

FS-TER-006

**TECHNICAL SHEETS
FOR EFFLUENT TREATMENT PLANTS
IN TEXTILE INDUSTRY**

FENTON REACTIONS

SERIES: TERTIARY TREATMENTS

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FENTON REACTIONS (FS-TER-003)

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INDEX

1.- INTRODUCTION

2.- FENTON ADVANCED OXIDATION PROCESSES

- 2.1.- Fenton processes
- 2.2.- Process fundamentals: Fenton reaction
- 2.3.- Advantages related with the classic Fenton process
- 2.4.- Drawbacks of the classical Fenton process

3.- DESIGN CRITERIA FOR CONVENTIONAL FENTON PROCESS

- 3.1.- Stage description
- 3.2.- Effluent pH adjustment
- 3.3.- Fenton oxidation
- 3.4.- Neutralization
- 3.5.- Coagulation and flocculation
- 3.6.- Sludge treatment line
- 3.7.- Fenton systems sizing parameter values

4.- FACTORS DETERMINING THE EFFICIENCY OF FENTON PROCESSES

- 4.1.- pH influence
- 4.2.- Temperature influence
- 4.3.- H₂O₂ dosage
- 4.4.- Influence of catalyst Fe²⁺ concentration
- 4.5.- Stoichiometric relation of the reagents [H₂O₂]/ [Fe²⁺]
- 4.6.- Wastewater composition and pollutants nature
- 4.7.- Contact time

5.- CHANGES OVER CLASSIC FENTON PROCESS

- 5.1.- Interesting changes leading to textile industry effluents treatment
- 5.2.- Electrochemical Fenton methods: Fered-Fenton process
- 5.3.- UV Photo-Fenton processes
- 5.4.- Solar Fenton processes
- 5.5.- Fenton processes in Fluidized Bed Reactors (FBR Fenton)
- 5.6.- Fenton process selection criteria

6.- FENTON PROCESSES APPLICATIONS TO EFFLUENT TREATMENTS: CASE STUDIES

- 6.1.- Fenton process with thermic intensification in *Schoeller Textiles AG*
- 6.2.- Fenton process in the dyeing effluent treatment plant of Bamwol Dyeing Industrial Complex

7.- COSTS ANALYSIS OF FENTON PROCESS APPLIED TO WASTEWATER TEXTILES TREATMENT

- 7.1.- Conditioning factors
- 7.2.- Specific cases review

BIBLIOGRAPHY

COMMERCIAL TECHNICAL REFERENCES



1.- INTRODUCTION

Industrial effluents pose specific concerns due to its low biodegradability and possible toxicity both for biological treatments or for receiving natural media. As a result, innovative treatments have been developed. These new processes are capable to degrade recalcitrant compounds present in wastewater. The advanced oxidation processes (AOPs) are included among these alternative treatments.

Overall, this is a diverse set of techniques that share the ability to generate highly energetic radicals, preferably hydroxyl radicals ($\text{HO}\cdot$). The high oxidation potential ($E_0 = 2.81$ volts) of the $\text{HO}\cdot$ radical facilitates the oxidation of numerous organic compounds highly refractory to conventional physical-chemical and biological processes.

The generation of $\text{HO}\cdot$ radicals, a highly reactive and unstable species, must take place *in situ* at the time of application. Depending on the AOP process, different precursor species are used, such as oxygen, ozone (O_3) or hydrogen peroxide (H_2O_2), which undergo chemical, photochemical, electrochemical, sonochemical... reactions, whether or not in the presence of a catalyst, both at homogeneous and heterogeneous systems. Different precursors, reactions and catalysts combinations generate multiple treatment schemes based on AOPs, with different current scale development. Advanced oxidation processes are described in detail in **FS-AVA-001-AOPs** sheet.

Ideally, the ultimate target of the AOPs would be the total conversion of organic matter into CO_2 , water and inorganic ions. In practice, advanced oxidation processes provide compounds more biodegradable than their predecessors, reducing toxicity, color, COD and sometimes the smell of the water under treatment. These features make the AOPs a set of particularly interesting techniques for the treatment of effluents from the textile industry processes.

2.- FENTON ADVANCED OXIDATION PROCESSES

2.1.- Fenton processes

Fenton process family is among the AOPs using H_2O_2 as a precursor reagent of $\text{HO}\cdot$ radicals. A first classification of these processes is:

- Classic Fenton (homogeneous) process at atmospheric pressure and room temperature.
- Heterogeneous Fenton processes, with a wide variety of catalysts, both solid and in supported media.
- Modified Fenton processes, in which process energy is provided by increasing the process temperature (thermal enhanced Fenton), visible or ultraviolet radiation (photo-Fenton processes), electric power (electro-Fenton process) or ultrasound (sono-Fenton process).

Each of these three categories supports multiple subdivisions depending on the reactor configuration, catalyst and/or employed carrier, treatment schemes adopted, working temperature, combinations with other AOPs and so on. Nowadays, technical development differs among the different types of Fenton processes. The newest, such as those with ultrasonic energy supply, are still in an experimental phase of development.

Fenton processes with full scale operation references for industrial wastewater treatment are:

- Classical homogeneous Fenton processes, either at atmospheric or higher pressures and temperatures above 100°C
- Heterogeneous Fenton processes, carried out at industrial scale in fluidized bed reactors (FBR process Fenton)
- Electro-Fenton processes, with external catalyst supply or *in situ* generation of Fe^{2+} through sacrificial anodes
- Photo-Fenton processes, both UV and visible (Solar).

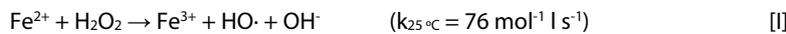
Fenton oxidation processes have been successfully applied to a variety of aqueous media treatments including natural waters, industrial wastewaters, landfill leachates, mining effluents, groundwater and contaminated soils. It has also been applied to volatile organic compounds degradation, oil industry wastes, explosives, pesticides and herbicides, as well as a long list of substances and individual chemical compounds; among them, numerous additives and dyes commonly used in the textile industry. Some detailed relations of compounds susceptible to

Fenton degradation can be found in US EPA (1998, 2001); Gernjak (2006); Rodriguez *et al.* (2010) or Oller *et al.* (2011).

In addition to its high capacity to mineralize refractory organic compounds and to reduce the toxicity of the effluent, the Fenton processes are especially effective in the removal of color, thanks to the high affinity of HO· radicals towards chromophoric groups. This feature makes Fenton processes idoneous for advanced treatment of wastewater from the textile industry, supporting the growing development and industrial application of Fenton processes over the past two decades.

2.2.- Process fundamentals: Fenton reaction

The possibility of generating HO· radicals at atmospheric pressure and room temperature from the so-called Fenton reaction, described in the late nineteenth century, has been known since the thirties in the twentieth century. Classical Fenton reaction occurs when hydrogen peroxide and Fe²⁺ ions are brought into contact in aqueous solution at acidic pH. The ferrous ion initiates the reaction of peroxide decomposition, resulting in the generation of highly reactive HO· radicals, water and heat, since the overall reaction is exothermic:



The successive reaction steps (initiation, propagation, termination), the coupling of successive oxidation and reduction reactions, the simultaneous formation of other radical species of lower oxidizing power, in addition to the multiple interactions between them and the rest of chemical species which may be present in the aqueous matrix, make the commonly known as 'Fenton reaction' a highly complex chemical system. The detailed description of the process is still subject to controversy (Bautista *et al.*, 2008; Barbusinski, 2009).

On the other hand, the participation of ferrous ion Fe²⁺ in the Fenton reaction should be of catalytic nature because, theoretically, the oxidized specie Fe³⁺ would react again with hydrogen peroxide, while generating hydroperoxyl radicals (HO₂·), with lower oxidizing power (E_o = 1.76 V). In the process, iron would return to its reduced form, to start back to reaction [I]:



In practice however, ferric ions (Fe³⁺) formed in reaction [I], much faster than reaction [II], are progressively accumulated in the aqueous solution up to their solubility product, leading to the appearance of ferric hydroxide Fe(OH)₃ precipitates with a characteristic reddish-brown color and colloidal appearance.

This particular aspect of the Fenton reaction should be especially considered when selecting and sizing the process, since:

- Iron precipitation requires keeping the pH of the mixture around 3, the range in which iron remains dissolved as Fe²⁺
- Effluents acidification requires a subsequent neutralization step.
- In order to maintain the reaction, the non-regeneration of Fe²⁺ forces its continuous addition.
- The appearance of ferric precipitates demands a separation step and sludge conditioning and final management after the oxidation reaction. Depending on the characteristics of the wastewater treatment flow, the sludge management can make the process uneconomical.

2.3.- Advantages related with the classic Fenton process

The main advantages of a classic Fenton process as a feasible alternative for industrial effluents treatment are:

- Wide range of applications to various types of effluents, contaminants and organic loads
- High affinity towards chromophore compounds, resulting in a rapid removal of color with relatively low contact times
- Facilitates the biodegradation of refractory organic compounds
- Simple design of equipment and facilities
- Operational simplicity

- Scalability of the process
- Lower investment and operation costs in comparison to other AOPs
- Reagents purchase and handling is easy
- No toxic byproducts (AOX) generation
- Toxicity reduction of effluents and final discharge
- Low surface occupation.
- Valid at industrial scale
- It provides a coagulation treatment associated with the co-precipitation of some contaminants along with iron (III)

2.4.- Drawbacks of the classical Fenton process

The classic Fenton process has three main drawbacks, essentially related to operational factors:

- **Sludge production:** It is the main drawback from an operational point of view. Fenton process sludge is a colloidal reddish-brown precipitate, which must be separated from the liquid mixture after the oxidation step and, subsequently, has to be properly managed as solid waste.
- **pH control:** the optimum pH for the reaction, close to 3, limits its application unless a prior acidification of the effluent is made, which implies an additional step of neutralization after the Fenton oxidation.
- **Reagents consumption:** the lack of Fe^{2+} regeneration requires the continuous supply of the catalyst during the reaction. The consumption of hydrogen peroxide may increase excessively the operating costs in case of large wastewater flows or high organic loads, to the point of being economically disadvantageous. In such cases, it may be necessary to establish an appropriate segregation strategy for the Fenton treatment flows, in order to optimize AOPs treatment application to the most cost-effective flows.

In real practice, the presence of sludge is the biggest drawback of the classic Fenton process, and is the fundamental reason to perform changes in the process. In general, the designed improvements are focused on two objectives intrinsically linked to each other:

- The reduction in iron (III) sludge production.
- The continuous Fe^{2+} catalyst regeneration during the process

The main characteristics of the classic Fenton processes are briefly exposed in Table 1. related to other advanced oxidation processes which are also frequently used to treat industrial wastewater.

Table 1. Comparison between Fenton and other AOPs processes

	Non-photochemical Fenton processes	Electrochemical oxidation	Ozone-based AOPs	UV photo-oxidation processes
Effluent treatability	Wide COD range. It is not affected by color or turbidity presence. pH adjustment is critical.	Optimized to high COD values. Adequate for specific segregated effluent treatment.	Suitable for effluent decoloring. Ozone transfer is diffculted by organic matter presence.	Limited to effluents with very low turbidity. Not applicable to highly colored effluents nor strong loaded flows.
Installation	Conventional. It allows facilities reuse. It can be incorporated in any treatment stage. Flow rate variability is supported.	Electrode selection and design are critical to optimize the process.	Relatively easy. Adapted to commercial ozonation equipment.	Adapted commercial UV equipment.
Sludge production	Yes	No	No	No
Commercial technology availability	Yes. Both homogeneous and heterogeneous treatments available	Yes. Electrode selection is definitive.	Yes	Yes. Limited experience at real scale with textile effluents
Investment costs	Low	High	High	High
Operation costs	Moderate	High	High	High
Operation & Maintenance	Easily acquired reactors equipment and H ₂ O ₂ and pH adjustment chemicals	Chlorine generation in treated effluents can represent a problem. Electricity consumption.	It requires oxygen and H ₂ O ₂ supply. Ozonation equipment O&M requires specialized personnel.	Limited UV lamps lifetime. A commercial catalyst is needed. Biofouling reduces process efficiency.
Textile effluent experience	Yes. Extended experience at real scale.	Yes.	Yes, moderate	Yes, moderate.

3.- DESIGN CRITERIA FOR CONVENTIONAL FENTON PROCESS

3.1.- Stage description

The scheme of a classic or conventional Fenton treatment, in homogeneous phase, is shown in Figure 1. It consists of a sequence of three stages, where sludge generation, separation and treatment processes are indicated.

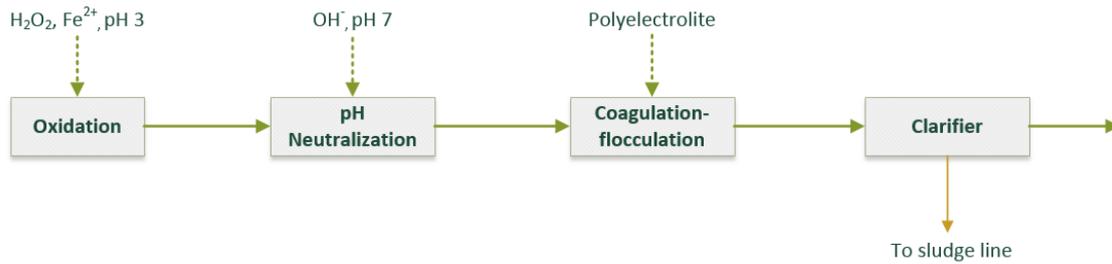


Figure 1. General scheme of an advanced oxidation Fenton process for wastewater treatment.

The successive stages consist in an oxidation reaction process itself, which takes place at a pH around 3, followed by an effluent neutralization step and coagulation/flocculation of the suspended solids. Each stage occurs in a separate reactor operating in sequential mode.

The general characteristics of the reactors and the design criteria for each of these unit operations are similar to those of any process of mixing and stirring, and are described in **FT-PRI-001-Coagulation-Flocculation** and **FT-PRE-004-Neutralization Sheets**.

Mixing steps end in a settling operation, where the oxidized effluent is separated from the ferric sludge generated during the Fenton process. Settling operations are considered in **FT-PRI-002-Primary Settling** and **FT-PRI-004-Lamella settling**.

Settled sludge requires further treatment. The use of iron as a coagulant allows the use of gravity thickening, turning 1% sludge to a concentration around 10% by weight. Sludge is then subject to drying operations (press filter) to reduce humidity to values compatible with the final destination.

Fenton process facilities include also deposits required for the storage, preparation and reagents dosage, as well as the corresponding sensors and automated controls for the whole process.

3.2.- Effluent pH adjustment

Before undergoing oxidation, wastewater must be acidified to a pH value around 3, optimal in order to develop the Fenton reaction. Usually, technical grade sulphuric acid is added in an appropriate dilution.

Depending on the wastewater treatment flow and the configuration of the treatment plant, acidification can be made:

- Into a specific acidification tank
- Into an effluent homogenization tank
- Directly in the oxidation tank

3.3.- Fenton oxidation

The reagents used for production of HO· radicals are dosed directly into the wastewater oxidation tank. Hydrogen peroxide and ferrous sulfate 35% are commonly used in any suitable commercial variety. HO· radicals production starts immediately after the addition of the ferrous catalyst mixture, resulting in the complex system of reactions known collectively as 'Fenton reaction'.

Hydroxyl radicals generated by Fenton reaction react non-selectively with virtually all organic compounds, both aliphatic and aromatic, carrying out the partial or total degradation of contaminants through various reaction mechanisms. Only some very stable low molecular weight compounds resist the attack, such as acetone, acetic acid and oxalic acid, plus some paraffins and organohalogen compounds.

Depending on the nature and chemical structure of the pollutants, and on their susceptibility to be attacked by HO· radicals, contact times ranging from thirty minutes to over two hours are required in a full scale oxidation tank. The mineralization degree achieved is also variable, being specific to each substance, aqueous matrix and

working conditions. Therefore, optimal doses of each reagent and process kinetics can only be determined from pilot studies for each particular effluent.

It is very important to ensure good mixing conditions in the oxidation tank. Given the short HO· radicals half-life within aqueous solution, the maintenance of the Fenton reaction in the oxidation tank for long contact times implies the need to establish an adequate system of reagents addition to the wastewater. Mixing conditions and dosage control are usually carried out automatically.

3.4.- Neutralization

Once HO· radicals oxidation is finished, the mixture of wastewater and residual reagents is sent to a conventional neutralization step, through lime or sodium hydroxide addition to the liquid. Even a possible excess of H₂O₂ is removed this way. The neutralization step is performed in a specific reactor, and requires a typical contact time of about 90 minutes.

pH rise to neutral values has an immediate consequence the generation of reddish iron (III) precipitates, which have a colloidal appearance and are difficult to manage..

3.5.- Coagulation and flocculation

The generation of precipitated iron (III), characteristic of the Fenton reaction, requires the advanced process treatment to be completed with a third stage in which the flocculation of the coagulated ferric sludge is accelerated by addition of a suitable polyelectrolyte. The stage is carried out in a mixing reactor for a minimum contact time of 15 minutes.

Coagulation and flocculation with iron (III) may also contribute to the elimination of possible particulate matter present in the wastewater.

3.6.- Sludge treatment line

At the outlet of the flocculation stage, the treated water is sent to settling. The sludge obtained present a typical solids content between 1 and 2% by weight. It is then necessary to submit the sludge to successive thickening and drying operations, to reach the right conditions for its disposal.

Since iron is not consumed during the reaction, the amount of produced iron (III) sludge can be estimated theoretically from the amount of Fe²⁺ dosed in the oxidation tank. Üstün *et al.* (2007) estimated a ferric sludge production of 0.014 m³ per m³ of water treated with a dose of 20 mg/L FeSO₄ added to dyeing operation textile effluent.

3.7.- Fenton system sizing parameter values

Fenton process performances vary greatly between different effluents, both qualitatively and quantitatively. For this reason, it is necessary to consider them individually, making previous pilot studies to determine the values of optimum design parameters for each wastewater flow according to:

- The wastewater composition and characteristics of the contaminants
- The susceptibility of the pollutants of interest to oxidation with HO·
- The quality objectives being pursued with the treatment: detoxification, partial or complete mineralization of organic matter; avoiding of biological process overloading; color removal in flow discharge; allowance of direct discharge to sewer or natural media..

Table 2. Some typical parameter operation values of advanced oxidation Fenton processes.

Stage	Operation pH	Contact time (min)	COD removal (%)
Fenton oxidation	3 (2 – 4)	30 – 120	30 – 80
Neutralization	7 (6.5 – 7.5)	60 – 100	-

Coagulation/flocculation	7 (6.5 – 7.5)	15 – 20	10 – 50
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The stoichiometry of the degradation reactions by Fenton processes is very complex. Besides radical HO·, the pair Fe²⁺/Fe³⁺ and hydrogen peroxide may also form other radical species, such as hydroperoxyl radical (HOO·), ferryl radical (FeO²⁺), dissolved molecular oxygen, organic hydroperoxides and other intermediate species formed during the course of the oxidation reactions. Despite these potential limitations for the development of a precise kinetic model for the design of a Fenton process, in practice the overall reaction can be adequately described by a pseudo first order kinetics with respect to the contaminant of interest (color, TOC, COD...) assuming stationary conditions of the reactants.

The kinetic parameters of the pseudo first order reaction should be established experimentally for each effluent at laboratory or pilot scale.



Figure 2. Industrial wastewater treatment using advanced oxidation Fenton process. Reagents required in each stage are supplied to successive reactors from storage tanks in a fully automated treatment process. The compactness of the system is enhanced by the use of lamellar sedimentation units. (Source: TECNA, s.l.r., Italy, www.tecna-italy.com)

4.- FACTORS DETERMINING THE EFFICIENCY OF FENTON PROCESSES

4.1.- pH influence

As mentioned above, AOPs based on the Fenton reaction are critically affected by pH because this parameter modifies the prevalence of various iron species coexisting in aqueous solution. The optimal value for the degradation of organic pollutants by the classical Fenton process lies in a narrow range of pH about 3 (2-4).

Below pH 2 an iron complex generation occurs, reducing the concentration of free Fe²⁺ remaining available in the aqueous mixture. Above pH 4, Fe(OH)₃ precipitates begin to appear, which are of colloidal nature and very stable, removing the catalyst substance from solution.

Consequently, the low efficiency of Fenton process above pH 4 is attributed to the low rate of HO· radicals production owing to the disappearance of Fe²⁺ in the reaction phase. Even higher pH values would result in decomposition of hydrogen peroxide into oxygen and water, dramatically reducing the formation of HO· and consequently, the overall efficiency of the process.

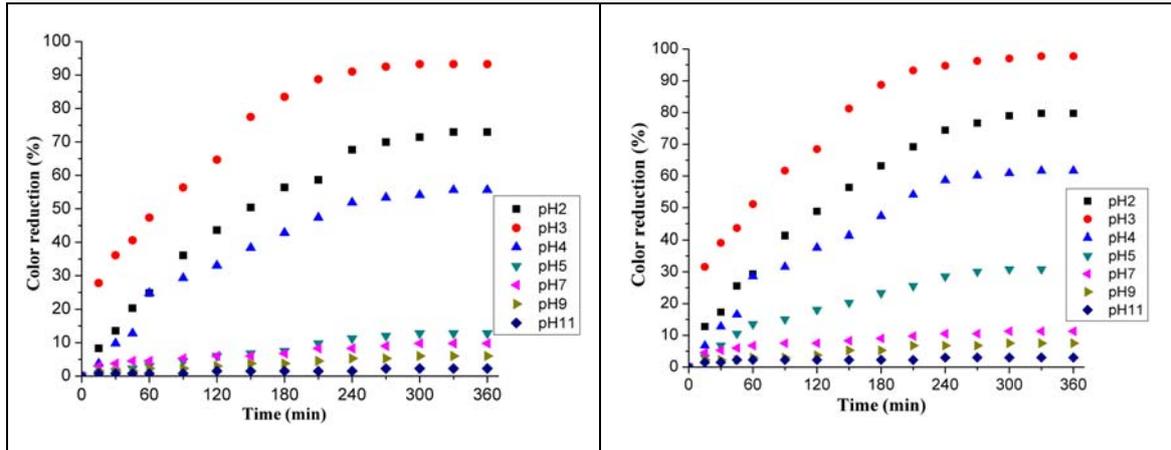


Figure 3. Effect of pH on color removal in an aqueous solution of Reactive Blue 19 ($C_0 = 20 \text{ mg/L}$) by Fenton process (left) and photo-Fenton UV (right). $[\text{H}_2\text{O}_2] = 50 \text{ mg/L}$; $[\text{Fe}^{2+}] = 4 \text{ mg/l}$. (From Bharadwaj and Saroha, 2015)

4.2.- Temperature influence

Being a radical mechanism, the initiation of the Fenton reaction does not require a high activation energy, which means it can proceed in a wide range of ambient temperatures, but more efficiently above 20°C .

A temperature increase would favor, at first, the rate of the reaction. However, high temperatures also favor the dismutation of hydrogen peroxide to water and oxygen. It also contributes to the solubility of oxygen, which participates in numerous stages of organic compounds mineralization, decreasing rapidly with temperature.

Several authors have established optimum temperatures as those in the range between 40°C and 50°C for Fenton processes carried out at atmospheric pressure. Table 3 provides some specific references evaluating the temperature influence on the efficiency of the conventional Fenton process, for different types of textile effluents.

Table 3. Optimal temperatures for conventional Fenton process at atmospheric pressure, for different types of textile process effluent.

Reference	Optimal performance temperature	Kind of textile effluent	Type of essay
Gulkaya <i>et al.</i> , 2006	$40 - 70^\circ \text{C}$	Real carpet dyeing process effluent	Batch (t: 30 min.)
Bouafia, 2010	40°C	Synthetic, basic dyes	Photo-Fenton, pilot scale
Rodrigues <i>et al.</i> , 2014	$30 - 50^\circ \text{C}$	Synthetic, polyester dyeing effluent reply	Jar test (t: 60 min)
Wu y Wang, 2012	35°C	Real dyeing and printing process effluent	Batch (t: 4 hours)
Pérez <i>et al.</i> , 2002	70°C	Real hypochlorite bleaching process effluent	Batch. Fenton and photo-Fenton with xenon lamp at pH 3. (t: 30 - 120 min)

Temperature dependence can restrict the use of Fenton reactions under cold environmental conditions. A modification to avoid this possible limiting factor makes use of the exothermic nature of the process, taking place in a closed vessel at a pressure of 3 to 5 atmospheres. Under these conditions, once initiated the reaction by the ferrous ion and hydrogen peroxide, the mixture easily reaches temperatures above 100°C without the occurrence of a violent hydrogen peroxide decomposition, which would take place at atmospheric pressure. The process continues in an autothermal way, without the need for external energy supply, achieving high removal

efficiencies of color and mineralization of organic compounds with moderate contact times (Schömberger and Schäfer, 2003).

4.3.- H₂O₂ Dosage

HO· radicals react with most organic and inorganic substances, with low selectivity for all species available. Therefore, the optimal dosage of H₂O₂ required for the Fenton oxidation of a given effluent must be established empirically, through specific tests both in laboratory and pilot scale. Dose will depend on the nature and concentration of contaminants in the treated water, together with the stoichiometric relationships established between substances and reagents.

The dose of H₂O₂ required will also be conditioned by the oxidation process objective (degradation of refractory material prior to biological treatment, tertiary effluent polishing after the biological elimination of perceptible color, total organic matter mineralization...), as well as the quality criteria for discharge.

In any case, the concentration of hydrogen peroxide is a significant factor in the overall efficiency of the degradation process of organic matter. Usually, and as a rule, it will be increased with increasing peroxide contribution. However, the determination of the optimal dose for the process must consider that the residual fraction of unreacted hydrogen peroxide contributes to raise the COD of the mixture. Unconsumed peroxide also acts as a sink for HO· radicals, thereby reducing the efficiency of the overall process. Therefore, excess reagent should be avoided for this reason, in addition to logical economic considerations.

The dosage of hydrogen peroxide must be adjusted so that the total supplied amount reacts efficiently during Fenton oxidation process. Determining the optimal dosage can only be made from the testing results with each specific effluent. As a guiding rule, the dose calculation corresponding to the theoretical stoichiometric ratio between effluent COD and hydrogen peroxide H₂O₂ may initially be applied.

In Table 4, some illustrative doses of H₂O₂ used in real conditions with different colored effluents from dyeing processes are listed.

Table 4. Some H₂O₂ dosage references in real operation conditions for Fenton process aimed to remove color and COD.

Effluent type	COD, mg O ₂ /L	H ₂ O ₂ dosage	Fe ²⁺ dosage	Reference
Schoeller Textiles AG (Switzerland). Highly COD loaded segregated effluent	8500	13 L H ₂ O ₂ (35%)/m ³	120 g Fe ²⁺ /m ³	Schömberger and Schäfer, 2003
Matches dyeing mil with acid dyes (Poland)	1000 – 3000	0.4 – 0.6 to 1,0 – 1.5 g H ₂ O ₂ /L	[Fe ²⁺] : [H ₂ O ₂] = 1:3	Barbusinski, 2009b
Effluent from a textile industry in Zanjan (Iran)	1800	1 – 2.5 g H ₂ O ₂ /L	0.05 – 0.35 g Fe ²⁺ /L	Eslami <i>et al.</i> , 2013
Dyeing effluent of polyester and acetate (Turkey)	930	0,3 g H ₂ O ₂ /L	0,3 g FeSO ₄ /L	Azbar <i>et al.</i> , 2004

Theoretically, the stoichiometric ratio between the oxidant and soluble organic matter should be between 2 and 10. However, in current practice this relationship can be one or two orders of magnitude greater, because of the competition between multiple reactions established with HO· radicals in the aqueous matrix.

4.4.- Influence of catalyst Fe²⁺ concentration

Excessive concentration of Fe²⁺ in the mixture does not increase the rate of oxidation of organic matter by Fenton process. This behavior is justified by the appearance of parasitic reactions between Fe²⁺ and available HO· radicals. The optimum concentration of catalyst that determines the process rate is fixed by the dose of hydrogen peroxide. They are related through the optimum stoichiometric ratio of both reagents for each specific treatment water.

Table 4 also includes the dosages of catalyst employed in optimum conditions for dyeing process effluent treatment in order to illustrate their specificity.

4.5.- Stoichiometric relation of the reagents [H₂O₂]/ [Fe²⁺]

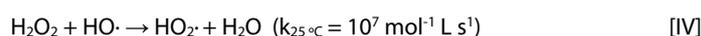
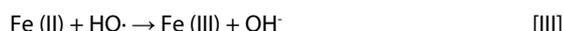
The optimum stoichiometric ratio of reagent concentrations [H₂O₂]/[Fe²⁺] is one of the determinants of the Fenton reaction efficiency as well as one of the main control parameters of this process.

Despite the numerous experimental studies and various industrial applications of the Fenton reaction, there is no agreement on an universal optimum value for the molar ratio [H₂O₂]/[Fe²⁺]. The high variability of water and pollutants, as well as the reaction conditions, make the relation [H₂O₂]/[Fe²⁺] to be determined empirically for each effluent.

In general, increasing the concentration of ferrous ion (Fe²⁺) accelerates the rate of reaction, but does not affect its performance. By contrast, increasing the concentration of H₂O₂ in the reaction media results in increased efficiency of oxidation, but without influencing the reaction rate. Determining the optimal ratio between the concentrations of both reactants provide a maximum reaction efficiency, along with the optimized kinetics for the overall process.

Reference values often used molar ratios [H₂O₂]/[Fe²⁺] between 1.2 and 2.5, although these values are only indicative. The ratio [H₂O₂]/[Fe²⁺] for each effluent can be fixed at the start of the oxidation reaction, or it can also be maintained during the course of the reaction by continuous or intermittent addition of the oxidant.

Moreover, excess concentration of any reactive has to be considered with care as it has an inhibitory nature of the reaction due to the capture of HO· radicals by excesses of both reagents, according to reactions [III] and [IV]. Thereby, mineralization process extent achieved in the aqueous mixture can be limited.



4.6.- Wastewater composition and pollutants nature

The effect of the aqueous matrix on the overall Fenton processes development also affects their performance. High levels of salinity commonly found in industrial effluents, especially from textile industries, can cause negative effects on the formation of the interesting reactive species (hydroxyl radicals and others), due to the appearance of competitive reactions with the organic matter oxidation.

The carbonate anion is an important sink for HO· radicals. Other anions such as phosphates, react with iron to form complexes, both in their ferrous and ferric state. Chloride ions also form complexes with iron, along with acting as hydroxyl radicals sinks.

The results obtained by De Laat *et al.* (2004) suggest that a significant presence of inorganic anions in effluent reduces the hydrogen peroxide decomposition rate in HO· and the oxidation of organic compounds, owing to competitive reactions that reduce the rate of HO· generation, even at optimal conditions of pH 3 and in catalyst excess.

Specifically, it was determined that the abundance of chloride ions produce sensitive reductions in the rate of oxidation of organic compounds as diverse as atrazine, nitrophenol and acetic acid, being lower the effect of nitrate ions (NO_3^-), perchlorate (ClO_4^-) and sulfate (SO_4^{2-}).

Although emphasizing that the extrapolation of these results to real operation conditions can only be achieved through pilot tests with every specific effluent, the study findings suggest the advantages of flow segregation strategies, or flow conditioning prior to Fenton treatment. This is specially necessary for effluents with an elevated content of inorganic salts, particularly carbonates and chlorides.

With respect to organic contaminants of particular concern from the point of view of the textile wastewater, practically all commercial dyes have shown susceptibility, in varying degree, to oxidation by Fenton process at reasonable contact times. As a summary, in Table 5 some discoloration percentages obtained for various commercial dyes commonly used in the textile industry are introduced, adapted from Gupta *et al.* (2015),.

The performance in terms of organic matter mineralization, expressed as removal percentage of COD or COT, varies greatly depending on the characteristics of each effluent and specific process conditions, but is usually above 60% in removed COD in very loaded water, treated before the biological treatment. The removal efficiency can reach more than 90% in secondary effluent refining operations with modern Fenton systems.

Table 5. Susceptibility to Fenton oxidation reaction of different aqueous mix of commercial dyes (Gupta *et al.*, 2015)

Dye/Dyes mixture	Color removal (%)
C. I. Reactive Red 195, C. I. Reactive Yellow 84 and C. I. Reactive Blue 69	High
Remazol Red RR, Remazol Blue RR	100
Cationic: Basic Blue 41, Basic Yellow 28 , Basic Red 46	100
C.I. Acid Yellow 36 (AY36), C.I. Acid Red 14 (AR14) and C.I. Basic Yellow 28 (BY28)	60
Methyl Orange, Reactive Black 5 and Fuchsin Acid Lissamine Green	43
Malaquite Green and Orange II	High
Yellow Drimaren, Congo Red and Methilene blue	90
Remazol Black 5, Remazol Red RB, Remazol Yellow 84, Remazol Brilliant Blue	99

4.7.- Contact time

The optimum contact time must also be set individually for each specific effluent. As a general rule, the period for the oxidation stage is in most cases around 60-120 minutes.

In addition, reaction times are also conditioned by the objective sought with the introduction of a Fenton process in the industrial wastewater treatment line. Oxidation of non-biodegradable organic matter, in order to raise the BOD_5/COD ratio before biological treatment, may require very different contact times than those required within a tertiary treatment after biological processing, especially in the treatment of very refractory chemical compounds, with very restrictive discharge limits, or when introducing the treated water reused as process water.

The contact time can be extended by intermittent dosing of hydrogen peroxide, with successive contributions to the mixture. The literature indicates that an intermittent oxidant injection improves the process performance compared to what would be obtained with a single initial dose.

5.- CHANGES OVER CLASSIC FENTON PROCESS

5.1.- Interesting changes leading to textile industry effluents treatment

Although highly efficient in removing organic pollutants, classic Fenton process associated drawbacks, already described, have prompted the introduction of modifications and alternative designs to the conventional process during the last two decades. The basic objective is to increase the efficiency of the process, trying to simultaneously reduce the formation of iron precipitates requiring the introduction of a sludge treatment line in the treatment configuration.

Among the numerous modifications and alternative methods, complex and hybrid, described in literature, the treatment of real scale textile effluents uses conventional Fenton processes, both homogeneous and heterogeneous, electrochemical Fenton processes and photo-Fenton processes.

Table 6. Description of industrial Fenton processes suitable for textile effluent treatment.

Fenton process	COD range (mg O ₂ /L)	Global reaction	Process characteristic
Classic Fenton (homogeneous)	50 – 1000	$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{HO}\cdot + \text{OH}^- + \text{Fe}^{3+}$	Formation of sludge and ferric hydroxide coprecipitates. Interference by parasitic reactions. Efficiency increases at high P and T.
Electro-Fenton (Fenton II)	50 - 300	a) $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$ b) $\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ c) $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{HO}\cdot + \text{OH}^- + \text{Fe}^{3+}$	Cathodic H ₂ O ₂ production from oxygen or air. The catalyst may be generated by anode oxidation (sacrificial anode)
Electrolytic reduction Fenton (Fered-Fenton, Fenton III)	1000 – 50000	a) $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ b) $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{HO}\cdot + \text{OH}^- + \text{Fe}^{3+}$	Electrolytic reduction of Fe (III) at the cathode allows catalyst recovery and reduces sludge production up to 80%
Fluidized bed Fenton (FBR-Fenton, Fenton IV)	50 - 1000	a) $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{HO}\cdot + \text{Fe}(\text{OH})^{2+} \rightarrow \dots \rightarrow \text{FeOOH}$ b) $\text{H}_2\text{O}_2 + \text{FeOOH} \rightarrow \dots$	Heterogeneous catalysis promotes crystal growth on the solid phase. The overall efficiency is increased, and iron sludge formation is reduced by up to 70%. The separation and recovery of iron is simpler.
Photo-Fenton processes (visible, UV)	Broad range. Limited to water	a) $\text{H}_2\text{O}_2 + h\nu \rightarrow 2 \text{HO}\cdot$ b) $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{HO}\cdot + \text{OH}^- + \text{Fe}^{3+}$ c) $\text{FeOH}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{HO}\cdot$	The photocatalytic reduction of iron (III) allows the recovery of the catalyst and prevents the formation of sludge. Method conditioned by the effluent transmittance.

5.2.- Electrochemical Fenton methods: Fered-Fenton process

At practical scale, the oxidation of Fe²⁺ catalyst species to Fe³⁺ during the Fenton process results in the drawbacks already mentioned: production of colloidal mud, catalyst consumption and the need of acidifying and neutralizing sequentially the effluent in order to separate the precipitates. Therefore, any modification of Fenton process that facilitates the conversion of Fe³⁺ to Fe²⁺ speeds up the process and stimulates the reduction in the amount of sludge produced. This modifications will help to maintain proper iron concentration levels in the effluent flow, without adding a new pollutant contribution to the treated effluent.

In modern electrochemical Fenton processes, called Fered-Fenton, this objective is achieved by applying an electric current to the aqueous mixture to provoke the cathodic reduction of Fe³⁺. Despite the existence of other

usually reserved for the specific treatment of segregated flows comprised of high or very high COD, containing presence of highly refractory pollutants or subject to very strict quality criteria.

The configuration changes of Fered-Fenton treatment in relation to a conventional Fenton process are minimal. The size of the Fered-Fenton reactor is usually quite small, so it can be adapted to any existing system, as shown in Figure 5. In Table 7 some references, reactor dimensions and COD removal efficiencies for effluents from various industrial sectors after Fered-Fenton treatment are included. This relation considers the information provided by the *Taiwan Center of Industrial Technology Research Institute* (www.itri.org.tw).

At full-scale, the performances obtained with these processes are about 90% in reduction of the influent COD. As for operating costs, some India references (2011) were established in the range of 120 to 170 rupees (about 1.7 to 2.4 euros at current exchange rate) per kg of COD removed (XH2O Solutions, www.xh2osolutions.com).



Figure 5. Fered-Fenton reactor for the oxidation of non-biodegradable COD from a printboard factory in Taiwan (Ref.: ITRI, www.itri.org.tw)

Table 7. Performances and features of some Fered-Fenton facilities in current operation in Taiwan. (Ref.: ITRI, www.itri.org.tw)

Industry typology	Fered-Fenton reactor size (m)	Operation start	Flow rate (m ³ /d)	Influent COD (mg/l)	COD removal (%)
Printboard manufacture	1 x 1 x 2	1998	30	2000	80
Chemical laboratory	0,7 x 0,7 x 2	1999	0,5	20000	85
Surface treatments	0,7 x 0,7 x 2	2000	10	10000	80
Synthetic fibers production	1 x 1 x 2 (x 2 units.)	2001	100	1000	90
Electronic industry	0,7 x 0,7 x 2	2002	1	18000	90
Printboard manufacture	0,32 x 0,32 x 1,80	2006	50	500	80
Energy generation	0,47 x 0,27 x 1,80	2007	15	20000	70
Precision equipment manufacture	0,24 x 0,7 x 2	2009	2 (weekly)	47000	90
Photo-voltaic industry	0,7 x 0,7 x 2	2010	5	30000	90

5.3.- UV Photo-Fenton processes

Another modification of the Fenton process that has been brought to the actual practice of Industrial wastewater treatment is based on the use of ultraviolet radiation to achieve the photoreduction of Fe³⁺ generated as a result of the production of HO· radicals. This entails an improvement in the efficiency of the process and, above all, a marked reduction in the Fe³⁺ amount of produced sludge.

UV radiation is able to substantially accelerate the reduction reaction of Fe^{3+} to Fe^{2+} increasing, simultaneously, the rate of $\text{OH}\cdot$ radicals formation, and the subsequent organic matter degradation. It also contributes, to a lesser extent, in the production of $\text{HO}\cdot$ radicals via direct photolysis of the hydrogen peroxide and in the possible photolysis of contaminants capable of being photodegraded.

As in the conventional Fenton process, the optimum pH of the photo-Fenton process is in the range between 2 and 4. In this pH range the predominant iron (III) species in aqueous solution is the cation FeOH^{2+} , which has an absorption band between 200 and 410 nm (between UV and visible spectra). In the presence of UV radiation, the cation FeOH^{2+} results in the generation of hydroxyl radicals according to the following photochemical reaction:



The maximum quantum yield of the reaction [VII] is obtained around 313 nm (US EPA, 1998) in the UV-C range, which determines the selection of UV lamps used in photo-Fenton processes.

The photocatalytic reaction is carried out in UV reactors similar to those used in other applications of UV radiation for wastewater treatment. The photo-Fenton stage is coupled to a conventional Fenton treatment system, as seen in Figure 6.

The high costs in investment (acquisition of UV equipment) and operation (power consumption, lamp replacement, UV reactors cleaning) associated with such systems, in addition to operating costs of a conventional Fenton arrangement, reduce the scope of this kind of treatment application to low flow rates.

Moreover, an excessive turbidity and coloration of effluents are technical factors discriminant for the selection of a photo-Fenton process, as to any other UV treatment. Therefore, the photo-Fenton UV systems are usually reserved for tertiary treatment of effluents subjected to a restrictive discharge quality in order to ensure the elimination of refractory contaminants at low concentrations escaping the biological treatment, avoiding the formation of toxic oxidation-by products.



Figure 6. UV Photo-Fenton treatment system applied to an industrial effluent tertiary treatment (Ref.: Enviolet GmbH, Karlsruhe).

As with any other UV photochemical process, system efficiency depends on the design of the reactor, which in turn will be influenced by factors such as:

- The type of UV lamps used
- The number of lamps
- Reactor geometry
- Hydrodynamic conditions

Commercial photo-Fenton systems are acquired as turnkey projects, making it difficult to establish general investment costs associated with treatment efficiency.

Regarding the operating costs of UV photo-Fenton systems, the estimation made by Rodrigues et al. (2014) for direct treatment of textile effluent from a cotton and synthetic fibers dyeing mill is in a range between 10 and 20 euros per cubic meter of treated effluent, using the radiation intensity, obviously very high, which guarantees the quality objective (no visible color; COD \leq 250 mg/L) for direct discharge of the effluent into a river. Meanwhile, Taner (2011) extracts tertiary treatment operating costs of textile effluents from a UV photo-Fenton system in the range between 1.2 and 4.6 dollars per cubic meter for local conditions in Turkey.

5.4.- Solar Fenton processes

Since the main drawback of photo-Fenton processes UV applied on an industrial scale lies in the high investment costs, maintenance and power consumption of UV lamps, an alternative arising great interest in the field of treatment of industrial wastewater is the oxidation process using photo-Fenton in which solar radiation replaces UV radiation.

Iron (III) formed during the Fenton reaction also forms complexes which have absorption bands in the UV-visible up to 600 nm, and which are capable to generate hydroxyl radicals under mechanisms similar to those of the reaction [VII] with acceptable quantum yields, although inferior to the UV-C radiation. Solar photo-Fenton process presents great interest, especially in those latitudes under a total insolation above 1700 kWh/ m²-year (Nascimento *et al.*, 2007).

Currently, some promising studies are being developed in practice at different scales. A noteworthy pilot scale is situated at *Plataforma Solar de Almería* (www.psa.es) using solar photo-Fenton process, in various solar photoreactor configurations (Gernjack., 2006; Bautista et al, 2008; Bouafia , 2010).

At demonstration scale, during 2014 the solar photocatalysis installation of agricultural waste processing company Albaida SL (La Mojonera, Almería) came into operation, in which a solar photo-Fenton process was applied to the degradation of pesticide residues from pesticide containers washing water. Albaida S.L. plant has 150 m² of solar surface of cylindrical-parabolic collectors coupled to a conventional Fenton process in order to minimize the production of ferric precipitates. The power consumption required by the plant is minimal and its operation is fully automated.

Like any other photochemical process, the applicability and performance of the solar photo-Fenton process is subject to the transmissivity properties of treated water, in addition, in this case, to the variation in atmospheric conditions and night periods.



Figure 7. Solar Photo-Fenton facilities in Albaida, S. L. in La Mojonera (Almería, Spain), dedicated to pesticide waste washing water treatment. Please observe the reddish tone caused by Fe (III) precipitates (www.psa.es).

5.5.- Fenton processes in Fluidized Bed Reactors (FBR Fenton)

Fenton fluidized bed reactors are a modification of the conventional Fenton method (homogeneous) for degradation of contaminants in aqueous solution. Operating results have confirmed the advantages of this method. Some of these advantages are (Tisa et al, 2014.):

- A higher rate of pollutants degradation
- Lower reaction time for similar performances
- Best recirculation of Fe^{2+} catalyst

Thus, the disadvantages resulting from the appearance of ferric precipitates in Fenton homogeneous processes can be reduced by introducing a solid phase in the system. On a commercial scale, Fenton treatment systems incorporating a fluidized bed reactor for the development of the reaction are denominated FBR Fenton or also Fenton IV systems.

The specific characteristics of fluidized bed reactors, applied to biological effluent treatment, are described in **FS-BIO-007**. Dissolved heavy metals recovery is included among the unit operations carried out advantageously with this type of reactor. This is possible through the crystallization around the bed particles, facilitating phase separation.

Thus, FBR Fenton systems' main advantage is the improvement in phase separation of the colloidal iron compounds (III) generated during the Fenton reaction. The bed particles serve as a support and nuclei for iron (III) compounds crystallization, being thus removed from the liquid phase.

The bed fill of the FBR Fenton reactor usually consists on readily available materials such as silica sand or brick construction ceramic particles. There are also known pilot scale experiences with glass beads of larger diameter, with different types of clay and activated carbon, and other materials (Tisa et al., 2014). The bed particles act as crystallization nuclei for iron (III), which is deposited in the form of $\text{FeO}(\text{OH})$, an iron oxy-hydroxide. The crystal growth is favored under suitable reagent supersaturation conditions, which implies a good control over the concentrations of hydrogen peroxide and ferrous ions within the mixture.

In Figure 8 a process of industrial effluent treatment based on FBR Fenton is outlined. The primary effluent, along with Fenton process reagents, is pumped upflow into the fluidized bed reactor. Once the reaction is complete, the Fenton-by oxidized effluent is extracted by the top of the reactor and sent to sedimentation process to remove settled suspended solids.

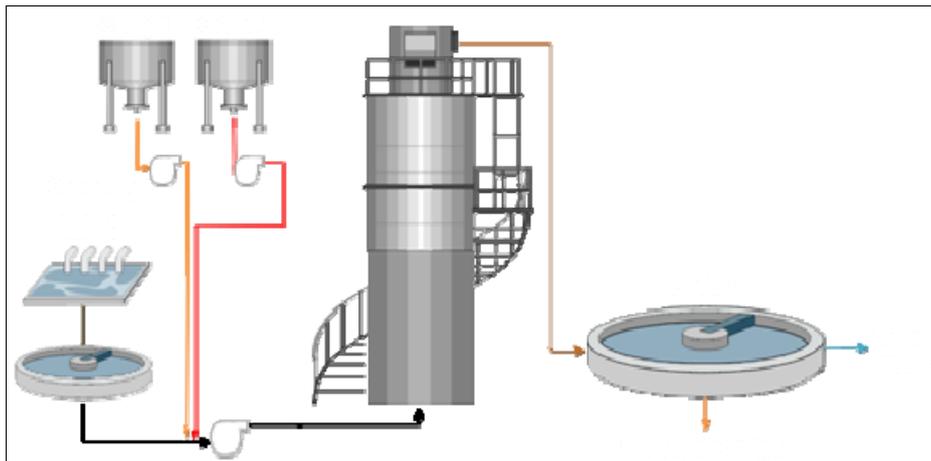
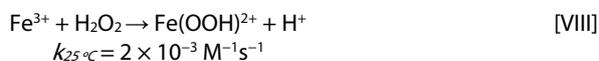


Figure 8. Wastewater treatment FBR Fenton scheme (XH2O Solutions, www.xh2osolutions.com).

The crystals of oxides and hydroxides of iron (III) growing on the bed particles are removed from the reactor when they reach a diameter between 1 and 2 mm. According to market references, as well as providing a better solid-liquid phase separation, FBR Fenton systems are able to reduce by up to 70 - 80% the sludge production compared to conventional Fenton process. Furthermore, iron (III) also exerts a certain catalytic activity, facilitating the generation of more HO· radicals through reaction [VIII], which would initiate those processes known as pseudo-Fenton reactions (with different species of Fe²⁺):



FBR Fenton processes are usually applied to the treatment of effluents containing high pollution loads, non-biodegradable compounds and/or intense color, allowing also the handling of large treatment volumes. The main advantages associated with FBR Fenton process are:

- Reduction of up to 70% in the sludge production
- Lower required area than a conventional Fenton process
- Ability to handle high organic loads
- Ability to handle high flow rates at a reasonable cost
- Lower operating costs than Fered-Fenton and photo-Fenton UV.
- Scalable process

In table 8 references, dimensions and characteristics of some FBR Fenton treatment processes in several wastewater treatment plants from various industrial sectors of Taiwan (ITRI, www.itri.org) are listed. While organic loads are not as high as those indicated in the Fered-Fenton processes, they include water flows with contaminants especially recalcitrant to biological oxidation. Overall COD removal performance with this type of process is superior to that of conventional Fenton process, although lower than the Fered-Fenton process.

Table 8. References, dimensions and performances of various FBR Fenton reactors in operation in Taiwan. (Ref.: ITRI, www.itri.org.tw)

Effluent type	FBR Fenton size (m)	Operation start year	Flow rate (m ³ /d)	Influent COD (mg/l)	COD removal (%)
Polyurethane weaving and dyeing	Φ 1 x h 7	2000	150	3500	70
ABS resins	Φ 2,5 x h 9 (x2 units)	2001	4000	130	70
ABS resins	Φ 2 x h 9 (x2 units)	2001	2000	120	60
TFT – LCD	Φ 1,2 x h 8,5	2001	400	500	30
Electronic industry	Φ 2, 5 x h 9 (x2 units)	2002	4000	130	70
Leather manufacturing	Φ 1,9 x h 9	2003	1200	300	67
Shoe manufacturing	Φ 2,8 x h 13	2004	4800	250	68
Paper mil	Φ 3,1 x h 13 (x2 units)	2006	12500	180	61
ABS resins	Φ 2,6 x h 9 (x2 units)	2007	5000	140	29
ABS resins	Φ 2 x h 9	2007	1050	120	50
Paper mill	Φ 3,35 x h 13 (x4 units)	2008	30000	350	71
Paper mill	Φ 3,6 x h 13 (x12 units)	2008	86000	800	88
Paper mil	Φ 2,85 x h 13	2008	5700	180	67
Electronic industry	Φ 2,6 x h 9	2008	3000	210	62





Figure 9. FBR Fenton reactor. (Century Envirotech Co., Taiwan)

With regard to its design, FBR Fenton reactors run as turnkey projects adapted to the specific characteristics of the treatment effluent. The hydrodynamic characteristics of the reactor can be established from the current fluidized bed reactors models. Contaminants degradation in a FBR Fenton reactor includes multiple chemical reactions involving solid-liquid-gas exchange systems. From theoretical considerations on the physical features of each phase, Tisa *et al*/ (2014) proposed a calculation method for bed and flow characteristics in the reactor to develop the process. As a result, velocities are set for each phase in order to ensure optimal mixing conditions in the reactor. The dimensions of the reactor and the bed can be determined from general formulas for the design of fluidized bed reactors.

As with other Fenton processes, the optimal reaction conditions (concentration of reagents, temperature, pH ...) in the FBR Fenton reactor are established experimentally by pilot scale studies.

5.6.- Fenton process selection criteria

Below, a summary table is included with a comparative evaluation of each of the diverse commercial Fenton processes known as applicable to textile effluent treatment.

Table 9. Selection criteria on diverse commercial Fenton processes.

Criteria	Classic Fenton	High temperature Fenton	FBR Fenton	Fered-Fenton	UV Photo-Fenton
High treatment flow	++	+	+++	-	-
High organic load	++	+++	++	+++	++
Application prior to biological treatment	+	+++	++	+++	-
Implementation as tertiary treatment	++	++	++	-	+++
Refractory compounds mineralization	+	++	++	+++	+++
Intense color, effluent opacity	++	+++	+++	+++	+++
Turbidity, suspended solids presence	+++	+++	+++	++	-
Sludge production control	-	-	+++	+++	++
Moderate investment costs	+++	++	++	+	-
Moderate O&M costs	++	++	++	+	-
Process automation	+++	+++	+++	+++	++
Moderate Electric consumption	++	+++	++	+	-

6.- FENTON PROCESSES APPLICATIONS TO EFFLUENT TREATMENTS: CASE STUDIES

6.1.- Fenton process with thermic intensification in *Schoeller Textiles AG, Sevelen (Switzerland)* (Schömberger and Schäfer, 2003)

The company Schoeller Textiles AG, in Sevelen (Switzerland), has a thermally enhanced Fenton reactor (operates at 130°C) for oxidative treatment of the segregated fraction of effluents from various operations carried out in the mill. Wastewater from various processes is subjected to different treatment lines depending on their origin, flow and composition, in order to optimize treatment costs. Consequently, only the contributions from desizing operations with non-biodegradable agents and dyeing are directed to Fenton advanced oxidation process.

The Fenton reactor operates in continuous mode, treating an average flow rate of 4 to 5 m³/h with an average organic load of 8500 mg O₂/L. The reactor, a pressure vessel made of stainless steel (Figure 7), operates at pressures between 3 and 5 bar and temperatures above 100°C. All operations of monitoring and dosage are automated. The amounts of reagents used per cubic meter of treated wastewater are:

- 13 L of hydrogen peroxide solution 35% (equivalent to 1.53 L of hydrogen peroxide, which provide an increase of COD of 1000 mg O₂/L)
- 35 mL of 30% sulfuric acid
- 120 grams of Fe²⁺

Depending on the contact time, the temperature and pressure conditions employed and the particular characteristics of the wastewater, the COD removal performance ranges between 70 and 85%. With regard to color, obtained discoloration exceeds 90%, with practically colorless effluent discharges to the municipal sewer. It is assumed that during the Fenton process effluent biodegradability increases, so that its subsequent biological treatment in municipal plant can raise total COD removal above 95% to the segregated flow.



Figure 10. Photograph and scheme of the treatment reactor for the catalytic Fenton oxidation treatment of segregated flow with high organic load in Schoeller Textiles AG (Switzerland), in operation since 1996 (Schömberger and Schäfer, 2003).

6.2.- Fenton process in the dyeing effluent treatment plant of Bamwol Dyeing Industrial Complex in Ansan, South Korea (Bae et al., 2015)

The centralized wastewater treatment of Dyeing Industrial Complex Bamwol district, located in the city of Ansan (South Korea), is the world's largest of its characteristics. It is a specific facility for the wastewater treatment from a total of 61 textile dyeing and finishing factories before the discharge to the municipal sewer system. Bamwol treatment plant receives a flow around 100,000 m³/d. The influent carries pollutants present in baths containing acidic, basic, disperse, azo, diazo and anthraquinone dyes along with metal complexes, and numerous textile additives.

The configuration of Bamwol treatment plant consists of a primary treatment with sieving, primary settling and neutralization. Then the primary effluent is led to a homogenization tank prior to the entry of a secondary activated sludge reactor with pure oxygen, followed by a tertiary treatment consisting of a conventional Fenton process, coagulation, flocculation and secondary clarifier. The clarified effluent is finally discharged to the urban sewage, receiving further treatment in a municipal treatment plant of urban waste water.

The characteristics of the wastewater coming into the Bamwol plant are quite variable, given the multiple flow sources and textile processing changes. In average, pH values oscillate between 10 and 12, the average temperature is 40°C, an average COD of 1150 mg O₂/L, with 1100 mg O₂/L corresponding to soluble COD, and a color intensity estimated in 1180 ADMI units. It is highly refractory to wastewater biodegradation, with a BOD₅/COD ratio of between 0.1 and 0.3.

Tertiary treatment stage is effected by Fenton oxidation at atmospheric pressure and room temperature, at pH 3.5 and with a hydraulic retention time of 30 minutes. Hydrogen peroxide at a 4.0 mM concentration is injected sequentially in the oxidation tank: 30% of the dose in the minute 12, and the remaining 70% in minute 16 in order to prolong the contact time. 4.2 mM ferrous sulfate is added in a single dose, entering to rapid mixing process to complete 30 minutes of contact time. The molar ratio of reactants in this case is close to 1.

The Fenton reactor effluent is subsequently subjected to coagulation for 15 minutes, at pH 5.8 - 6.0, using the generated iron (III) during the process as a coagulant. After the final clarification, the effluent is considered suitable for discharge to urban sewerage network. This treatment line meets the objective of the elimination of all biodegradable organic matter in biological treatment before Fenton process, in order to limit the demand for oxidant and to use generated ferric salts as a coagulant.

Average yields for color and organic matter removal obtained in both treatment steps are specified in Table 10.

Table 10. Treatment yields obtained in Bamwol Dyeing Industrial Complex ETP in Ansan, South Korea (Bae et al., 2015).

Stage	Soluble COD Renoval (%)	Color reduction (%)
Biological treatment	53	13
Fenton process	66 (*)	73 (*)

(*) Respect to secondary clarifier effluent

Regarding the mineralization of the effluent, although the known affinity of the HO· radical to chromophoric groups provided an almost complete color removal by Fenton treatment, the effluent analysis with HPLC/MS after each treatment stage revealed molecular compositions analogous to the input and output of the plant, indicative of poor mineralization of organic matter in the operating conditions of Bamwol plant.

7.- COSTS ANALYSIS OF FENTON PROCESS APPLIED TO TEXTILE EFFLUENT TREATMENT

7.1.- Conditioning factors

In a real scale advanced oxidation process, costs are strongly influenced by (Azbar *et al.*, 2004):

- Treatment effluent flow rate
- Reactor configuration: conventional or modified Fenton
- Effluent nature
- Treatment target

Data regarding investment and operating costs of Fenton processes applied to the textile effluents treatment are so specific to individual facilities as the treatment wastewater. Moreover, the differences between countries require a specific cost analysis for each individual process. It should be noted that operating costs, including salaries, electricity, reagents and final disposal of sludge are absolutely specific to each country, in addition to being subject to scaling factors.

7.2.- Specific cases review

7.2.1.- Fenton process with thermal intensification in Switzerland (Schömberger & Schäfer, 2003)

The presence of non-biodegradable organic matter and color in effluent from Schoeller Textiles AG company in Sevelen (Switzerland) made the flow unacceptable for direct discharge to the municipal sewer. The investment costs for the Fenton treatment at high pressure and temperature described in section 5.1, for a flow of 4-5 m³/h, amounted to 230,000 euros in 2003 in local Switzerland conditions. This amount includes the reactor, the reagent mixing and addition system the heat exchanger, piping and automation of the process.

Operating costs, including reagents consumption, maintenance, power consumption and human labor, amounted 3 euros/m³ of treated water (2003). This value corresponds only to the treatment cost of segregated high load flows.

7.2.2.- Conventional Fenton process in Turkey (Yonar, 2011)

The detailed estimate of the costs (investment, operation and maintenance) under local conditions in Turkey for a wastewater treatment plant of a manual printing mill, with a flow rate of 200 m³/day, compares the costs of a conventional system, with physical, chemical and biological treatment processes, against the alternative of a physical treatment followed by an advanced oxidation Fenton process. The treatment plant occupies a total area of 200 m² where a small laboratory, preparation and dosing of reagents areas, tanks, sludge conditioning zone and sludge filter presses are included.

Table 11. Comparison between the investment costs of two treatment schemes in Turkey (2011).

Concept*	Conventional treatment system (euros)	Physical + Fenton system (euros)
Civil Works	47.800	37.400
Electromechanical equipment	64.600	55.800
Electrical equipment	12.600	10.700
Indirect costs	26.000	22.800
Total without taxes	151.000	126.700

(* All concepts include human labor)

Regarding the operation and maintenance costs for this treatment plant, Yonar estimated that those associated with the Fenton process are 3% higher (1,485 euros/m³ to 1.452 euros/m³), because of the increased chemicals consumption. However, considering this slight difference, the investment savings would be amortized over a period of fifteen years of operation.

7.2.3.- Operation costs of different AOPs applied to textile effluents in Turkey

Azbar *et al.* (2004) performed estimates of the operating costs for the effluent treatment of homogenization tank (pH 9.2; COD: 930 mg/L BOD₅ 375 mg/L; SS: 95) of a polyester and acetate fabric dyeing mill situated in Bursa (Turkey).

Different advanced oxidation treatment alternatives were essayed in batch test at laboratory scale. The estimated costs in US dollars (2004) corresponded to operation, excluding replacement of the UV lamps when applicable, and labor in all cases. Taking into account only the reagents and electricity consumption costs under optimal conditions of performance for each process, the estimates presented in Table 12 were obtained.

Table 12. Operation costs estimated for different AOPs in Turkey (2004).

Process	Operation costs estimation 2004 (USD/m ³)	COD removal (%)	Color removal (%)
Coagulation with FeSO ₄	0.07	60	40
Conventional Fenton	0.23	96	94
H ₂ O ₂ /UV	1.26	90	85
O ₃	5.28	92	90
O ₃ /UV	6.38	94	93
O ₃ / H ₂ O ₂ /UV	6.54	99	96

In view of Table 12, the authors concluded that the conventional Fenton process offers the best cost-performance because slight efficiency increase obtainable by more complex AOPs does not justify the increase in operating costs. It is noteworthy that this estimate does not include the treatment of sludge produced by the Fenton process.

With the above data in addition to own and other authors estimates, Taner (2011) presented the following comparative table of operational costs, which again puts the Fenton processes as the most cost-effective for the treatment of textile effluents in Turkey local conditions, especially when used as pretreatment step with a reduction objective of an order of magnitude of COD or color. Again, Table 13 operating costs do not include the sludge management.

Table 13. Operation costs estimation of different textile effluent treatment operations in Turkey (Taner, 2011).

<i>Process</i>	<i>Operational cost in 2011 (USD/m³)</i>
Coagulation with FeSO ₄	0.07 – 0.20
Classic Fenton	0.23 – 0.59
Fenton with Fe (III)	0.48 – 0.57
H ₂ O ₂ /UV	1.26 – 4.56
O ₃	4.21 – 5.35
O ₃ / H ₂ O ₂	5.02 – 5.85
O ₃ /UV	6.38 – 8.68
O ₃ / H ₂ O ₂ /UV	6.54 – 11.25

Also in Turkey, Üstün *et al.* (2007) estimated operating wastewater treatment costs from a textile industrial district in the city of Bursa. The treatment goal, consisting of a conventional Fenton process followed by coagulation with powdered activated carbon and ion exchange, was to regenerate the effluent and reuse it on manufacturing operations. The estimations performed, including in this case the generated sludge management, are shown in Table 14.

Table 14. Operational cost estimation of some textile effluents alternative treatments in Turkey (Üstün et al., 2007).

<i>Process</i>	<i>Operational cost in 2007 (USD/m³)</i>
Fenton process	0,124
PAC coagulation	0,006
Ionic Exchange	1,21
Sludge management	1,20
Total cost	2,54

The sludge is generated both in Fenton and in coagulation with powdered activated carbon (PACT). Daily generation rates were 29.6 and 66.3 m³/d, respectively. Management costs include sludge filter press operation, consumption of lime and polyelectrolyte, storage and transport to an external incineration plant.

7.2.4. Operation cost estimation for Fenton and Photo-Fenton treatment to dyeing processes in Portugal (Rodrigues et al., 2013, 2014)

Rodrigues et al. (2014) compared the costs associated with the use of a coagulation/flocculation stage, a Fenton process, and both combined, using the residual iron from coagulation/flocculation stage as a catalyst for the Fenton reaction. The treatment objective was to test the feasibility of different configurations to achieve direct river discharge quality, without biological treatment.

The three treatments were applied to a synthetic wastewater with a polyester dyeing average effluent composition (pH: 8.3; COD: 520 mg/L BOD₅: 130; alkalinity: 775 mg CaCO₃/L; sulphates: 885 mg/L, no visible color). In optimum performance conditions, the Fenton process alone managed to reduce the pollutant load to the permissible conditions for direct discharge (absence of color; COD ≤ 250 mg/L) after a contact time of 60 minutes.

Estimated operating costs, taking into account only the consumed reagents, and excluding the final disposal of sludge, are shown in Table 15.

Table 15. Operation costs estimated by Rodrigues et al. (2014) for Fenton and coagulation+Fenton in a polyester dyeing effluent.

Treatment Configuration	Experimental conditions	COD removal (%)	DOC removal (%)	BOD ₅ removal (%)	Estimated cost (euros/m ³)
Conventional Fenton	[H ₂ O ₂]: 2500 mg/L; [Fe ²⁺]: 350 mg/L; pH: 3,5; 60 min	57	56	52	2,7
Coagulation/ flocculation + conventional Fenton	[H ₂ O ₂]: 2500 mg/L; [Fe ²⁺]: 350 mg/L; pH: 3,5; 60 min	79	83	73	3,1
	[H ₂ O ₂]: 1250 mg/L; [Fe ²⁺]: 175 mg/L; pH: 3,5; 60 min	63	73	59	1,3
	Minimum requirement for effluent discharge	55	60	48	0,7

The same authors (Rodrigues et al., 2013) made operating costs estimation for photo-Fenton processes UV and solar under working conditions to reduce the pollution load of three different dyeing process effluents (acrylic, cotton and polyester) in order to achieve minimum discharge quality requirements (absence of color; COD ≤ 250 mg/L). The obtained values related to reagent consumption and electric power in optimum operating conditions are set forth in Table 16.

Table 16. Operation costs estimated by Rodrigues et al. (2013) for UV and solar Photo-Fenton for diverse fiber dyeing effluents treatment.

Process	Dyeing effluent	Optimum conditions	COD removal (%)	BOD ₅ removal (%)	Estimated operation cost (euros/m ³)
UV Photo- Fenton	Acrylic	[H ₂ O ₂]: 10 g/l; F: 220 W·m ⁻²	70	-42	17,4
	Cotton	[H ₂ O ₂]: 10 g/l; F: 7 W·m ⁻²	33	2	9,6
	Polyester	[H ₂ O ₂]: 2,5 g/l; F: 7 W·m ⁻²	52	52	2,9
Solar Photo- Fenton	Acrylic	[H ₂ O ₂]: 6,5 g/l; F: 500 W·m ⁻²	72	-31	5,8
	Cotton	[H ₂ O ₂]: 3,75 g/l; F: 500 W·m ⁻²	30	2	3,5
	Polyester	[H ₂ O ₂]: 0,94 g/l; F: 500 W·m ⁻²	55	53	1

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