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Photocatalytic processes on the oxidation of organic compounds in water

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1. Introduction

This chapter aims to give the reader an overview of the application of semiconductor photocatalysis, as well as of the Fenton process, as new technologies employed for the decontamination of chlorinated organic compounds in liquid waste.

Advanced oxidation processes (AOPs) constitute an effective technology for the treatment of wastewaters containing non-easily removable organic compounds and among these AOPs photocatalysis in particular is the most promising. Therefore, in this chapter the theoretical aspects of semiconductor photocatalysis will be discussed, followed by a review on the applications. Since the most commonly used semiconductor photocatalyst is TiO_2 , efforts on the modification of TiO_2 in order to improve the catalyst's efficiency will also be presented. Finally, the high efficiency Fenton process that it is being increasingly used in the treatment of contaminated water, will be presented, along with applications in the decontamination of synthetic wastewaters.

2. General

As it is generally known, water constitutes the elementary ingredient of life on our planet. Despite its great importance, until a few decades ago it was treated by mankind as an abundant and cheap raw material, which will never run scarce. During the last years, however, we all realize that our philosophy towards water has changed dramatically. Water is at present considered as a valuable good that becomes easily polluted and disperses into all layers of the biosphere, while, on the other hand, it is difficult to decontaminate. Human activity has led to a huge production of liquid waste, which aggravates particularly the urban and industrial areas.

The pollution induced to water due to the increased production of liquid waste in combination with the increased consumption as the planet's population increases in great numbers, lead mankind to take action in two basic directions: (a) cleaning polluted water found on the surface as well as underground in order to make it potable, and (b) to the decontamination of liquid waste containing ingredients toxic to the ecosystem.

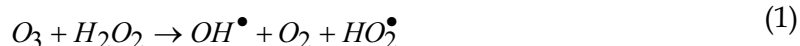
Particularly, chlorinated organic compounds constitute a group of contaminants with a complex diversity of biologic effects that has been designated as priority pollutants. The domestic use and industrial activity generate high amounts of residual wastewater containing chlorinated organic compounds, whose direct disposal to natural channels causes a considerable effect in the environment. Therefore, the need arises to develop processes for the purification of water.

Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of wastewaters containing non-easily removable organic compounds and are at present considered to have great potential in degrading chlorinated organic compounds.

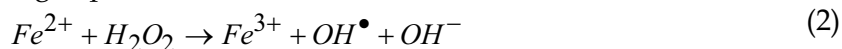
Hydrogen peroxide is a strong oxidant (standard potential 1.80 and 0.87 V at pH 0 and 14 respectively) and its application in the treatment of various inorganic and organic pollutants is well established. Numerous applications of H_2O_2 in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, cyanides, and chlorine are known (Venkatadri and Peeters, 1993).

Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants such as highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides), because of low rates of reaction at reasonable H_2O_2 concentrations. Transition metal salts (e.g. iron salts), ozone and UV-light can activate H_2O_2 to form hydroxyl radicals which are strong oxidants:

- Ozone and hydrogen peroxide



- Iron salts and hydrogen peroxide



- UV-light and hydrogen peroxide



AOPs make use of different reacting systems, including photochemical degradation processes (UV/ O_3 , UV/ H_2O_2), photocatalysis (TiO_2 /UV, photo-Fenton reagent), and chemical oxidation processes (O_3 , O_3/H_2O_2 , H_2O_2/Fe^{2+}). The light driven AOPs involve the production of hydroxyl radicals, which react almost non-selectively with the organic pollutants at very high rates. Chemical treatment of wastewaters by AOPs can result in the complete mineralization of the pollutants to carbon dioxide, water, inorganic compounds or, at least, in their transformation to harmless end products.

3. The Fenton Process

The oxidation processes utilizing activation of H_2O_2 by iron salts is referred to as Fenton's reagent. Fenton's reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s (Huang et. al, 1993). Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2 , water and inorganic salts. The Fenton reaction causes the dissociation of the oxidant and the formation

of highly reactive hydroxyl radicals that attack and destroy the organic pollutants.

The Fenton process, in one or other of its various forms, is being increasingly used in the treatment of contaminated water and soil. The conventional “dark” Fenton process involves the use of one or more oxidizing agents [usually hydrogen peroxide and /or oxygen] and a catalyst (a metal salt or oxide, usually iron), while the photo-Fenton (or photo-assisted Fenton) process also involves irradiation with sunlight or an artificial light source, which increases the rate of contaminant degradation by stimulating the reduction of Fe(III) to Fe(II). The reactions produce a range of free radicals, which can react with most organic compounds. Reactions involving the highly reactive hydroxyl radical ($\bullet\text{OH}$) (or “hydroxyl radical-like” species) are the most important, and are characteristic of all advanced oxidation processes.

Fenton-type processes can be divided into two categories: homogeneous processes (Fe(II)/H₂O₂/dark, Fe(III)/H₂O₂/dark, Fe(II)/H₂O₂/light, Fe(III)-ligand/H₂O₂/light, Fe(III)-ligand/light) and heterogeneous processes (Fe(III)oxide/H₂O₂/dark, supported iron catalysts, electrochemical Fenton processes).

Fenton’s reagent is a mixture of H₂O₂ and ferrous iron, which generates hydroxyl radicals according to the reaction (Kitis et al.,1999; Yoon et al., 2001; Lu et al., 2001)



The ferrous iron (Fe²⁺) initiates and catalyses the decomposition of H₂O₂, resulting in the generation of hydroxyl radicals. The generation of the radicals involves a complex reaction sequence in an aqueous solution

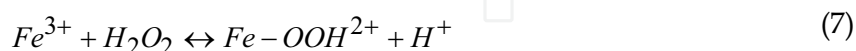


K₅=70 M⁻¹s⁻¹ (Rigg et al., 1954)



K₆=3.2 M⁻¹s⁻¹ (Buxton and Greenstock, 1988)

Moreover, the newly formed ferric ions may catalyse hydrogen peroxide, causing it to be decomposed into water and oxygen. Ferrous ions and radicals are also formed in the reactions. The reactions are as shown in Eqs. (3)–(7).



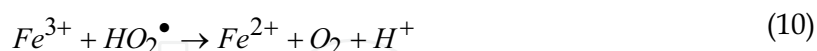
K₇=0.001-0.01 M⁻¹s⁻¹ (Walling and Goosen, 1973)



The reaction of hydrogen peroxide with ferric ions is referred to as a Fenton-like reaction [reactions (7) and (8)] (Walling and Goosen, 1973; De Laat and Gallard, 1999).



$K_9 = 1.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (at pH=3, Bielski et al., 1985)



$K_{10} = 1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (at pH=3, Bielski et al., 1985)



$K_{11} = 3.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (Buxton and Greenstock, 1988)

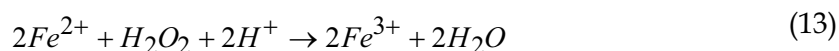
As seen in reaction (11), H_2O_2 can act as an OH^{\bullet} scavenger as well as an initiator [reaction (7)].

Hydroxyl radicals can oxidise organics (RH) by abstraction of protons producing organic radicals (R^{\bullet}), which are highly reactive and can be further oxidised (Walling and Kato, 1971; Venkatadri and Peters, 1993; Lin and Lo, 1997)

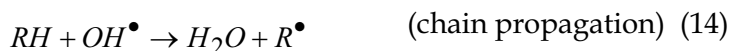


If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2 , water and in the case of substituted organics, inorganic salts if the treatment is continued.

Walling, 1975, simplified the overall Fenton chemistry by accounting for the dissociation of water



This equation suggests that the presence of H^{+} is required in the decomposition of H_2O_2 , indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. Previous Fenton studies have shown that acidic pH levels near 3 are usually optimum for Fenton oxidations (Hickey et al., 1995). In the presence of organic substrates (RH), excess ferrous ion, and at low pH, hydroxyl radicals can add to the aromatic or heterocyclic rings (as well as to the unsaturated bonds of alkenes or alkynes). They can also abstract a hydrogen atom, initiating a radical chain oxidation (Walling, 1975; Lipczynska-Kochany et al., 1995)



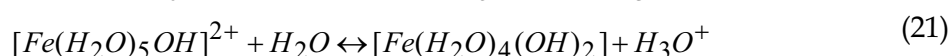
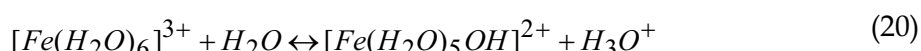
The organic free radicals produced in reaction (14) may then be oxidised by Fe^{3+} , reduced by

Fe^{2+} , or dimerised according to the following reactions (Tang and Tassos, 1997)

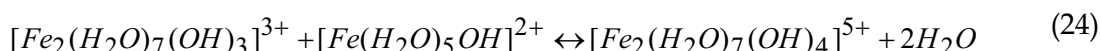
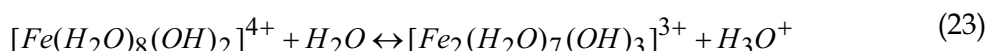


The sequence of reactions (1), (2), (10) and (13) constitute the present accepted scheme for the Fenton's reagent chain.

The ferrous ions generated in the above redox reactions (8) and (9) react with hydroxide ions to form ferric hydroxo complexes according to (Walling and Kato, 1971, Lin and Lo, 1997)



Within pH 3 and 7, the above complexes become



which accounts for the coagulation capability of Fenton's reagent. Dissolved suspended solids are captured and precipitated. It should be noted that large amounts of small flocs are consistently observed in the Fenton oxidation step. Those flocs take a very long time, sometimes overnight, to settle out. Chemical coagulation using polymer is therefore necessary. Fenton's reagent is known to have different treatment functions, as mentioned earlier, depending on the $\text{H}_2\text{O}_2/\text{FeSO}_4$ ratio. When the amount of Fe^{2+} employed exceeds that of H_2O_2 , the treatment tends to have the effect of chemical coagulation. When the two amounts are reversed, the treatment tends to have the effect of chemical oxidation.

Reaction (13) competes with both the chain termination reaction [reaction (2)] and with the propagation reaction (10) of Fenton chemistry. This competition for hydroxyl radical between Fe^{2+} , RH and Fe^{3+} leads to the non-productive decomposition of hydrogen peroxide and limits the yield of hydroxylated (oxidised) organic compounds. Therefore, the stoichiometric relationship between Fe^{2+} , RH and Fe^{3+} has to be established to maximize the efficiency of the degradation process.

3.1 Applications of the Fenton Process

Fenton's reagent can be employed to treat a variety of industrial wastes containing a range of organic compounds like phenols, formaldehyde, pesticides, wood preservatives, plastic additives, and rubber chemicals [Barbeni et al., 1987; Gau and Chang, 1996; Lipczynska-Kochany and Bolton, 1992; Lipczynska-Kochany, 1991, 1994; Lipczynska-Kochany et al., 1995; Miller et al., 1996; Murphy et al., 1989; Pignatello, 1992; Pera-Titus et al., 2004; Pouloupoulos et al., 2008] resulting to a reduction of toxicity, an improvement of

biodegradability, and odor and color removal. In Table 1 is given a list of compounds degraded by the Fenton and photo-Fenton processes as well as the reaction conditions and the value of the pseudo-first order kinetic rate constant .

Fenton's Reagent					
Compound	Initial Concentration (mM)	[H ₂ O ₂] ₀ (mM)	[Fe ²⁺] ₀ (mM)	K (min ⁻¹)	Reference
2-CP	0.50	5.00	0.20	1.67	Tang and Huang, 1996
2-CP	0.39	2.20	0.008	1.92x10 ⁻²	Lu, 1999
3-CP	0.80	4.00	0.020	-	Shul'pin et al., 1997
4-CP	0.50	4.00	0.040	0.320	Linsebigler et al., 1995
4-CP	0.80	4.00	0.020	-	Shul'pin et al., 1997
4-CP	2.00	6.00	0.30	1.55	Kwon et al., 1999
4-CP	0.30	7.50	0.10	1.88	Benítez et al., 2000
4-CP	10.00	30.00	0.005	-	Yoon et al., 2000
4-CP	0.30	0.50	0.010	0.007	Benítez et al., 2001
4-CP	2.27	8.20	0.054	0.007	Chamarro et al., 2001
2,4-DCP	0.50	5.07.500	0.20	0.995	Tang and Huang, 1996
2,4-DCP	0.30	4.00	0.010	0.0007	Benítez et al., 2001
2,4,5-TCP	0.80	5.00	0.020	-	Shul'pin et al., 1997
2,4,6-TCP	0.50	5.90	0.20	0.15	Tang and Huang, 1996
2,4,6-TCP	0.30	0.50	0.010	0.0005	Benítez et al., 2001
PCP	0.80	4.00	0.020	-	Shul'pin et al., 1997
Photo-Fenton's Reagent					
Compound	Initial Concentration (mM)	[H ₂ O ₂] ₀ (mM)	[Fe ²⁺] ₀ (mM)	K (min ⁻¹)	Reference
4-CP	0.30	0.50	0.010	0.642	Benítez et al., 2001
4-CP	10.00	30.00	0.005	-	Yoon et al., 2000
4-CP	0.80	4.00	0.020	-	Shul'pin et al., 1997
4-CP	0.30	0.50	0.010	0.642	Benítez et al., 2000
4-CP	1.00	10.00	0.25	1.25	Bauer et al., 1999
2,4-DCP	0.80	4.00	0.020	-	Shul'pin et al., 1997
2,4-DCP	0.30	0.50	0.010	0.088	Benítez et al., 2000
2,4-DCP	0.30	0.50	0.010	0.088	Benítez et al., 2001
2,4,5-TCP	0.80	4.00	0.020	-	Shul'pin et al., 1997
2,4,6-TCP	0.30	0.50	0.010	0.078	Benítez et al., 2000
2,4,6-TCP	0.30	0.50	0.010	0.078	Benítez et al., 2001
2,3,4,6-TTCP	0.30	0.50	0.010	0.058	Benítez et al., 2000
2,3,4,6-TTCP	0.30	0.50	0.010	0.058	Benítez et al., 2001
PCP	0.80	4.00	0.020	-	Shul'pin et al., 1997

Table 1. Pseudo-first order kinetic rate constants and under different initial experimental conditions for 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP), pentachlorophenol (PCP).

4. Heterogeneous semiconductor photocatalysis

The most important among the Advanced Oxidation Processes is heterogeneous photocatalytic oxidation, often referred to as photocatalysis. This method deals with the oxidation mostly of organic molecules, with the use of a solid catalyst, which is activated by the incidence of radiation of an appropriate wavelength. It can take place both in the aqueous phase as well as in the gas phase. In the past years it is gaining considerable interest in comparison to homogeneous catalysis due to disadvantages of the latter. The most important are the separation process of the products that may be implicated, and that in most cases is economically and/or technically impracticable, as well as the inappropriate, from an environmental point of view, use of some homogeneous catalysts, such as metal salts. These disadvantages have given a boost to the development of heterogeneous catalytic processes, despite the fact that controlling such a process is difficult, since it comprises of five stages:

1. the transfer of the reactants from the liquid phase on to the catalytic surface,
2. the adsorption of at least one of the reactants,
3. the reaction in the adsorbed phase,
4. the desorption of the products,
5. the transfer of the products away from the diphasic area.

The photocatalytic reaction takes place in the adsorbed phase (stage 3). The difference from classic catalysis is that instead of the thermal activation of the catalyst, we have a photonic activation from the incident radiation.

In photocatalytic reactions in the aqueous media the most commonly used process is the photocatalytic degradation of organic pollutants in the presence of a semiconducting solid catalyst (mostly TiO_2).

4.1 The Photocatalytic mechanism

The last decade has seen the emergence of a major new initiative in the area of water and wastewater treatment, namely semiconductor photocatalysis. In semiconductor photocatalysis, the light-absorbing species is a semiconducting material. The electronic structure of most semiconductor materials comprises a highest occupied band full of electrons called the valence band (VB), and a lowest unoccupied called the conductance band (CB). These bands are separated by a region that is largely devoid of energy levels, and the difference in energy between two bands is called the bandgap energy, E_{bg} . Ultra-bandgap illumination of such semiconductor materials produces electron-hole pairs, $h^+ e^-$, which can either recombine to liberate heat, or make their separate ways to the surface of the semiconductor material, where they have the possibility of reacting with surface absorbed species.

The major processes that occur on a semiconductor photocatalyst particle upon ultra-bandgap excitation in an aqueous solution containing dissolved oxygen and an oxidizable pollutant are: (a) electron-hole recombination in the bulk, (b) electron-hole recombination at the surface, (c) direct or indirect (through trap sites) reduction of oxygen, or oxidizing intermediates by the photogenerated electron at the surface of the semiconductor and (d) direct or indirect (through trap sites) oxidation of the pollutant, or an oxidized intermediate by the photogenerated hole at the surface of the semiconductor, leading eventually to the mineralization of the pollutant.

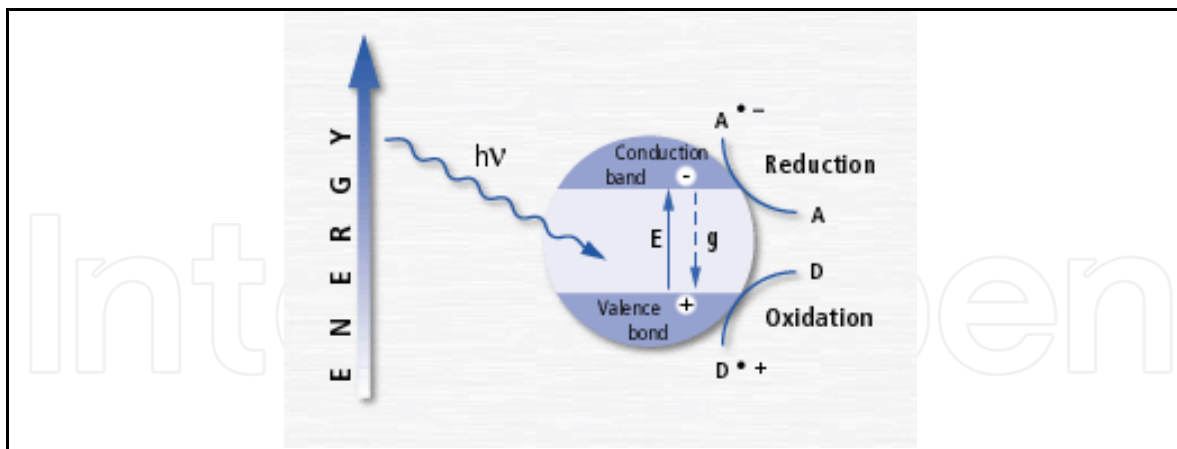


Fig. 1. Photocatalysis on a semiconductor

Ideally, a semiconductor photocatalyst for the purification of water should be chemically and biologically inert, photocatalytically active, easy to produce and use, and activated by sunlight. TiO_2 is currently considered as the most promising photocatalyst because of its reasonable photocatalytic activity, relatively low cost, and high stability toward photocorrosion (Peternel et al., 2007; Serpone et al., 2005; Chen and Dionysiou, 2007; Dionysiou et al., 2006). However, recent research questions the absence of toxicity of TiO_2 indicating that nanosize TiO_2 could pose a risk to biological targets that are sensitive to oxidative stress damage [dcp19]. However, the very positive features of TiO_2 as a semiconductor photocatalyst far outweigh the limitations of its spectral profile and thus, it has become the semiconducting material for research in the field of semiconductor photocatalysis for water purification.

It must be noted that the process of electron transport (or equally for holes) is more effective, if the electron acceptors (or donors) are adsorbed on the particle surface. Their transport rate depends upon the relative positions of the conduction and valence bands, as well as upon the redox potential of the adsorbed species.

The efficiency of a photocatalytic process is measured by quantum yield, which is the ratio of the stimulation incidents per absorbed photon. In the heterogeneous processes, however, there is a difficulty in measuring the exact amount of the absorbed radiation, because a part of it is scattered by the semiconductor's surface. Therefore, it is assumed that all the incident radiation is absorbed and an apparent quantum yield is calculated instead.

An alternative definition for the efficiency (based on the reaction kinetics) is that the efficiency is equal to the ratio of the photocatalytic reaction rate (mols^{-1}) to the absorbed radiation flux (photons s^{-1}). In order to calculate the process quantum yield, all possible interaction phenomena between electrons and holes must be taken into account. Therefore the quantum yield is defined as:

$$\Phi \propto \frac{k_{M\Phi}}{k_{M\Phi} + k_{EP}} \quad (20)$$

where $k_{M\Phi}$ and k_{EP} the charge transfer rate (electrons or holes) and the recombination rate respectively. It is obvious that if it were not for charge recombination, the quantum yield of the process would be equal to unity. In this case, the transfer rate would depend solely upon electron and hole diffusion to the surface. This is however an ideal case, because in fact

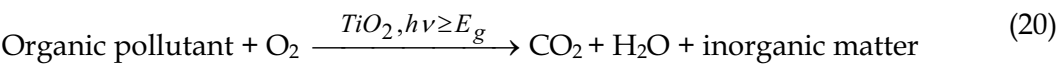
recombination takes place and the electron and hole concentration on the surface of the semiconductor is not uniform. In order to reduce the electron-hole recombination rate and to increase the efficiency of the photocatalytic process, researchers are trying to modify the semiconductor surface with various ways, such as metal addition, in combination with other semiconductors and so on.

Finally, it should be noted that the knowledge of the parameter Φ is very important mainly for three reasons:

- a) it provides the capability of comparing the efficiency of different catalysts for a given reaction
- b) it provides an estimation means of the relative applicability of different reactions
- c) it calculates the energy efficiency of a process as well as the relative cost.

4.2 Mechanism of the photocatalytic degradation of different organic pollutants in the presence of semiconductors

The reaction describing the process for the implementation of semiconductor photocatalysis on the degradation of organic pollutants is given by the following equation:



One of the major products of this reaction is carbon dioxide, as the result of the oxidation of organic compounds. Organic compounds contain inorganic atoms and so during their oxidation inorganic compounds are produced.

Studying the mechanism implied in this reaction, the most important steps of the process are given in Table 2.

Initial steps of the photocatalytic process process	Indicative Time
Charge carrier generation (electrons-holes) $TiO_2 + h\nu \rightarrow h^+ + e^-$	fs (very fast)
Charge carrier trapping $h^+ + Ti^{IV}OH \rightarrow Ti^{IV}OH^{\bullet+}$ $e^- + Ti^{IV}OH \rightarrow Ti^{III}OH$ $e^- + Ti^{IV} \rightarrow Ti^{III}$	10ns (fast) 100ps (surface trapping- dynamic equilibrium) 10ns (bulk trapping- irreversible)
Charge carrier recombination $e^- + Ti^{IV}OH^{\bullet+} \rightarrow Ti^{IV}OH$ $h^+ + Ti^{III}OH \rightarrow Ti^{IV}OH$	100ns (slow) 10ns (fast)
Charge transfer to the interfacial region $e^- + Ti^{IV}OH^{\bullet+} + P \rightarrow Ti^{IV}OH + P^*$ $Ti^{III}OH + O_2 \rightarrow Ti^{IV}OH + O_2^{\bullet-}$	100ns (slow) ms (very slow)
P: organic pollutant, P*: oxidized organic pollutant	

Table 2. Initial steps of the photocatalytic process

At this point, it should be mentioned that the exact mechanism of the process, as well as the role of each component in the reaction course, still remains a research field. For example, the role of oxygen has not been yet clearly defined. It is possible that among the different chemical species arising from oxygen reduction, some of them play an important role in the organic compound oxidation. Hydrogen peroxide has also been proven to be very effective and as a result it is used in many processes as a strong oxidant. Most researchers converge to the fact that the organic substance does not undergo direct oxidation by the produced holes, but the oxidation takes place through a hydroxyl radical on the surface, such as $Ti^{IV}OH^{\bullet+}$. Some researchers suggest the direct oxidation of the organic radical by the produced hole, before the latter is trapped in the bulk or on the surface of the semiconductor.

Photocatalytic processes employing TiO_2 can be divided into two categories:

(a) Semiconductor photocatalysis using TiO_2 powder dispersions. The use of such slurries obviously requires a subsequent separation step involving either filtration, centrifugation or coagulation/flocculation which instantly compromises the system's economical viability. However, slurry reactor photocatalytic systems are usually very efficient in terms of photons (relative to thin film reactors) and easy to make and maintain.

(b) Photocatalytic reactors utilizing a fixed bed of a semiconductor material. These systems are usually less photo-efficient for pollutant destruction, due to an intrinsic low surface area to volume ratio; in addition, such systems are difficult to make, can be difficult to maintain (if passivation of the photocatalyst occurs) and are costly to replace. However, the major advantage of such fixed-film photoreactors is that no subsequent separation step is required. However, the application of TiO_2 for photocatalytic oxidation of organic molecules is limited by both high charge carrier recombination rates and, usually, the need for ultraviolet excitation.

4.3 Applications using TiO_2 powder dispersions

TiO_2 photocatalysis is now considered an increasingly attractive approach for the degradation of organic compounds. To increase the activity of TiO_2 and to extend the wavelength range response of TiO_2 to the visible region, different methods have been developed for the modification of TiO_2 nanoparticles. These methods include the modification through noble metals in order to enable TiO_2 nanoparticles to be active in the energy range of visible light and to enhance the photocatalytic activity. However, TiO_2 modification with noble metals as a practical remediation technology is restricted because noble metals are expensive. In contrast, modification of TiO_2 with transition metals provides a successful and cost effective alternative, also leading successfully to the complete degradation of organic compounds. In Table 3 are summarized the results of several studies employing TiO_2 particles modified with noble and transition metals.

Type of catalyst	Reaction Conditions and degradation efficiency for organic dyes	Reference
1 wt. % Ag- TiO_2	Under UVC (254 nm) irradiation 100mL of 19 mg L ⁻¹ MV, 95% in 4 min (pH 7) 100mL of 19 mg L ⁻¹ GRL, 88% in 5 min (pH 11) 100mL of 100 mg L ⁻¹ FMR, 90% in 30 min (pH 3.5)	Sökmen et al., 2001

1 at. % Ag-TiO ₂	Under 300-450 nm irradiation 60mL of 5x10 ⁻⁵ M AO7, 100% in 45 min, 60mL of 5x10 ⁻⁵ M tartrazine, 89% in 20 min, 60mL of 4x10 ⁻⁵ M 3-nitrobenzenesulfonic acid, 100% in 2.5 h	Kambala et al., 2003
1 wt. % Ag-TiO ₂	Under UVC (254 nm) irradiation 100mL of 20 mg L ⁻¹ SG-GC, 97% in 8 min (pH 3.5) and 95% in 10 min (pH 7)	Özkan et al., 2004
2 at.% Ag ⁰ -TiO ₂ nanosol	Under visible light irradiation 50mL of 1x10 ⁻⁵ M RB, 90% in 4 h	Sung-Suh et al., 2004
0.05 wt. % Ag-TiO ₂	Under UVA (365 nm) irradiation 500mL of 20 mg L ⁻¹ X-3B, 98% in 60 min (pH 4)	Qi et al., 2005
Ag-AgBr-TiO ₂	Under visible light irradiation, 60mL of 50 mg L ⁻¹ of the dyes: 88% for ARB, 92% for K-2G, 32% for X-GRL, 98% for X-3B in 1 h	Hu et al., 2006
1 at. % Ag ⁺ -TiO ₂	Under UVA (365 nm) irradiation, 60 mL of mixed CV (5x10 ⁻⁵ M) and MR (7.5x10 ⁻⁵ M), >99% degraded (>86% mineralized) in 1.5 h)	Gupta et al., 2006
Ag-TiO ₂ nanotube, Au-TiO ₂ nanotube	Under UVA (360 nm) irradiation, 3 mL of 2.5x10 ⁻⁵ M AO7, 80% with Ag-TiO ₂ and 67% with Au-TiO ₂ in 1 h	Paramasivam et al., 2008
Ag (2 wt. %)- In ₂ O ₃ (1.9 wt. %)- TiO ₂	Under UVB (313 nm) irradiation, 90 mL of 25 mg L ⁻¹ RB, 100% decolorized in 45 min (100% mineralized in 105 min)	Yang et al., 2008
0.5 at.% Au-TiO ₂ , 0.5 at.% Au ³⁺ -TiO ₂	Under visible light irradiation (400-800 nm), 165mL of 12 mg L ⁻¹ MB, 100% with 0.5 at.% Au ³⁺ -TiO ₂ , and 96% with 0.5 at.% Au-TiO ₂ in 1 h	Li and Li, 2001
2 wt.% Pt-S ⁶⁺ -TiO ₂	Under 340-420 nm irradiation, 15 mL of 1x10 ⁻⁴ M AO7, 97% in 30 min	Kryukova et al., 2007
PtCl ₄ ²⁻ -TiO ₂ , PtCl ₆ ²⁻ -TiO ₂ , [Pt ₃ (CO) ₆] ₆ ²⁻ -TiO ₂	Under UV-vis irradiation, 1x10 ⁻⁴ M RB, 100% with [Pt ₃ (CO) ₆] ₆ ²⁻ modified P25 TiO ₂ in 15 min, 100% with PtCl ₆ ²⁻ modified TiO ₂ (sol-gel synthesized) in 20 min. Under visible irradiation (>450 nm), 1x10 ⁻⁴ M RB, 90% with PtCl ₄ ²⁻ modified P25 TiO ₂ in 2 h, 100% with [Pt ₃ (CO) ₆] ₆ ²⁻ modified TiO ₂ (sol-gel synthesized) in 70 min	Kowalska et al., 2008
Fe ³⁺ - TiO ₂ , Fe ²⁺ - TiO ₂	Under UV irradiation, 60mL of 100 mg L ⁻¹ XRG, 60% with 0.09 at.% Fe ²⁺ - TiO ₂ , and 70% with 0.09 at.% Fe ³⁺ - TiO ₂ in 1 h; Under visible light irradiation, 60mL of 100 mg L ⁻¹ XRG, 25% with 0.09 at.% Fe ²⁺ - TiO ₂ , and 41% with 0.09 at.% Fe ³⁺ - TiO ₂ in 7 h	Zhu et al., 2004
Fe ³⁺ - TiO ₂	Under visible light (>420 nm) irradiation, 15 mL of 1x10 ⁻⁷ M SRB, 60% in 90 min	Kumbhar and Chumanov, 2005
0.1 wt.% Fe- TiO ₂	Under UV irradiation (365 nm), 500mL of 20 mg L ⁻¹ X-3B, 97% in 60 min (pH 4)	Qi et al., 2005
0.15 at.% Fe ³⁺ - TiO ₂	Under visible light (>380 nm) irradiation, 60 mL of 100 mg L ⁻¹ XRG, 82% in 7h	Zhu et al., 2006

N- 0.5at.% Fe ³⁺ - TiO ₂	Under visible light (>420 nm) irradiation, 50 mL of 20 mg L ⁻¹ RB, 100% in 4 h	Cong et al., 2007
Fe(OH) ₃ - TiO ₂ , Cu(OH) ₂ - TiO ₂	Under UV irradiation, half-time of 250 mL of 10 mg L ⁻¹ MO at pH 6 was decreased from 332 min for unmodified TiO ₂ to 63 min for Fe(OH) ₃ - TiO ₂ and 65 min for Cu(OH) ₂ - TiO ₂ , respectively (pH 3-7)	Wang et al., 2008
1 at.% Cu-TiO ₂	Under UV irradiation (254 nm), 400 mL of 2x10 ⁻⁴ M AO7, 100% (99%) mineralized in 150 min	Wong et al., 2005
Cu ⁺ -, Cu ²⁺ - TiO ₂ nanotubes	Under UV irradiation, 100 mL of 3 mg L ⁻¹ RB, 97.5% in 50 min	Li et al., 2008
Titamium-niobium mixed oxide	Under UV irradiation, 25 mL of 14.24 mg L ⁻¹ BG, 100% in 18 min (pH 2.1)	Saupe et al., 2005
1 mol% V-TiO ₂	Under UV-vis irradiation, 450 mL of 19 mg L ⁻¹ MB, 75% in 4 h	Bettinelli et al., 2007
0.1 at.% Zn-TiO ₂	Under UV irradiation, 700 mL of 20 mg L ⁻¹ MO, 100% in 30 min	Chen et al., 2008
Sr-TiO ₂ , (SrTiO ₃ -TiO ₂)	Under UV irradiation (325 nm), 100 mL of 40 mg L ⁻¹ RBB, 95% in 3 h	Lv et al., 2008
3 mol% Bi ³⁺ -TiO ₂	Under UV irradiation, 25 mL of 20 mg L ⁻¹ MO, 94.4% in 90 min	Yu et sl., 2008
Bi-\S-TiO ₂	Under visible light (>410 nm), 100 mL of 20 mg L ⁻¹ IC, 100% in 40 min	Wang et al., 2008

Table 3. TiO₂ particles modified with noble and transition metals.

4.4 Applications using TiO₂ thin films

In the case of TiO₂ powder slurries, the major problems are: the need for separation or filtration steps, the problematic use in continuous flow systems and the particles aggregation, especially at high concentrations. To overcome these drawbacks, investigations on TiO₂ photocatalysis have been oriented towards the photocatalyst immobilization in the form of a thin film in recent years. However, the overall photocatalytic performance of TiO₂ thin films decrease in comparison with corresponding slurry solution. The photocatalytic process is a surface and not a volume or mass phenomenon. Easy access to illuminating light and organic compound is essential for successful photocatalytic degradation. In the case of the film this only corresponds to its external surface which is much lower than the TiO₂ powder surface area. A proficient solution to enhance the photocatalytic reaction rate is the modification of TiO₂ thin films with noble metals, transition metals and non-metals. Such modifications aim to hinder the photo-generated electron-hole pair recombination and accelerate the photoexcitation and formation of oxidizing species. In Table 4 are listed indicatively a number of researches along with the results on the photocatalytic degradation of organic compounds using TiO₂ thin films modified with noble and transition metals.

Type of catalyst	Reaction conditions and degradation efficiency	reference
Ag ⁺ -TiO ₂ thin film	Under UV irradiation (350 nm), 5 mL of 1.9x10 ⁻⁵ M MO, 90% in 2 h (initial pH 9.2)	Arabatzis et al., 2003
Au-TiO ₂ thin film	Under UV irradiation (350 nm), 4 mL of 2.056x10 ⁻⁵ M MO, 100% in 2.5 h	Arabatzis et al., 2003b
Pt-TiO ₂ thin film	Under visible light illumination, 30 mL of 10 mg L ⁻¹ MO, 97% in 2 h	Zhang et al., 2006
Fe ³⁺ -TiO ₂ thin film	Under UV irradiation (365 nm), 25 mL of 1.53x10 ⁻³ M MO, degradation rate 9.3x10 ⁻⁴ min ⁻¹	Yu et al., 2006
Sn ⁴⁺ -TiO ₂ thin film	Under UV irradiation, 2 mg L ⁻¹ RB, 80% in 160 min	Zheng et al., 2002
N-TiO ₂ thin film	Under visible light illumination, 47.2% and 46.4% degradation of 30 mL of 20 mg L ⁻¹ MB and MO solutions was achieved	Zhao et al., 2008
1 wt.% Ag/0.5 wt.% InVO ₄ -TiO ₂ thin film	Under visible light irradiation (>400 nm), 30 mL of 10 mg L ⁻¹ MO, 45% in 15 h	Ge et al., 2006
CdO/ZnO-TiO ₂ thin film	Under visible light irradiation, 500 mL of 100 mg L ⁻¹ textile blue azo dye, 100% in 2 h (pH 3)	Suárez-Parra et al., 2003

Table 4. TiO₂ thin films modified with noble and transition metals

5 Future Research

Titanium dioxide photocatalysts are widely employed in the photocatalytic technologies for the removal of organic compounds removal from water. However, in this promising research area, the following problems need to be addressed in order to achieve further progress: (a) the loss of TiO₂ nanoparticle surface area throughout the growth of TiO₂ nanocrystallites during high temperature calcination process and serious aggregation of prepared nanoparticles when dispersed in aqueous solution, (b) the efficiency of recycled TiO₂ photocatalysts is reduced after several cycles of use, (c) Development of pilot scale treatment systems in order to provide useful information for further large-scale application especially for huge amount of real wastewater purification needs to be fully explored. It is worthwhile to indicate that no universal TiO₂ photocatalytic system is available for a complete treatment encompassing the essential features such as high mineralization efficiency for wastewaters, easy retrieval from treated solution and visible light photo-active. The degradation of organic compounds using the Fenton process is strongly dependent on the concentration of hydrogen peroxide, the reaction temperature, the pH and the Fe²⁺-concentration in the oxidative treatment. Drawbacks associated with the use of Fenton oxidation are the safety hazards associated with using H₂O₂ and the need to firstly reduce the pH, followed by a subsequent neutralisation. Even though these techniques can provide the conversion of contaminants to less harmful compounds, usually oxygenated organic products and low molecular acids, they are limited to treat waters which contain low concentrations of organic or inorganic scavenging material. Even though titanium dioxide photocatalysts and Fenton’s reagent are promising techniques for water and wastewater treatment, showing high efficiencies, they actually

work at high cost, and appear to be suitable for Chemical Oxygen Demand contents lower than 5 g L⁻¹, since higher COD contents would require the consumption of too large amounts of reactants. In order to make these processes economically viable without reducing their efficiency, the scientific interest is currently directed to the combination of an Advanced Oxidation Process as a preliminary treatment, followed by an inexpensive biological process.

6 Conclusions

Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water and have been also reported to achieve the degradation of organic compounds in a short period of time. In this chapter we reviewed briefly the various reactions which constitute the overall kinetic scheme and we presented some applications proving the efficiency of this process in the degradation of chlorinated organic compounds.

On the other hand, titanium dioxide has long been used to remediate organic substances present in wastewater and significant effort has been directed towards the modification of this semiconductor material. In this chapter, we have summarized the theoretical aspects of titanium dioxide heterogeneous photocatalysis as well as some applications demonstrating the use of TiO₂ and modified TiO₂ photocatalysts for the degradation of organic compounds, and especially aiming at high efficiency, activity in visible range of the solar spectrum and effective reuse of the catalyst.

The applications presented in this chapter confirm the efficiency of TiO₂ photocatalytic oxidation and of the Fenton process in water purification in laboratory scale, and it is apparent that the need to develop pilot scale treatment systems and to apply these techniques in cost effective purification processes stipulates continued indepth research. Thus extensive possibilities exist in this promising area of research, which need to be given full attention and outcome of such exploration should benefit commercial sector both in terms of ecology and economy.

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