expensive and unsafe process [14], while the major drawbacks of UV-C ($\lambda < 300$ nm)-driven treatment systems such as O₃/UV-C, H₂O₂/UV-C and Fenton/UV-C are the limited reactor configurations and high operational costs [15].

Among the AOPs, the homogeneous photo-Fenton (Fe²⁺/³⁺/H₂O₂/UV) reaction [16-18] and titanium dioxide-mediated heterogeneous photocatalytic (TiO₂/UV-A) treatment process [19-21] have shown recently great promise for the treatment of industrial wastewater, groundwater and contaminated air. They are capable of absorbing in the near-UV spectral region (300 nm < λ < 400 nm) to initiate radical

reactions. The photo-Fenton system has been shown to be the most promising for the remediation of contaminated water containing dyes [22, 23]. Moreover, as UV radiation generation by lamps or ozone production is expensive, photo-Fenton driven by solar radiation is of special interest, making the development of suitable technologies very attractive for practical applications [24, 25].

Advanced Oxidation Processes (AOPs) are very promising methods for the remediation of contaminated wastewaters containing non-biodegradable organic pollutants. Although AOPs generally can produce high quality effluent and cheaper than incineration or wet oxidation technologies, nevertheless, one of the major drawbacks of these AOPs is that their operating costs exceed those of biological treatment. However, the use of AOPs as a pre-treatment step to enhance the biodegradability of waste water containing recalcitrant or inhibitory pollutants can be justified if the resulting intermediates are easily degradable by micro-organisms in further biological treatment [26].

Previous studies have attempted the strategy of combining chemical and biological processes to treat contaminants in wastewater. Many reports have focused on the study of new chemical oxidation technologies as a pre-treatment for non-biodegradable or toxic waste water combined with a conventional biological treatment [27-28]. These results suggest potential advantages for water treatment. Recently, very attractive combined systems have been proposed to treat different kinds of industrial waste water [29-33].

Today combined photo-assisted AOP and biological processes are gaining in importance as treatment systems, as one of the main urban waste water treatment obligations imposed by European Union Council Directive 91/271/EEC is that waste water collecting and treatment systems (generally involving biological treatment), must be in place in all agglomerations of between 2000 and 10,000 population equivalents by 31st December 2005. Smaller agglomerations which already have a collecting system must also have an appropriate treatment system by the same date [34]. In a near future, AOP plants developed in the EU could be discharging pre-treated waste water into a nearby conventional biological treatment plant.

This work evaluates the feasibility of enhancing the biological treatment of the textile wastewater employing photo-Fenton pre-treatment step. The goal of this paper is to use an experimental design for the choice of minimum photo-Fenton reactant doses and in a reasonable length of time able to convert the wastewater taken under the study into biocompatible effluents, seeking the subsequent coupling to a biological step for complete organic load removal.

2. EXPERIMENTAL

2.1. Material & Analysis

GP grad chemicals namely, ferrous sulfate (FeSO₄ · 7H₂O), hydrogen peroxide (H₂O₂) 30%, sulfuric acid and sodium hydroxide were used without any purification were provided by Merck. The original real wastewater used was produced from industrial plant for textile at Germany. These effluents were characterized and analyzed for COD, BOD₅, TOC, other physical chemical analysis, according to the procedures described in Standard Methods for the Examination of Water and Wastewater (1998) [35].

2.2. Set-up

A laboratory photocatalytic oxidation unit was used for the batch experiments. The schematic diagram of the experimental set-up used is shown in Figure (1). It consists of an external stirred vessel 1 liter with a variable speed stirrer, combined with a cylindrical photo reactor (0.85 L), made from quartz, with a coaxial and immersed medium pressure UV mercury lamp was used as the UV emitter and light source (Heraeus TQ150, input energy of 150 w) emitting a polychromatic radiation in the range from 100 to 280 nm wavelength. The lamp emitted a power of 6.2 W in the UV-C ($100 < \lambda < 280$ nm) range (indication Heraeus), corresponding to 1.32×10^{-5} Einstein s^{-1} . The UV lamp is equipped with a cooling water jacket to maintain the temperature of the reaction of wastewater at room temperature. There is one cooling circle for cooling UV lamp. The UV system is placed positioned coaxial inside the reactor vessel. The reaction chamber is filled with the wastewater, which is between the reactor walls and UV lamp system. The reactor was designed for different flow rates, organic loads, recalculation rates, and oxidant addition rates. Mixing was accomplished by means of a closed external circulating loop through the illuminated part of the photoreactor by the use of a peristaltic pump. The flow system was assembled with polytetrafluorethylene or glass tubing and connectors.

2.3. Procedures

The laboratory unit was filled separately with 0.85 L of wastewater under study. The optimum conditions for photo-Fenton treatment as a pre-treatment step for biological treatment were investigated for the textile wastewater. In the photochemical oxidation, the pH of the industrial wastewater was adjusted to the desired value with sulfuric acid addition before start-up, and kept at the same value during the reaction. Then appropriate amount of ferrous sulfate was added into the mixing vessel and was re-circulated in batch mode through the illuminated part of the photoreactor by means of peristaltic pump for ten minutes. Then the desired volume of H_2O_2 was injected continuously to the solution by using a dosing pump during the period of the reaction to insure the continuous reaction of hydrogen peroxide with ferrous ions along the irradiation time. The time at which the UV lamp was turned on was considered time zero simultaneously with starting the addition of hydrogen peroxide. The hydrogen peroxide dos-

age was based on the stoichiometric ratio with respect to COD. The solution was circulated at a flow rate of $180 L h^{-1}$. After 60 min reaction time the lamp was turned off. The pH of the photo-Fenton treated effluent was adjusted to 7 and the photo-oxidation effluent was centrifuged before the analysis of BOD_5 the analysis of the other parameters.

2.4. Analytical methods

Samples were taken periodically at regular time intervals from the reaction vessel and were analyzed immediately to avoid further reaction. As reported in the literature [10], Fenton and photo-Fenton reactions cannot proceed at $pH > 10$. Therefore, the reaction was stopped instantly by adding NaOH to the reaction samples before H_2O_2 analysis. One drop of $Na_2S_2O_3$ (0.1 N) was also added to each sample to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with organic substrates during the analysis. Hydrogen peroxide was detected by a modified iodometric titration method [36]. Total organic carbon measurements (TOC) were carried out by using a Shimadzu-TOC analyzer 5000 equipped with an auto-sampler ASI-5000. The pH was measured by means of a WTW pH-meter 537 equipped with a pH combination electrode E56. Chemical oxygen demand (COD) was carried out via a digester LT 148 from Firma Lange using a dichromate solution as the oxidant in strong acid media [37]. The effluent of the photo-Fenton treatment was subjected for the analysis of biochemical oxygen demand (BOD_5) to evaluate its biodegradability. BOD_5 was measured using a respirometry system [38]). Hydrogen peroxide analysis was carried out by iodometric titration, although, since this method is very time consuming (around 45 min), it was frequently determined in fresh sample solutions using Merckoquant Paper (Merck Cat. No. 1.10011.0001) just to get an idea of overall H_2O_2 consumption and to detect any significant decrease.

3. RESULTS AND DISCUSSION

3.1. Wastewater characterization and assessment of biological treatment

The environmental and physicochemical characterization of the 3 fold diluted textile wastewater taken in this study is given in Table (1). Selection of this dilution rate was also based upon the fact that for light induced treatment systems the very poor visible- and UV-light transmission of the actual (undiluted) dye bath is the major drawback for an effective treatment via AOPs. The effluent exhibits very low BOD_5 , high COD and high TOC and is highly colored. These values indicated that wastewater generated from the company contained toxic pollutants such as azo dyes which may inhibit the process or pass through biological application because of their refractory and toxic properties [39]. These data indicated that the industrial wastewater is highly loaded with organic matter. Some of these compounds are poorly biodegradable and consequently, they often remain in the effluent from biological treatment processes and depress treatment efficiency of city treatment plant.

One interesting alternative that is gaining importance among the potential techniques for non-biodegradable or toxic wastewater treatment is the combination of an AOP with a subsequent biological step. In this way the use of the AOP, the expensive part of the global procedure is re-

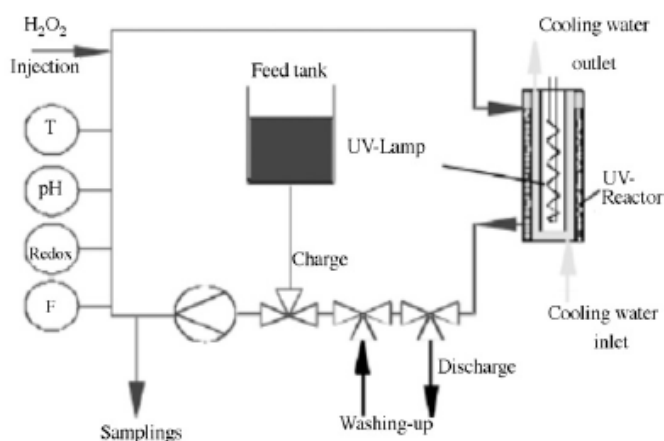


Figure 1. Schematic diagram of photocatalytic oxidation system experimental set-up.

duced to the attainment of a non-toxic and/or biodegradable solution, being the rest of the organic matter removed in the biological step.

Table 1
Environmental characterization of the
3 fold diluted wastewater

Permissible Limits [40]	Value	Parameter
160	2500	COD (mg/L)
	1570	TOC (mg/L)
	0.09	BOD ₅ /COD
7	38.1	UV _{436nm} (1/m)
5	41.7	UV _{525nm} (1/m)
3	13	UV _{620nm} (1/m)
6-9	10.9	pH

a Below the detection limit of the standard BOD₅ test.

The ratio of BOD₅/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD₅/COD is more than 0.3, the wastewater has a better biodegradability. Whereas the ratio is less than 0.3, the wastewater is difficult to be biodegraded [41,42]. The non-biodegradability of a wastewater have to be confirmed before apply a photochemical treatment, since classical biological treatments are, at the present, the cheapest and most environmentally compatible.

Table (1) shows that, the ratio of BOD₅/COD of the wastewater is non detectable, equals 0.09 (less than 0.3). This indicating that, the wastewater is poorly biodegradable and can't be biodegraded by activated sludge. These results reveal that the biorecalcitrance of this effluent, in the tested conditions, is associated with the structural stability of compounds towards microbiological attack but no with the toxicity of the solution. Furthermore the value of BOD₅ of the raw wastewater is very low; indicating that wastewater containing azo dyes inhibits the respiratory activity of bacterial seed. Therefore, they not only can not be biodegraded but also decrease the efficiency of biological treatment. The obtained results indicate that the wastewater generated from the industry does not comply with the environmental laws

3.2. The photo-Fenton reaction as end of pipe pre-treatment process

Wastewater from textile processing is characterized by a remarkable content of organic dyes. Biological processes alone are not always able to reach effluent standards for the discharge into municipal sewer or into surface waters, so a pretreatment is required. Therefore, the treatment process was designed to cover two main objectives: destruction of the toxic dyes and pollutants present in the wastewater and convert them into biodegradable compounds. The treatment system was carefully investigated using advanced oxidation processes, (Photo-Fenton), as a pretreatment step followed by biological treatment. Photo-Fenton system, UV/Fe²⁺/H₂O₂, is one of the most interesting promising oxidative techniques for the abatement of refractory and toxic organic pollutants in water and wastewater particularly containing dyes [43]. In this technique, the strong oxidizing agent OH• radical is produced. The formation of OH• radical depends on several parameters such as pH, initial amount of Fe²⁺, initial concentration of H₂O₂, the organic loads and the irradiation time. Because these parameters are the most influential variables and determine the oxidation efficiency, it is important to optimize

the initial amounts and conditions of these reagents and the operating conditions. One of the aims of this study was mainly to reach the optimum operating conditions such as: irradiation time, optimum pH (acidity), optimum initial amounts of both H₂O₂ and Fe²⁺ respectively for the best TOC and COD removals of the effluent of the textile industry by photo-Fenton process. Other factors like BOD₅ and the biodegradability ratio (BOD₅/COD) of the pre- photo-treated effluent with the different reactant doses were also assessed. Experimental design was applied.

3.2.1. Effect of irradiation time

The photo-treatment time must be as short as possible to avoid a high electricity consumption, which represents about 60% of the total operational cost when using electric light sources [44]. However, if the fixed pretreatment time is too short, the intermediates remaining in solution could still be structurally similar to initial biorecalcitrant compounds and therefore, non-biodegradable. Furthermore, at short photo-treatment times, the residual H₂O₂ concentration may be high enough to inhibit the biological stage of the coupled reactor. This oxidant is not required for all the photochemical processes but, whenever utilized it has to be eliminated before the biological stage. Figure (2) indicates that the optimum irradiation time was 60min. Within this time, about 90 and 95 % removal of TOC and COD of the wastewater respectively were achieved.

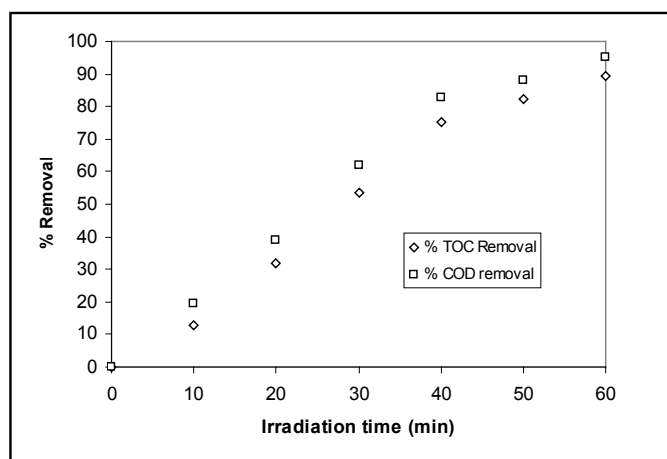


Figure (2). Effect of irradiation time on TOC and COD removal. [initial TOC=1570 mg/L, initial COD=2500 mg/L, H₂O₂= 1000 ppm, Fe²⁺=50 ppm, pH=3].

3.2.2. Effect of the pH

The photo-Fenton systems have a maximum catalytic activity at pH of about 2.8-3. The pH value influences the generation of OH• radicals and thus the oxidation efficiency. For pH values above 4 the degradation strongly decreases since iron precipitates as hydroxide derivate, reducing the Fe²⁺ availability and the radiation transmission [15, 16]. The decrease of activity for pH values below the optimum is understandable taking into account that Fe²⁺ forms different complex species in solution, and the quantum yield of light absorption by Fe²⁺ is directly depending on the specific species responsible for the absorption. Therefore, the all experiments of this work are performed at pH 3.

3.2.3. Mode of addition of hydrogen peroxide

Hydrogen peroxide was added in two different modes either batch or continuously to determine the optimum

mode of its addition. Two separated experimental runs were carried out with the same of conditions of irradiation time, the same amounts of added hydrogen peroxide and ferrous ion, the same pH and the same initial of TOC of the wastewater but in different modes of hydrogen peroxide addition. Figure (3) illustrates the decrease of TOC of wastewater as a function of irradiation time at different modes of addition of hydrogen peroxide either batch or continuous. The addition of hydrogen peroxide in continuous mode gave rather moderate results in TOC reduction of the textile wastewater comparing with its addition in a batch mode. As can be seen from Figure (3), the decrease in TOC of the wastewater was faster in the first 15 minutes of the irradiation time when the amount hydrogen peroxide was added one time on the start of the experiment and after that the decrease of TOC was slowly. On the opposite, when hydrogen peroxide was added continuously the decrease of TOC was slowly in the first period of the experiment but along the irradiation time of the experiment the decrease of TOC was faster and at the end of the experiment the decrease of TOC was greater than that in case of addition of hydrogen peroxide at the batch mode. This can be explained with continuous production of free hydroxyl radicals during the whole experiment in case of addition of hydrogen peroxide was added in a continuous mode while in case of addition of hydrogen peroxide in a batch mode the amount of produced free hydroxyl radicals was consumed in the first stage of the experiment. Consequently the amount of hydrogen peroxide was adjusted at this work to be added continuously by using dosing pump.

3.2.4. Effect of initial amount of Fe²⁺

There are two important factors affecting the rate of photo-Fenton reaction once the photon source is fixed: hydrogen peroxide dose and iron concentration. The hydrogen peroxide dose is important in order to obtain quantitative degradation, while the iron concentration is important for the reaction kinetics [45]. Nevertheless, formation of different scavengers of reactive species when an excess of reactants is added to the solution can be detrimental. Thus, the most efficient reagent concentration needs to be carefully determined. Multivariate experimental design has been used to accomplish such a goal.

To elucidate the role of Fe²⁺ concentration on the mineralization of the effluent, a series of experiments varying the concentration of iron and keeping fixed the other param-

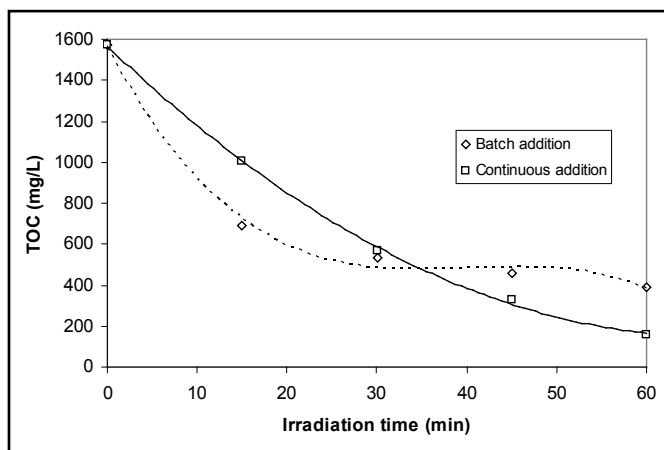


Figure (3). Mode of addition of hydrogen peroxide (batch and continuous). [initial TOC=1570 mg/L, H₂O₂= 1000 ppm, pH=3, Fe²⁺=50 ppm].

eters, were carried out. Figure (4) shows the TOC evolution (i.e., mineralization process) as a function of Fe²⁺ concentration. The best (%) mineralization was obtained with Fe²⁺ concentration of 50 mg/L. At 0 ppm of Fe²⁺ concentration, the % removal of TOC reached only 20 % after 60 minutes using UV/H₂O₂ process. As can be seen, the TOC removal was mainly influenced by Fe²⁺ concentration. Nevertheless, an excess of ferrous ions in the system produced a decrease in mineralization yield. The possible formation of futile intermediate iron (IV) species (ferryl iron FeO²⁺) could be the cause of this negative behavior, producing a possible side reaction that interferes with the formation of hydroxyl radicals that are critical for the oxidation of organic matter (Reactions 1-3) [46].

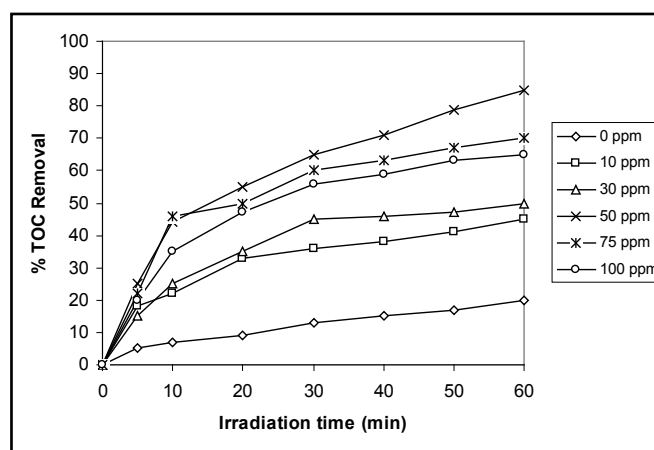
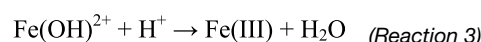
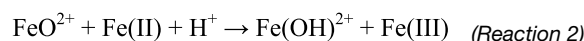
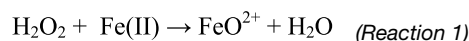


Figure (4). Effect of initial amount of Fe²⁺ on TOC removal. [initial TOC=1570 mg/L, H₂O₂= 1000 ppm, pH=3].

3.2.5. Effect of the initial hydrogen peroxide concentration

To further elucidate the role of H₂O₂ concentration on the photo-catalytic degradation of the wastewater in the photo-Fenton system, some experiments are carried out by varying the initial H₂O₂ concentrations at constant COD & TOC and initial Fe²⁺. Figure (5) shows the % removal of TOC as a function of reaction time when different concentration of H₂O₂ was used. At 0 ppm of hydrogen peroxide, the % removal of TOC reached only 10 % after 60 minutes due to the adsorption of the dyes present in the wastewater by the effect of the presence of Fe²⁺ ions. As shown from Figure, significant enhancement of the degradation efficiency represented by %TOC removal is demonstrated when H₂O₂ concentration increases from 0 to 1000 ppm, which is explained by the effect of the additionally produced OH[•] radicals [15,16,26,47]. Nevertheless, the small difference between the TOC removal attained with 1000, 1500 and 2000 ppm of H₂O₂ indicates that improvements of reaction rate may not compensate the large amounts of oxidant consumed. In all these cases around 75 % TOC reduction after 40 min irradiation time and around 90% after 60 min irradiation time were obtained.

However, when the H₂O₂ concentration is larger 2000 ppm, the degradation rate slightly slows down and sometimes is negatively affected, by the progressive increase of the

hydrogen peroxide. This may be due to auto-decomposition of H_2O_2 to oxygen and water and recombination of OH^\bullet radicals (Reactions 4,5). Excess of H_2O_2 will react with OH^\bullet competing with organic pollutants and consequently reducing the efficiency of the treatment, the H_2O_2 itself contributes to the OH^\bullet radicals scavenging capacity. It is found that, the optimal H_2O_2 concentration is 1000 ppm for the treatment of the wastewater under study with 90% TOC removal after 60 min irradiation time as shown in Figure (5). Therefore, H_2O_2 should be added at an optimal concentration to achieve the best degradation. This optimal H_2O_2 concentration depends on the nature and the organic load of the wastewater to be treated and on the iron concentration.

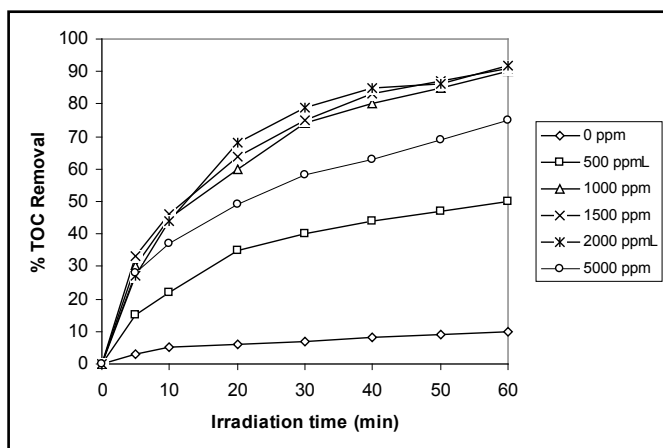
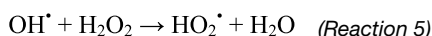
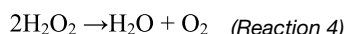


Figure (5). Effect of the initial hydrogen peroxide concentration on TOC removal. [initial TOC=1570 mg/L, Fe^{2+} =50 ppm, pH=3].

3.3. Decolorization and biodegradability relationship

The biodegradability of the pretreated solutions by photo-Fenton process of initial biorecalcitrant wastewaters is followed or assessed by means of: (i) analyzing global parameters, such as biological oxygen demand (BOD_5), chemical oxygen demand (COD); (ii) estimating the ratio BOD_5/COD is a crucial way to impulse the practical application and design of these coupled systems. BOD_5/COD ratio is the most used parameter to quantify the biodegradability of a contaminated effluent. The threshold value of such ratio for a wastewater to be considered easily biodegradable is 0.3 while a value between 0.2 and 0.3 corresponds to a partially biodegradable wastewater [48]. The key question concerning the combined use of an photo-Fenton process as a pretreatment step and a biological treatment is to probe that the biodegradability of the photo-treated effluent and, particularly, the BOD_5/COD ratio increases during the photo-Fenton process, approaching the value 0.3 that is considered the quantitative index for organic matter complete biodegradability. Thus, BOD_5 and COD analysis of the treated wastewater were carried out in order to characterize the evolution of the BOD_5/COD ratio. The biodegradability of the treated effluents within 60 min irradiation time of photo-Fenton reaction was also tested by incubating the pre-treated effluent over a 5-days pe-

riod. To verify the relationship between decolorization and biodegradability of the textile wastewater selected as case study, experiment was carried out to follow both BOD_5/COD ratio & colour removal along the irradiation time. As clear from Table (1), of the chemical property of the wastewater, it can not be biodegraded according to the ratio $BOD_5/COD = 0.09$. However, the color and COD of the wastewater were removed by photocatalytic treatment with photo-Fenton process as shown in Figure (6). The complete decolorization of wastewater with photo-Fenton process is achieved for about 30-min. irradiation. At the same time, the COD conversion of wastewater was 61%. Furthermore, 95% of the COD removal can be obtained after 60-min. irradiation.

The ratio of BOD_5/COD of the sample at treatment time 30min. increased from initial 0.09 to 0.3. The result indicates the biodegradability of photocatalytically treated wastewater with photo-Fenton process was enhanced, and the complete decolorization wastewater was biodegradable due to $BOD_5/COD > 0.3$. Therefore, the more appropriate photocatalytic treatment time was also the period of color disappearing completely for practical wastewater treatment. After 60 min irradiation time, the final values of COD and TOC were 125 and 337 mg/L respectively. These results show that the biodegradability tendency can be enhanced by the photocatalytic oxidation converting the non-biodegradable organic substrates into more biodegradable compounds. Also, these results indicated that the treated effluent comply with standards given by German Environmental laws [40], which regulates the disposal of industrial wastewater into the sewage system and the treated final effluent, can be used for water reuse purposes.

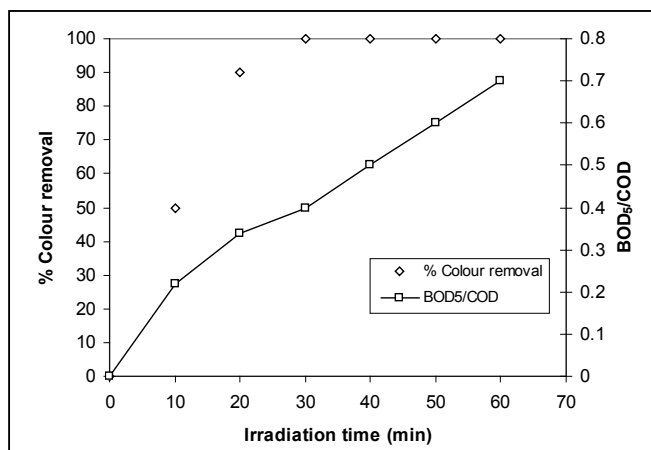


Figure (6). Decolorization and biodegradability relationship of pre-photo-oxidizing textile wastewater with irradiation time. [initial $BOD_5/COD=0.09$, initial COD=2500 mg/L, $H_2O_2 = 1000$ ppm, $Fe^{2+}=50$ ppm, pH=3].

3.5. Economic analysis

The economic assessment will be based on the expected capital cost for each alternative considering the operation and maintenance costs required for different components. The expected benefits will be quantified and evaluated in terms of money to perform the cost benefit analysis. The costs for the treatment of 30 m³/day of the wastewater of the company was estimated to be 50000 Euro as capital costs and to be 12000 Euros/year for the annual maintenance and operating costs for the treatment by using photo-Fenton process as a pretreatment accompanied by biological treatment.

4. CONCLUSION

A textile effluent was determined to be non-biodegradable since the biodegradability test indicated that the COD/BOD₅ ratio is very low. This study demonstrates the utility of the photo-Fenton process as a pretreatment method preceding a biological treatment for the complete mineralization of non-biodegradable organic substances. The photocatalytic treatment of the final effluent of one of the textile industry was successfully achieved with the photo-Fenton process. In this study, photo-Fenton degradation was considered as a pre-treatment step for an integrated photocatalytic-biological coupled system for removal of the biorecalcitrant dyes and colours. In particular, it was aimed to shorten the photo-treatment time in order to enhance the economical feasibility of the integrated process.

Multivariate experimental design has been applied to optimize photo-Fenton reactant doses. The results from this study showed that the rate of percentage of TOC degradation was strongly accelerated by photoassisted chemical oxidation processes. The oxidation rate was influenced by many factors such as irradiation time, initial amounts of both H₂O₂, Fe²⁺. The optimum operating conditions obtained for the best degradation treatment for 90 and 95% TOC and COD removal respectively were pH 3, 1000 and 50 ppm initial amounts of H₂O₂, Fe²⁺ respectively within 60 minutes reaction time. With these optimized reagent doses, colour disappears from wastewater under mild conditions, and more biodegradable effluent is formed, and could be successfully degraded by means of a biological treatment. COD/BOD₅ evaluation for biodegradability assessment was shown to be an important relevant indicator to determine the best moment for coupling. The obtained concomitant decrease of organic load and increase of biodegradability of the partially photo-treated solution of textile wastewater confirmed that photo-Fenton is a promising pre-treatment process capable to enhance the biotreatability of such wastewaters contaminated with dyes as biorecalcitrant chemicals.

Color removal of wastewater was achieved after 40 min. treatment. With the decolourization, COD and TOC in wastewater were also to 80 and 75% respectively at the optimum operating conditions. The BOD₅/COD of wastewater was generally more than 0.3 when their color disappeared completely within 40 min of reaction time. The result implies that the optimal exposing time to photocatalysis process is the period for complete decolourization. The photocatalysis process could be an alternative for decolourization and further TOC and COD removal of dyes from wastewater as pre-treatment of conventional biological process.

The results indicate that the biodegradability of the wastewater can be enhanced by photocatalytic oxidation. In this work, biodegradability analyses of the phototreated solutions of wastewater show that the solution resulting from the photodegradation biologically compatible and its complete mineralization can be performed by biological means.

BIBLIOGRAPHY

1. Correia VM, Stephenson T, Judd SJ. Characterization of textile wastewater-a review. *Environ Technol* 1994; 15: 917-29.

2. Chang S-H, Wang K-S, Chao S-J, Peng T-H, Huang L-C, Degradation of azo and anthraquinone dyes by a low-cost Fe⁰/air process. *Journal of Hazardous Materials* 166 (2009) 1127-1133
3. Reife A. Dyes, environmental. In: *Dyes, environmental chemistry*. Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed., vol. 8. John Wiley and Sons, New York, 1993. p. 753-84.
4. Pagga U, Brown D. The degradation of dyestuffs part II: behavior of dyestuffs in aerobic biodegradation tests. *Chemosphere* 1986, 15:479-91.
5. Parent Y, Blake D, Magrini-Bair K, Lyons C, Turchi C, Watt A, Wolfrum E & Prairie M. Solar photocatalytic processes for the purification of water: state of development and barriers to commercialization. *Solar Energy* 1996, 56(5): 429-437.
6. Malato S, Rodriguez M, Richter B, Blanco C, Galvez J & Vincent M. Photocatalytic degradation of industrial residual waters. *Solar Energy* 1996, 56(5): 401-410
7. Gözmen B, Kayana B, Gizir AM., Hesenov A, Oxidative degradations of reactive blue 4 dye by different advanced oxidation methods. *Journal of Hazardous Materials* 168 (2009) 129-136
8. Bahnemann D, Cunningham J, Fox M, Pelizzetti E, Serpone N. Photocatalytic treatment of waters, in *aquatic and surface photochemistry*. 1994, G.R. Helz, R.G. Zepp, and D.G. Crosby, Editors, Lewis Publishers: Boca Raton. p. 261-316.
9. Bolton JR and Cater SR. Homogeneous photodegradation of pollutants in contaminated water: an introduction. 1994, in *Aquatic and Surface Photochemistry*, G.R. Helz, R.G. Zepp, and D.G. Crosby, Editors, Lewis Publishers: Boca Raton. p. 467-490.
10. Ollis DF, Ekabi HA. Photocatalytic purification and treatment of water and air, in: *EDS*, Elsevier, Amsterdam, 1993.
11. Glaze WH, Kang JW, Chapin DH. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Oz Sci Eng* 1987, 9:335-52.
12. Mayer R, Haseneder R, Härtel G, Ghaly MY. Nas-oxidative Zerstörung kanzerogener und toxisch wirksamer Substanzen. Ein Vergleich der Effektivität verschiedener Verfahren. *TerraTech, Zeitschrift für Altlasten und Boden*, 1999, 4, Juli/August, 55-57.
13. Ghaly MY, Härtel G, Mayer R and Haseneder R. Effect of pH, UV irradiation and hydrogen peroxide on the ozonation process of p-Chlorophenol. *AFINIDAD LVII*, 2000, 490, November-December, 424-430.
14. Ghaly MY, Härtel G, Mayer R and Haseneder R. Aromatic compounds degradation in water by using ozone and AOPs. A comparative study. o-Nitrotoluene as a model substrate. *Ozone Science & Engineering*, 2000, Vol. 23, 127-138.
15. Ghaly MY, Härtel G, Mayer R and Haseneder R. Photochemical oxidation of p-chlorophenol by UV/H₂O₂ and photo-Fenton process. A comparative study. *Waste Management*. 2001, 21, 41-47.
16. Ghaly MY. Destruction of the Environmental organic pollutants through activated hydrogen peroxide oxidation. *Afinidad*, 2005, 62 (518), 314-320.
17. Ruppert G, Bauer R. The photo-Fenton reaction – an effective photochemical wastewater treatment process. *J Photochem Photobiol A: Chem* 1993; 73:75-8.

18. Zepp RG, Hoigne J. Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen peroxide. *Environ Sci Technol* 1992; 26:313-9.
19. Herrmann JM. Heterogeneous photocatalysis: state of the art and present applications. *Topics in Catalysis* 2005, Vol. 34, Nos. 1-4, 45-65.
20. Khataee AR, Pons MN, Zahraa O. Photocatalytic degradation of three azo dyes using immobilized TiO₂ nanoparticles on glass plates activated by UV light irradiation: Influence of dye molecular structure. *Journal of Hazardous Materials* 168 (2009) 451-457
21. Konstantinou IK, Albanis TA. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. A review. *Applied Catalysis B: Environmental* 2004, 49, 1-14.
22. Li Y, Lu Y, Zhu X. Photo-Fenton discoloration of the azo dye X-3B over pillared bentonites containing iron. *Journal of Hazardous Materials* 2006, B132, 196-201.
23. Neamtu M, Yediler A, Siminiceanu I, Kettrup A. Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes. *Journal of Photochemistry and Photobiology A: Chemistry*, 2003, 161, 87-93.
24. Chacon JM, Leal MT, Sanchez M, Bandala ER. Solar photocatalytic degradation of azo-dyes by photo-Fenton process. *Dyes and Pigments* 2006, 69, 144-150.
25. Kositzki M, Antoniadis A, Poullos I, Kiridis I, Malato S. Solar photocatalytic treatment of simulated dyestuff effluents. *Solar Energy* 2004, 77, 591-600
26. Badawy MI, Gad-Allah TA, Ghaly MY and Lopez A. Combination of photocatalytic and biological processes as an integrated system for treatment and recovery of industrial wastewater containing pesticides. *Afinidad*, 2006, 63 (526), 478-487.
27. Ska-Sobecka BS, Tomaszewska M, Morawski A W. Removal of micro-pollutants from water by ozonation/biofiltration process». *Desalination*, 2005, 128, 151-157.
28. Kitis M, Adams CD, Kuzhikannil J, Daigger GT. Effects of Ozone/Hydrogen peroxide pretreatment on aerobic biodegradability of nonionic surfactants and polypropylene glycol». *Environmental Science and Technology*, 2000, 34(11), 2305-2310.
29. Parra S, Sarria V, Malato S, Peringer P and Pulgarin C. Photochemical versus coupled photochemical biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon. *Applied Catalysis B: Environmental*, 2000, 27, 153-168.
30. Lapertot M, Pulgarin C, Fernandez-Ibanez P, Maldonado MI, Perez Estrada L, Oller I, Gernjak W, Malato S, Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton. *Water Research* 40 (2006) 1086-1094.
31. Chen C-Y, Wu P-S, Chung Y-C. Coupled biological and photo-Fenton pretreatment system for the removal of di-(2-ethylhexyl) phthalate (DEHP) from water. *Bioresource Technology* 100 (2009) 4531-4534
32. Scott JP and Ollis DF. Integration of chemical and biological oxidation processes for water treatment: II. Recent illustrations and experiences». *J. Adv. Oxid. Technol.*, 1997, 2(3), 374-381.
33. Lapertot M, Ebrahimi S, Dazio S, Rubinelli A, Pulgarin C. Photo-Fenton and biological integrated process for degradation of a mixture of pesticides. *Journal of Photochemistry and Photobiology A: Chemistry* 186 (2007) 34-40
34. EC, Implementation of Council Directive 91/27/EEC of 21 May 1991 concerning urban waste water treatment, as amended by Commission Directive 98/15/EC of 27 February 1998, Commission of the European Communities, COM (2004) 248 final, Brussels, 2004.
35. Eaton AD, Clesceri L.S. and Greenberg A.E. *Standard Methods for the Examination of Water and Wastewater*. 20th Edition, APHA, AWWA, WEF (1998).
36. [36] *Standard Methods for the Examination of Water and Wastewater*, 20th ed., AWWA, Washington, DC, 1998.
37. Lange for water quality LC. 400 CSB chemischer Sauerstoffbedarf.
38. Süßmuth R, Eberspächer J, Haag R, Springer W. *Mikrobiologisch-Biochemisches Praktikum*, 2 völlig überarbeitete Auflage, 1992.
39. Chun H, Yizhong W. Decolorization and Biodegradability of photocatalytic treated azo dyes and wool textile wastewater. *Chemosphere*, 1999, Vol. 39, No. 12, pp. 2107-2115.
40. Jürgen Trittin. Der Bundesminister für Umwelt, Naturschutz und Reaktorsicherheit. Bekanntung der Neufassung der Abwasserverordnung vom 17 Juni 2004. Anhang Textilherstellung, Textilveredlung. C Anforderung an das Abwasser für die Einleitungsstelle.
41. Hu C and Yizhong W. Decolorization and biodegradability of photocatalytic treated azodyes and wool textile wastewater. *Chemosphere*, 1999, 39, 2107-2115.
42. Sarria V; Parra S; Invernizzi M.; Peringer P and Pulgarin C. Photochemical- biological treatment of a real industrial biorecalcitrant wastewater containing 5-amino-6-methyl-2-benzimidazolone. *Wat. Sci. Tech.*, 2001, 44, 93-101.
43. Perez M, Torrades F, Dom'enech X, Peral J. Fenton and photo-Fenton oxidation of textile effluents. *Water Research* 2002, 36, 2703-2710.
44. Smalling K.L.; Aelion C.M. Biological and chemical transformation of atrazine in coastal aquatic sediments. *Chemosphere* 2006, 62, 188-196.
45. Chamarro E, Marco A, Esplugas S. Use of Fenton reagent to improve organic chemical biodegradability. *Water Res.* 2000, 35 (4), 1047-1051.
46. Chan KH, Chu W. The dose and ratio effects of Fe(II) and H₂O₂ in Fenton's process on the removal of atrazine. *Environ. Technol.* 2003, 24, 703-710.
47. Fernandez J, Bandara, J, Lopez, A, Buar Ph., Kiwi J. Photoassisted Fenton degradation of nonbiodegradable azo dye (Orange II) in Fe-free solutions mediated by cation transfer membranes. *Langmuir* 1999, 15, 185-192.
48. Sarria V, Parra, S, Nevenka A, Peringer P, Benitez, N, Pulgarin, C. Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds. *Catal. Today*, 2002 76, 301-315.