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Solar Photochemistry for Environmental Remediation – Advanced Oxidation Processes for Industrial Wastewater Treatment

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1. Introduction

Photochemistry is the chemistry induced by light. Being the sun the most abundant and widespread light (and consequently energy) source on earth, it is obvious that solar light can also induce chemical reactions. There are several classes of organic pollutants (organic dyes, pharmaceuticals, polycyclic aromatic hydrocarbons, polychlorinated pesticides, polychlorinated dibenzodioxins, dibenzofurans and biphenyls) that by the seriousness of the risks they pose to environment and human health are considered priorities for environmental monitoring by the most important environmental agencies. In this chapter we will show how solar light can be advantageously used for environmental remediation, leading to the destruction of environmentally relevant molecules, especially when they are present in industrial wastewaters. In fact, solar light can greatly contribute to the remediation (going from the partial decomposition to the complete destruction) of those environmental pollutants. This solar remediation action can be effective either through direct photolysis and photodegradation (light induced chemical bond cleavage leading to the formation of smaller compounds) or as being the photon source that triggers the processes of their photocatalytic degradation (solar photocatalysis through advanced oxidation processes).

Advanced Oxidation Processes (AOPs) are an emergent and promising methodology for the degradation of persistent environmental pollutants, refractory to other environmental decontamination / remediation treatments. AOPs are methods of advanced photocatalysis that use the highly oxidant and non selective hydroxyl radicals, which are able to react with almost all classes of organic compounds leading to their total (complete) mineralization or to the formation of more biodegradable intermediates. The method has the advantage that it

can be applied to a large set of different matrixes and that decontamination occurs through pollutants degradation instead of their simple phase transfer. These methodologies become even more attractive when they use the sunlight as energy source, and they are generally identified as Solar Photocatalysis. The most representative solar photocatalysis treatments are semiconductor photocatalysis (Titanium dioxide, TiO_2 , is the most used semiconductor) and photo-Fenton. Using TiO_2 or photo-Fenton, highly oxidant hydroxyl radicals are produced to promote the degradation of environmental contaminants.

Photochemistry is not only the aim of solar photocatalysis in what regards source energy and basic mechanism of action but it also furnishes powerful analytical tools for the study, monitoring and understanding of the main photodegradation processes and their mechanisms of action. So, many environmental pollutants and effluents which contain them had already their photolytic and photocatalytic photodegradation mechanisms investigated and have been treated through direct photolysis and/or solar activated advanced oxidation technologies in different environmental segments. Although most of the studies reported in literature are performed in laboratorial conditions, most often with artificial irradiation simulating solar light, there are also studies performed in pilot plants at industrial scale. In fact, there are several technological solutions using solar light and photocatalysis being applied in remediation / detoxification pilot plants. Those technologies (that use batch or continuous reactors) as well as the chemical substances or type of effluents that have already been treated with or without solar concentration capabilities will be revised in this chapter.

In our opinion solar photochemistry through advanced oxidation process is an elegant application of fundamental photochemistry that is close to reach a wide industrial use and that in this way well deserves to be included in a reference work on photochemistry and their most relevant applications in modern world. Despite the impressive volume of data published in the last 30 years, the questions related to the actual trends and future involvement of advanced oxidation processes in environmental remediation applications is a hot topic as reflected by the increasing number of publications on the filed in the most recent years.

1.1 Treatment of industrial wastewaters

Generally the term wastewater refers to any residual fluid released into the environment and that contains polluting potential. The equivalent term effluent, which means to spill, derives from the latin *effluente*.

In the last decades the growing environmental awareness led to the implementation of national, international and communitary legislation (Simonsen, 2007) which prohibits or severely restricts the discharge into the environment of untreated industrial effluents containing various classes of substances (a list of controlled or restricted organic pollutants is found in Metcalf & Eddy, 2003, chapter 2, pages 99 - 104). Therefore, particular attention has been devoted to the development of methodologies for industrial wastewater treatment able to destroy or reduce the concentration of restricted chemicals within the allowed legal limits (Davis & Cornwell, 1998; Eckenfelder, 2000; Kiely, 1998; Metcalf & Eddy, 2003; Tchobanoglous at al., 1986; Nevers, 2000).

Effluents discharges into the environment may be liquid and gaseous. Domestic sewage and several different industrial effluents are the main sources of liquid effluents. After treatment,

these effluents are generally released into water bodies (rivers or sea), being usually designated as wastewaters (industrial or domestic). Deficient or incomplete wastewater treatment can lead to surface and groundwater contamination. The extensive use of chemicals such as pesticide, fertilizers, pharmaceuticals, detergents, etc. and soil deposition of urban solid residues are the most important causes of water contamination (Tchobanoglous, et al., 1993). Because of the risk posed to public health by consumption of contaminated water, special care must be taken in water source preservation and water treatment.

Water and wastewater treatment sequences consists of several different mechanical, physical, chemical and biological treatments that frequently include harrowing, filtration, flocculation, sedimentation, sterilization and chemistry oxidation of organic pollutants, among others. After physical treatment (filtration and sedimentation) the water still has considerable amounts of organic matter (including organic contaminants), which, in general, can be efficiently degraded under biological treatment (Davis & Cornwell, 1998; Eckenfelder, 2000; Kiely, 1998; Metcalf & Eddy, 2003). The gaseous effluents are often released to the air through tall chimneys and their main treatments include masking, adsorption on active carbon, contact liquid method, combustion and biological treatment (Davis & Cornwell, 1998; Kiely, 1998; Nevers, 2000). The methods for the treatment of water and wastewater (Davis & Cornwell, 1998; Eckenfelder, 2000; Kiely, 1998; Metcalf & Eddy, 2003) and gases (Davis & Cornwell, 1998; Eckenfelder, 2000; Nevers, 2000) are deeply revised in the literature.

However, the treatment of wastewater containing some organic substances cannot be achieved by traditional processes, because they resist to biological degradation (biorecalcitrant or persistent organic pollutants - POPs) or they are not completely removed by traditional treatment.

1.2 Treatment of wastewaters containing persistent organic pollutants

Nowadays, the persistent organic pollutants (POPs) are a matter of great importance, because they cannot be eliminated by the ordinary water or wastewater treatments (Davis & Cornwell, 1998; Eckenfelder, 2000; Kiely, 1998; Metcalf & Eddy, 2003; Nevers, 2000).

POPs are xenobiotic chemicals of natural or anthropogenic origin which accumulated in the environment and biota, due to their highly refractory chemical structures and physical-chemical properties. Structurally they are polycyclic conjugated compounds (polycyclic aromatic hydrocarbons) or they have a high number of halogen atoms, especially chlorine or bromine (pesticides, polychlorinated dibenzodioxins - PCDDs -, polychlorinated dibenzofurans - PCDFs -, polychlorinated biphenyls - PCBs -, brominated flame retardants, etc). Because most POPs are semi-volatile they suffer long range transport and can be found anywhere, even in distant regions where they have never been produced or released. POPs have a lipophilic and hydrophobic characters and so they consequently bioaccumulate in fatty tissues of organisms and are capable of bioaccumulating or biomagnifying into food chains, reaching extremely high concentrations (in comparison with their environmental concentrations) on the top species (Baird, 1999). Many of these compounds are biologically active possessing mutagenic and/or carcinogenic or even endocrine disruption properties. Although several of them have natural sources, the fast industrial development since the

late nineteenth century lead to an enormous increase either on the quantity and on the diversity of the persistent organic pollutants from anthropogenic origin present in the environment. Conjugation of their above mentioned characteristics determines that these compounds represent a high risk to public and environmental health.

Several of those substances have already been classified as priority substances for environmental monitoring (see Baird, 1999, chapter 7, pages 293 to 379). Dibenzodioxins, dibenzofurans, polychlorinated biphenyls and organochlorinated pesticides join the list of priority organic pollutants of World Health Organization (WHO), United Nations Environmental Program (UNEP) and other Environmental Protection Agencies (Kiely, 1998; Metcalf & Eddy, 2003). The Stockholm Convention regulates this matter worldwide. This Convention presents a list of POPs (originally 12 substances: aldrin, dieldrin, endrin, chlordane, PCDDs, PCDFs, BHC, DDT, heptachlor, mirex, PCBs, toxaphene). Nowadays there are other under consideration: HCH, chlordecone, hexabromobiphenyl, hexa and heptabromobiphenyl ether, pentachlorobenzene tetra and pentabromodiphenyl ether e perfluorooctanosulfonic acid and its salts) which production, use and trading are banned or severely restricted (United Nations Environment Programme, 2005; Stockholm Convention on Persistent Organic Pollutants, 2005; Oliveira, et al., 2004, 2008, 2011). There are many other synthetic substances that have been identified as priority pollutants for environmental monitoring by the United States Environmental Protection Agency (USEPA) based on their probable or confirmed carcinogenic, mutagenic, teratogenic or acute toxicity characteristics. Among them we can mention volatile organic compounds, agricultural fertilizers and chlorinated residues resultant from disinfection processes at water public supply systems. Many of those substances can either be found in the air (as is the case of the volatile organic compounds) or in surface and groundwater and they reach the reception media through domestic or industrial wastewater systems or due to drain-off from agriculture (as happens with pesticides and fertilizers). There are also several substances (i.e. dyes, pharmaceuticals, etc) some of them specially synthesized to be resistant to degradation and conventional wastewater treatment processes are not able to remove them efficiently (Eckenfelder, 2000). Although these substances are not classified as priority pollutants, their negative impact in aquatic life and the changes of physical-chemical characteristics of the water bodies even when present in low concentrations make the control of their concentration very important.

Once the use and discharge of bioactive organic substances in the different environmental segments is not easy to eliminate and appears extremely difficult to control its essential to develop new powerful, clean and safe environmental remediation technologies for their treatment especially for the biorecalcitrant organic pollutants. One of the new most promising technologies available uses hydroxyl radical, a highly reactive chemical species that can attack and destroy organic molecules and is denominated advanced oxidation processes (Eckenfelder, 2000; Metcalf & Eddy, 2003).

2. Advanced oxidation processes

Advanced oxidation processes (AOPs) is the common name of several chemical oxidation methods used to remediate substances that are highly resistant to biological degradation. Although oxidation can be total, frequently a partial oxidation is sufficient to decrease the toxicity of the biorecalcitrant compound enabling their final treatment by conventional biological treatment. The complete oxidation leads to mineralization and yields CO_2 , H_2O

and inorganic ions. The partial oxidation can be enough to decrease toxicity enabling biological degradation, but is essential to verify if the intermediary products formed are not more toxic than the parent compound under treatment. In the last 30 years several books (Bahnemann, 1999; Halmann, 1995; Pelizzetti & Serpone, 1989; Schiavello, 1988) and reviews (Byrne, et al., 2011; Dusek, 2010; Gogate & Pandit; 2004a, 2004b; Legrini, et al., 1993; Linsebigler, et al, 1995) were published on the subject. Blake, 2001 contains more than 1200 references on the subject. AOPs can remediate all different types of organic pollutants in liquid, gaseous or solid media, reason why they are used on the remediation of contaminated waters, liquid or gaseous effluents and also on the treatment of different hazardous wastes namely on contaminated soils. Some of the above mentioned reviews present comprehensive compilations of the substances and residues already mineralized using different advanced oxidation processes (Blake, 2001, Legrini, et al., 1993).

2.1 Theory of advanced oxidation

Although different advanced oxidation processes use several different reaction systems, all of them have the same chemical characteristic: i.e., the production and use of hydroxyl radicals (OH•) (Eckenfelder, 2000; Metcalf & Eddy, 2003). Hydroxyl radicals are highly reactive species that are able to attack and destroy even the most persistent organic molecules that are not oxidized by the oxidants as oxygen, ozone or chlorine (Eckenfelder, 2000). Table 1 shows oxidation potential of the hydroxyl radical and compares it with others commons oxidants used in chemical oxidation (Fox & Dulay, 1993).

Oxidizing agent	Oxidation potential, Volt
Fluorine	3.06
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Molecular oxygen	1.23

Table 1. Oxidation potential of most common oxidizing agents.

Hydroxyl radical is the most powerful oxidant after fluorine; it is able to initiate several oxidation reactions leading to complete mineralization of the original organic substances and their subsequent degradation products. Hydroxyl radical reacts will all classes of organics mainly by hydrogen abstraction:



Hydrogen abstraction produces organic radicals able to react with molecular oxygen and originating peroxy radicals.



Electrophilic additions may also occur (Legrini et al., 1993).



Electron transfer reactions,



and reactions between hydroxyl radicals,



Hydroxyl radical is characterized by a non-selective attack; this is an extremely useful characteristic for an oxidant to be used on environmental remediation. Other relevant and important characteristics are the existence of several possible pathways for hydroxyl radical production and the fact that all reactions occur at normal temperature and pressure. AOPs advantageously promote complete degradation of pollutants being remediated while classical treatments usually only transfer target pollutants to another phase, leading to the production of secondary residues (slugs) that require further treatment or deposition. Therefore, the advanced oxidation process is a good method for environmental decontamination (Linsebigler et al., 1995).

AOPs versatility is favoured also by the existence of various pathways to produce hydroxyl radicals, which enables a high adaptability to any specific environmental remediation problem. The advanced oxidation process can degrade all types of organic compounds in water therefore they are widely used in industrial wastewater remediation.

2.2 Technologies used in the production of hydroxyl radicals

Advanced oxidation processes enclose several different treatments options: as ozone, hydrogen peroxide, ultraviolet radiation, ultrasound, homogeneous and heterogeneous photocatalysis, photocatalytic disinfection and also their combination (Hoffmann et al., 1995). The use of hydroxyl radicals to promote chemical oxidation it is the common feature of all AOPs. Table 2 shows several of the chemical oxidation technologies available.

Processes with ozone	Processes without ozone
Ozone at high pH (8-10)	$\text{H}_2\text{O}_2 + \text{UV}$
Ozone + UV	Photocatalysis (UV+ photocatalyst)
Ozone + H_2O_2	Ultrasound
Ozone + $\text{H}_2\text{O}_2 + \text{UV}$	Oxidation supercritical
Ozone + TiO_2	$\text{H}_2\text{O}_2 + \text{UV} + \text{iron salts}$ (Foto-Fenton)
Ozone + $\text{TiO}_2 + \text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2 + \text{iron salts}$ (Fenton reagent)
Ozone + Ultrasound	

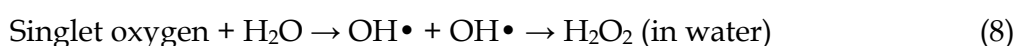
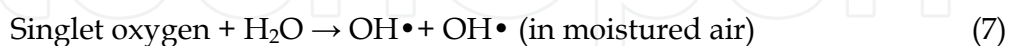
Table 2. Technologies used in the production of hydroxyl radicals.

The AOPs classification is frequently based on the use or not of ozone on the production of hydroxyl radicals. The classification can also be based on the use or not of irradiation and on the number of phases (homogeneous or heterogeneous). Ozone + UV, ozone + hydrogen

peroxide, ozone + UV + hydrogen peroxide and hydrogen peroxide + UV are the most used commercial processes (highlighted in *italic* in Table 2) and its use will be analyzed below (Metcalf & Edie, 2003).

2.2.1 Ozone + UV

The hydroxyl radical production is achieved by ozone irradiation (O_3) with ultraviolet radiation (UV) according to:



Ozone photolysis in air with moisture produces two hydroxyl radicals by each ozone molecule while when the same reaction occurs in water the hydroxyl radicals produced suffer rapid recombination and hydrogen peroxide is readily formed. Due to this later reaction, the process in water is not economically viable, since a lot of energy as to be imparted to the system to keep the adequate hydroxyl radical concentration. However, ozone + UV process is efficient on degradation in gaseous phases. The efficiency is even higher if the compounds also undergo direct photolysis by ultraviolet radiation. Figure 1 presents a scheme of an advanced oxidation treatment unity using ozone and UV radiation (Ikehata & El-Din, 2004; Mills & Hunte, 1997).

2.2.2 Ozone + hydrogen peroxide

For compounds that do not efficiently absorb ultraviolet radiation the yield of the degradation processes can be increased adding hydrogen peroxide once the latter when in contact with ozone undergoes an additional reaction, further promoting hydroxyl radical formation.

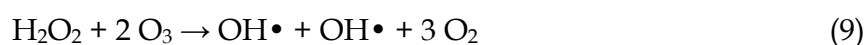


Figure 2 presents a scheme of an advanced oxidation unity using ozone and hydrogen peroxide.

2.2.3 Hydrogen peroxide + UV and ozone + UV + hydrogen peroxide

UV irradiation of water with hydrogen peroxide also leads to hydroxyl radical formation (Galindo et al., 2000, Ikehata & El-Din, 2006).

However, frequently the process is not economically viable due to the low absorption extinction coefficient of hydrogen peroxide; this fact determines the use of high concentrations of hydrogen peroxide so that hydroxyl radicals are produced in the adequate amount. The combination of the later process with ozone promotes a better efficiency on the use of UV radiation. Figure 3, presents a scheme of an advanced oxidation unit using ozone, hydrogen peroxide and UV radiation.

Although the technologies presented above have reached commercial application, especially in industrial wastewater treatment and water disinfection all of them use high amounts of

expensive reagents (hydrogen peroxide and ozone) and consume a lot of energy on UV radiation generation. So, their application is restricted to processes where more economic alternatives are not viable.

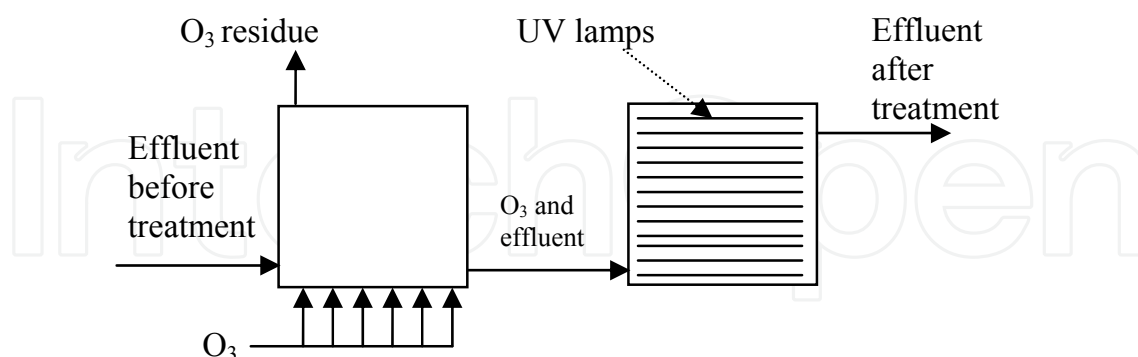


Fig. 1. Scheme of advanced oxidation treatment unit using ozone and UV radiation.

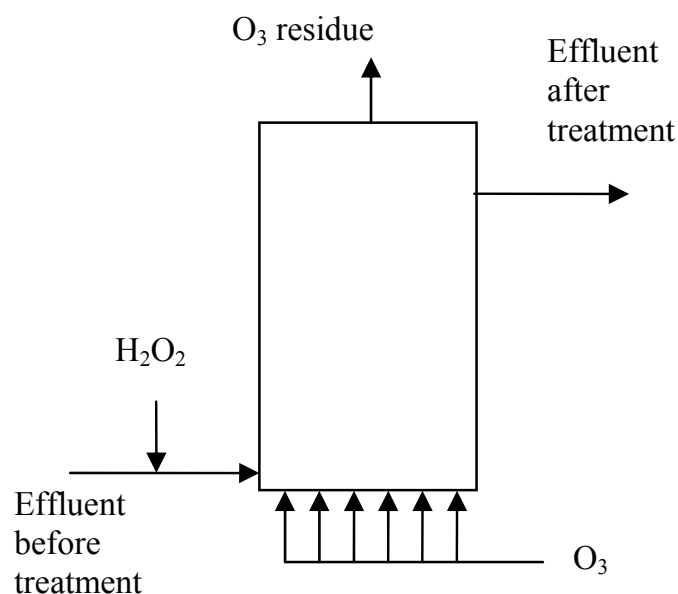


Fig. 2. Scheme of advanced oxidation unit using ozone and hydrogen peroxide.



Taking in account their cost, advanced oxidation processes can be used in integrated treatment systems for water, and domestic or industrial wastewaters where prior to biological treatment an advanced oxidative degradation of toxic and refractory substances is performed (Mantzavinos & Psillakis, 2004; Oller et al., 2007; Zapata et al., 2010). Frequently, the primary attack promoted by hydroxyl radical is sufficient to produce less toxic compounds that can already undergo biological treatment. This integrated treatment scheme can lead effectively to global treatment cost reduction. At different times of the advanced oxidative treatment it is advisable to perform toxicity tests with different microorganisms commonly used in biological treatment. These toxicity tests will help to determine the moment that the advanced oxidation process can already be substitute by the biological treatment (Fujishima et al., 2000).

However, because AOPs are essential for treatment of resistant substances in wastewater the most recent research efforts were on the development of more efficient energy processes. AOPs that do not need UV irradiation to activate hydroxyl radical production and that alternatively can use sunlight (wavelengths greater than 300 nm) for the same propose are extremely attractive (Byrne et al., 2011; Malato et al., 2002, 2009).

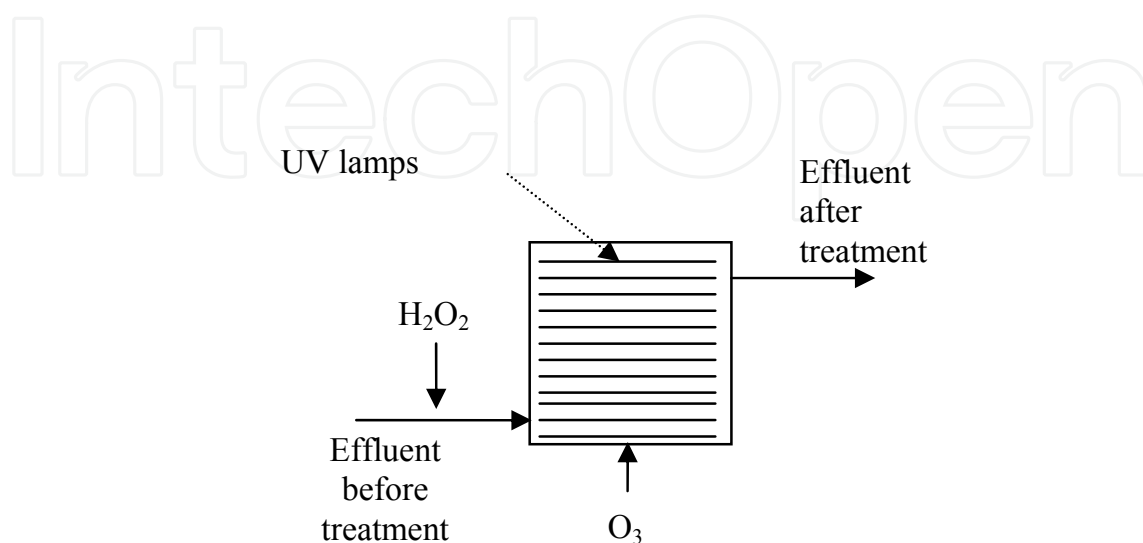


Fig. 3. Scheme of advanced oxidation unit using ozone, hydrogen peroxide and UV light.

3. Advanced oxidation processes with sunlight

The degradation of persistent organic pollutant using advanced oxidation processes with sunlight as energy source have as great advantage their lower costs. There are two advanced oxidation processes that enable the use of sunlight as energy source: heterogeneous photocatalysis using semiconductors and homogeneous photocatalysis using photo-Fenton processes (Fujishima et al., 2000; Pirkanniemi & Sillanpaa, 2002).

We can compare the solar emission spectra (starting at 300 nm) with the absorption spectra of titanium dioxide and of Fenton reactant (Malato et al., 2002). Heterogeneous photocatalysis activated by sunlight uses near ultraviolet solar spectrum (wavelength under 380 nm) and homogeneous photocatalysis by photo-Fenton uses a larger portion of solar spectrum (wavelength up to 580 nm). Both processes are efficient in the photodegradation of persistent organic pollutants, they are a innovative way of using a renewable energy and they are very promising technologies in what regards environmental remediation (Gogate & Pandit, 2004a, 2004b).

Photocatalysis is the combination of photochemistry and catalysis, a process where light and catalysis are simultaneously used to promote or accelerate a chemical reaction. So, photocatalysis can be defined as “catalysis driven acceleration of a light induced reaction”. Direct light absorption is one of photocatalysis bigger advantages compared to thermally activate catalytic processes.

Nowadays, photocatalysis appears as an excellent tool for final treatments of samples containing persistent organic pollutants (POPs) when compared to classical treatments (Doll & Frimmel, 2005; Hincapié, 2005). In a near future they can turn in one of the most used technologies for POPs remediation.

3.1 Heterogeneous photocatalysis using semiconductors – TiO₂/UV

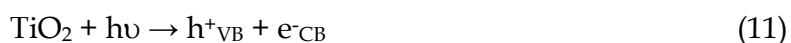
Heterogeneous photocatalysis is a (sun)light activated process that produces reducing and oxidizing species able to promote mineralization of organic pollutants using a semiconductor (TiO₂, ZnO, etc) as catalyst. The interaction of a photon with the catalyst produces an electron/hole pair on it. Excited electrons can be transferred to chemicals (reduction) into the semiconductor particle environment and at the same time the catalyst accepts electrons of oxidized specie. The net flux of electrons in both directions is null and the catalyst stays unaltered. The mechanism and the electron/hole generation processes of heterogeneous photocatalysis is addressed in several reviews (Davis & Cornwell, 1998; Eckenfelder, 2000; Kiely, 1998; Metcalf & Eddy, 2003; Nevers, 2000) that also present exhaustive list of organic residues remediated already by the method.

The ability of heterogeneous photocatalysis to eliminate organic pollutants from gaseous or aqueous (Eckenfelder, 2000; Kiely, 1998; Metcalf & Eddy, 2003) streams was largely demonstrated. Polycyclic aromatic hydrocarbons, pentachlorophenol, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 4,4'-DDT, dichlorobiphenyls and dichlorodibenzodioxins were already mineralized by heterogeneous photocatalysis (Blake, 2001; Pelizzetti & Serpone, 1989). Once TiO₂ only uses about 10% of the available solar radiation, several groups are working on improving TiO₂ visible light absorption (Anandan & Yoon, 2003; Chan et al., 2011; Fox & Dulay, 1993; Gupta & Tripathi, 2011; Janus & Morawski, 2010; Linsebigler et al., 1995; Mills & Hunte, 1997; Mourao et al., 2009; Reynaud et al., 2011; Roy et al., 2011; Zhang et al., 2004) to improve photocatalysis efficiency.

3.1.1 Heterogenous photocatalysis mechanism

Semiconductors (as TiO₂, ZnO, CdS, ZnS, etc.) have a typical electronic structure composed by a fully occupied valence band (VB) and an empty conduction band (CB). This typical semiconductor's electronic structure enable they can act as sensitizers of light induced oxidation processes. Photocatalysis action mechanism can be visualized on Figure 4. In this scheme the valence and conduction band of a semiconductor are represented over a spherical semiconductor particle.

The semiconductor (TiO₂) absorbs photons with enough energy to promote an electron from the valence band to the conduction band and on the process an electron/hole pair is formed. The energy of the absorbed photon has to be equal or higher than that of the semiconductor "band-gap". The process can be described in a simple way by the following set of equations:



While the electron is promoted to the conduction band a hole is produced in the valence band; this hole has a high oxidative power (+1 to +3.5 V, depending on semiconductor and pH) able not only to oxidize the water absorb on semiconductor surface producing hydroxyl radicals but also able to oxidize hydroxide ions, OH⁻, or the substrate itself, RX (Figure 4).

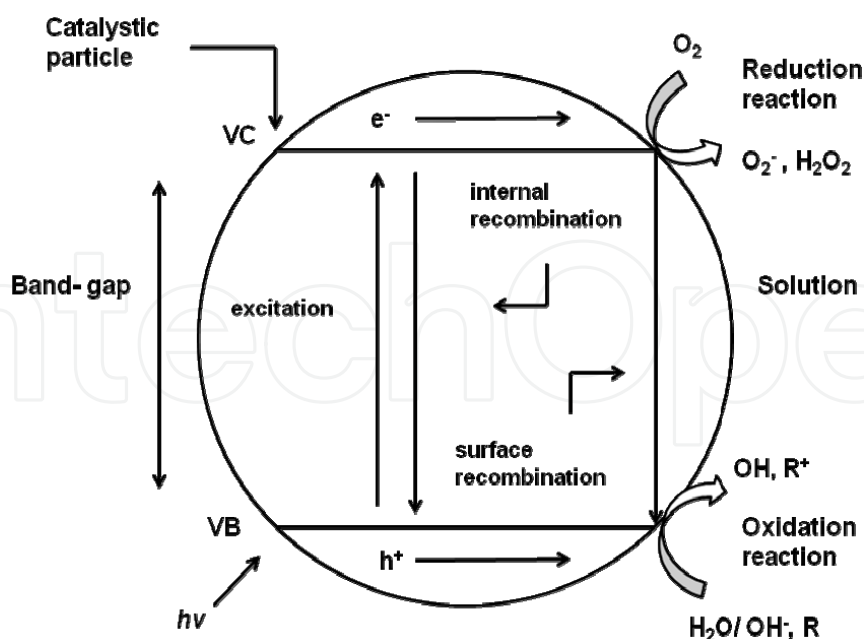


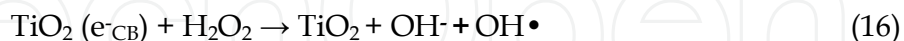
Fig. 4. Heterogeneous photocatalysis on a semiconductor (TiO₂) particle surface.



Once formed hydroxyl radicals promote the already mentioned oxidation reactions that degrade the persistent organic pollutants. The electrons promoted to the conduction band are also able to reduce the oxygen available in the surroundings to superoxide radicals. Presence of oxygen is essential in all oxidative degradation processes



When hydrogen peroxide is added the speed of the photodegradation significantly increase because its reaction with TiO₂ provides another hydroxyl radical source.



Although the nature of all oxidizing species formed on semiconductor surface after light absorption is controversial, all authors agree that hydroxyl radical is the main oxidizing species formed on semiconductor surface. Effectively all detected intermediary species during photodegradation of polycyclic aromatic hydrocarbons and halogenated organic compounds are typically hydroxylated structures (Bahnemann, 1999; Oliveira et al., 2004b; Xavier et al., 2005). More difficult to clarify is if oxidation proceeds by direct or indirect route, directly by holes or by hydroxyl radical formed from them, bonded to surface or in solution. On the other hand, the strong correlation between speed of degradation and the concentration of pollutants absorbed on catalyst surface also suggests and reinforces the hypothesis that the species responsible for the photodegradation are hydroxyl radicals formed on the surface of the photocatalyst. Laser flash photolysis and electronic

paramagnetic resonance proved to be helpful on the elucidation on the nature of intermediary species formed during photocatalytic degradation processes (Bahnemann, 1999; Botelho do Rego and Vieira Ferreira, 2001, Fox & Dulay, 1993, Oliveira et al., 2004b).

3.1.2 Photocatalysts

The ideal semiconductor to be used as photocatalyst must be photoactive, able to absorb ultraviolet and visible radiation, photostable, cheap and biologically and chemically inert. TiO_2 , ZnO e CdS are the most studied photocatalysts. Titanium dioxide has all above mentioned characteristics of a good photocatalyst and is in fact the photocatalyst with higher photocatalytic activity on organic matter decomposition. This quality of titanium dioxide made him the reference semiconductor to establish and compare the photocatalytic activity of other semiconductor materials. TiO_2 photocatalysis also obeys to green chemistry key principles (Anastas & Warner, 1998; Hermann et al., 2007).

TiO_2 occurs in three crystals forms: anatase, rutile and brookite. Anatase is the photocatalytic active form. However, different semiconductor batches have present different photocatalytic activities from batch to batch and between different producers. It is also difficult to reproduce the photocatalytic activity between laboratories. Because of that, TiO_2 P25 from Degussa is currently accepted as the standard titanium dioxide. TiO_2 Degussa P25 without any treatment is used on phenol degradation for comparative purposes of the photocatalytic reactors performance. Degradation of 4-chlorophenol is also a standard reaction for certification of titanium dioxide photocatalytic activity.

TiO_2 Degussa P25 is the standard form of TiO_2 ; it is a powder available commercially with a purity of 99.5% (70:30 anatase : rutile), with a superficial area of $50 \pm 15 \text{ m}^2/\text{g}$, its not porous and have cubic particles of rounded edges and a average particle diameter of 21 nm. However TiO_2 particles does not exist isolated but as complex irreducible primary aggregates of about 1 μm .

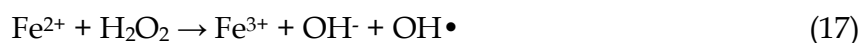
To perform a heterogeneous photocatalytic reaction activated by light it is necessary to use semiconductors with the adequate "band-gap" to be activated by solar energy. TiO_2 have a high band-gap, of 3.2 eV, being consequently activated only by radiation below 380 nm, i.e., using only 10% of the sunlight spectrum. However, metal oxides with high band-gap, as TiO_2 , go on being strongly used on photocatalysis since they are usually resistant to photocorrosion. Although photocatalysts with lower band-gaps present bigger sensitivity to solar spectrum, they are not frequently used because they experience strong photocorrosion, being globally less effective.

Maximizing the efficiency of photocatalysis is an object of great challenge for scientists. Many efforts have been devoted to extend the photocatalytic properties into the visible region (Anandan & Yoon, 2003; Asahi et al., 2001; Augugliaro et al., 2006; Chan et al., 2011; Emeline et al., 2008; Fox & Dulay, 1993; Gupta & Tripathi, 2011; Janus & Morawski, 2010; Linsebigler et al., 1995; Mills & Hunte, 1997; Mourao et al., 2009; Reynaud et al., 2011; Roy et al., 2011; Zhang et al., 2004). Approaches such as doping the TiO_2 with transition metal ions or the deposition of a noble metal on semiconductor particles have been successfully used. Inclusion of iron into TiO_2 particles, for example, has been effectively used in the degradation of chlorinated organic compounds. Additionally nanotechnology is providing

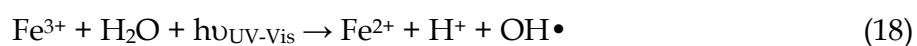
new insights in this subject with several classes of nanoscale materials (some of them including already titanium or other catalysts) that are being already evaluated as functional materials for water purification (Biswas & Wu, 2005; Wang et al., 2008; Xu et al., 2011): metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers (Savage & Diallo, 2005). The use of light to activate such nanoparticles opens up new ways to design green oxidation technologies for environmental remediation (Kamat & Meisel, 2002, 2003; Savage & Diallo, 2005). Due to their high-specific surface area, nanoparticles exhibit enhanced reactivity when compared with their bulk counterparts by several reasons such as the proportion of surface sites at edges or corners, the presence of distorted high-energy sites, contributions of interfacial free energies to chemical thermodynamics, the effects of altered surface regions, and quantum effects. Nanoparticles can be easily deposited or anchored onto various surfaces or used as a tailored film. These facilities can improve the adsorption of desirable chemicals, such as organics and heavy metals onto film surfaces. (Biswas & Wu, 2005; Kamat & Meisel, 2002, 2003). TiO₂ nanoparticles have been extensively studied for oxidative and reductive transformation of organic and inorganic species present as contaminants water (Wang et al., 2008; Xu et al., 2011). Ashasi et al. (2001) synthesized N-doped TiO₂ nanoparticles that were capable of photodegraded methylene blue under visible light and Bae & Choi (2003) have synthesized visible light-activated TiO₂ nanoparticles based on TiO₂ modified by ruthenium-complex sensitizers and Pt deposits.

3.2 Homogeneous photocatalysis - photo-Fenton process

Fenton's reagent is another extremely useful source of hydroxyl radicals and a potent oxidant of organic compounds. It was first described at the end of the XIX century and consists in a process in homogeneous phase, in which an aqueous hydrogen peroxide solution and Fe²⁺ (ferrous) ions, in acidic conditions (pH = 2-4), generate hydroxyl radicals, in a process that is not activated by light (Nogueira et al., 2007; Pignatello et al., 2006):



When Fenton process occurs under solar radiation, degradation rate increases significantly. Although the oxidizing power of Fenton reaction was known for more than one hundred years, only recently it was discovered that Fenton reaction can be accelerated by irradiation with ultraviolet or visible light ($\lambda < 580$ nm), making it a photocatalytic process (Fe²⁺ is regenerated). The so-called photo-Fenton reaction produces additional hydroxyl radicals and leads to the photocatalyst reduction by light (Nogueira et al., 2007; Pignatello et al., 2006):



The great advantage of this process when compared with heterogeneous photocatalysis with TiO₂ is its sensibility to light up to 580 nm. When compared with TiO₂ photocatalysis, this process allows a more efficient use of sunlight. The contact between the pollutant and the oxidizing agent is more effective once the process occur in homogeneous phase. The disadvantages of the photo-Fenton process are the treatment aggressivity due to low pH required (usually below 4), the high consumption of hydrogen peroxide and the need of removing iron at the end of the treatment.

The use of sunlight instead of artificial light for photo-Fenton activation, besides increasing the efficiency, also significantly decreases the cost of treatment. Therefore photo-Fenton is a great advance towards industrial implementation of photocatalysis processes (Brillas et al., 2009; Nogueira et al., 2007; Pignatello et al., 2006). Foto-phenton's process ability to treat water containing various pollutants (Kavitha & Palanivelu, 2004; Soon & Hameed; 2011; Umar et al., 2010) was already proved.

4. Industrial units of wastewater treatment by photocatalysis

4.1 Solar collectors for photochemical processes

The use of light activated advanced oxidation processes requires the development of dedicated photochemical solar technology that include the design of efficient solar photons collection technologies and the direction of those photons to the appropriate reactor in order to promote the photodegradation of the persistent organic pollutants to be remediated. For solar photochemical processes it is more interesting the collection of photons with high-energy and low wavelength, since typically the majority of the photocatalysis processes use solar radiation in the ultraviolet (300-400 nm). The exception is photo-Fenton process, which uses all sunlight below 580 nm. Usually radiation with wavelengths higher than 600 nm does not have any utility for photocatalysis processes. Solar flux at ground level is about 20 to 30 W per square meter, so sun approximately provides 0.2 to 0.3 moles of photons per square meter per hour (Bahnmamm, 1999; Malato et al., 2002).

The equipment that makes the efficient collection of photons is the solar collector. This equipment represents the largest source of operating costs of a photocatalysis unit for treatment of effluents. Solar collectors can be classified into three types according to the level of solar concentration achieved, which is usually directly related to the temperature reached by the system. So we have solar collectors which are non concentrators, moderately concentrators or highly concentrators. They can also be called concentrators of low (<150 °C), medium (150 - 400 °C) and high (> 400 °C) temperature.

The non concentrating collectors or low temperature collectors are static and usually consist of flat plates directed towards the sun with a certain inclination, depending on the geographic location. Its main advantage is their great simplicity and low cost.

The moderately concentrating collectors or medium temperature collectors concentrate the sun 5 to 50 times; to achieve this concentration factor the equipment must be able to continuously follow the sun. The parabolic and holographic are such type of collectors. Parabolic collectors have a parabolic reflecting surface which concentrates the radiation in a tubular collector located at the focus of the parabola and can have uni or biaxial movement. Holographic collectors consist of reflective surfaces like convex lenses that deflect radiation and concentrate it in a focus.

The highly concentrating collectors or high temperature collectors have a punctual focus rather than a linear one and they are based on a paraboloid with solar tracking. These reactors ensure solar concentrations from 100 to 10,000 times, reason why they require high precision optical elements.

As the temperature plays no role in photochemical reactions, their technological applications typically only use low and medium temperature collectors, which have a much more economical construction. An important difference between these two reactors is that the first type of concentrators uses both direct and diffuse radiation while the concentrators collectors only use direct radiation. In terms of collector and reactor design itself, the systems have much in common with that of conventional thermal collectors; however, as the effluent to be cleaned must be directly exposed to sunlight, the absorber must be transparent to the photons. As temperature is not important, the systems are not thermally isolated. Most photocatalytic remediation systems involve wastewaters (Duran et al., 2010, 2011; Malato et al., 2007a, 2007b; Marugan et al., 2007; Miranda-Garcia et al., 2011; Navarro et al., 2011; Oyama et al., 2011; Vilar et al., 2009; Zayani et al., 2009), but the appropriated technology for gas phase photocatalytic processes is also possible (Lim et al., 2009).

4.2 Reactors with solar collectors

Several types of solar reactors for effluents decontamination have been tested. We describe below the four most commonly used.

4.2.1 Thin film fixed bed reactor

This reactor, whose simplified diagram is presented in Figure 5, is one of the first non-concentrators solar reactors, so it can use the total solar radiation (direct and diffuse) for the photocatalytic process. Quantities of direct and diffuse radiation reaching earth are nearly identical, so concentrator reactors, by not using the diffuse radiation, profit from only half of the maximum radiation available.

The most important part of the reactor is a tilted fixed dish (0.6 m × 1.2 m) coated with a thin film of photocatalyst, typically Degussa P25 TiO₂, which is continuously washed with a film of about 100 μm from the wastewater to be treated at a rate of 1 to 6.5 liters per hour (Bahnmamm, 1999; Malato et al., 2002).

4.2.2 Parabolic trough reactor

This reactor directly concentrates sunlight by a factor from 5 to 50. Tracking of solar radiation is done by a single or dual motors system that allow the continued alignment of the solar concentrator with the sun and various reactors can be connected in series or in parallel. In the parabolic trough reactor, the reflector has a parabolic profile and the tube where the photocatalytic reaction takes place is in its focus, in this way, only the light that enters parallel in the reflector can be focused on the reaction tube (Figure 6). This type of reactor is being used in solar decontamination circuits installed in the United States (Albuquerque, Sandia National Laboratories, and California, Lawrence Livermore Laboratories) and Spain (Plataforma Solar de Almeria), Figure 7 (Navntoft et al., 2009).

The concentrated radiation is focused into a tube containing an aqueous suspension of TiO₂ and the effluent to be treated. In fact, only about 60% of the radiation collected is effectively used, the rest being lost by various causes.

At Almeria reactors, the total volume of effluent are about 400 liters, but the illuminated tube of about 180 meters contains only about half of that volume of effluent, which moves at speeds between 250 to 3500 liters per hour (Bahnemamm, 1999; Malato et al., 2002).

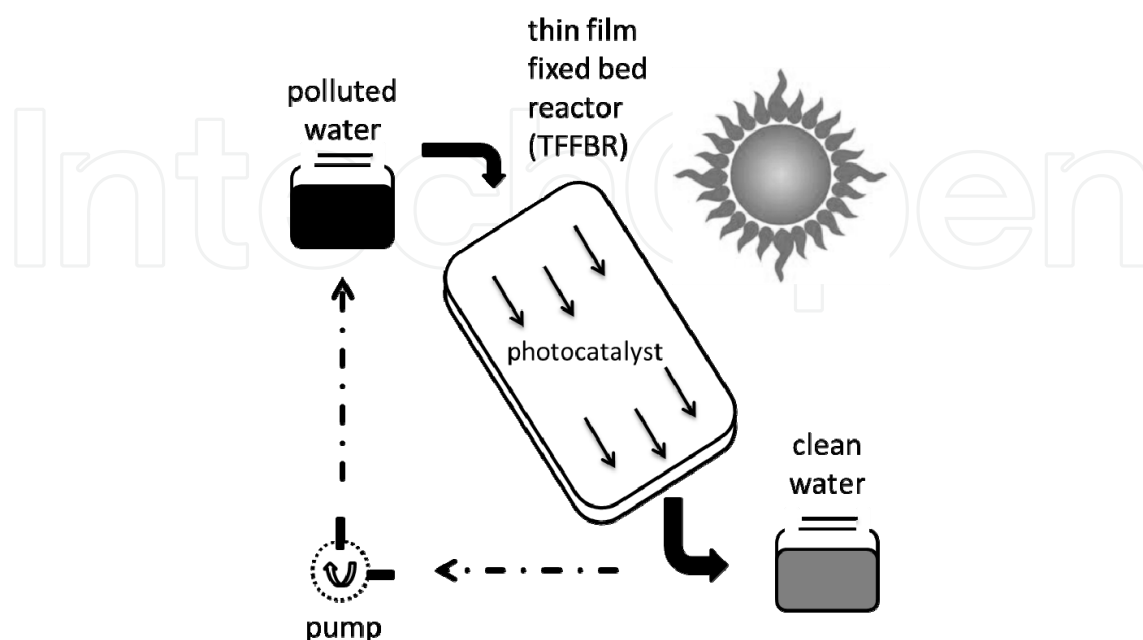


Fig. 5. Simplified diagram of a thin film fixed bed reactor.

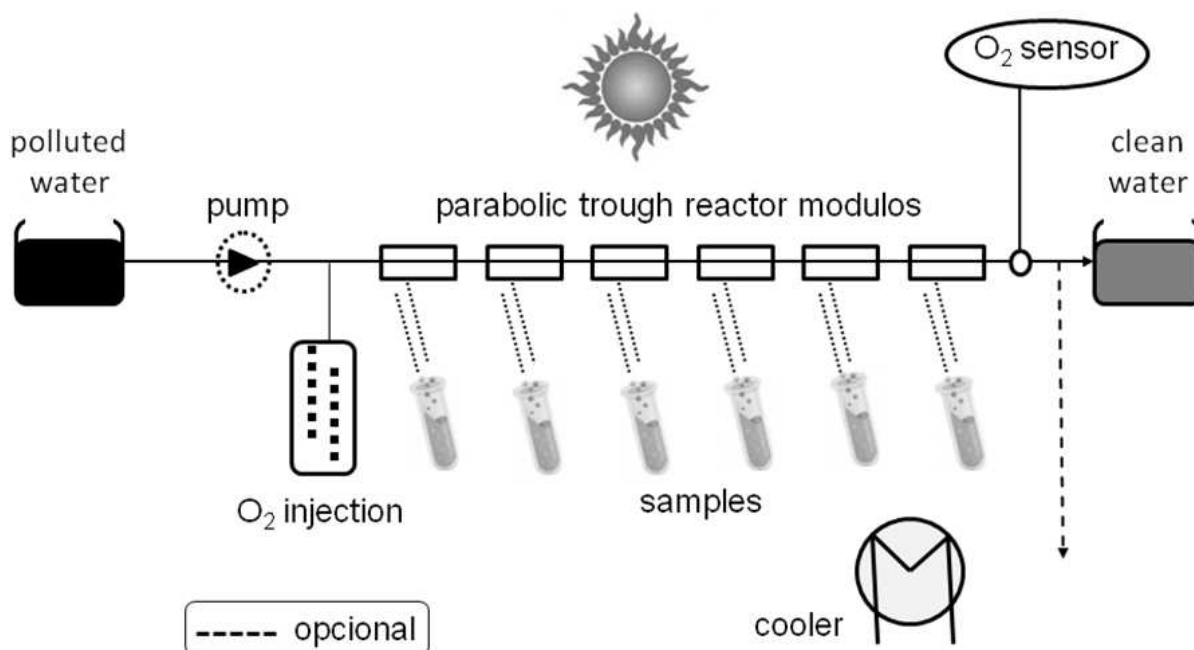


Fig. 6. Simplified diagram of a plant using parabolic trough reactors.

4.2.3 Compound parabolic collecting reactor

This reactor, whose simplified diagram is presented in Figure 7, is an open reactor without solar concentration. Basically this reactor differs from the conventional open parabolic reactor in the form of the reflectors. These reactors are static collectors with a reflective

surface that surrounds a circular reactor, as shown in Figure 7. They had shown to provide better efficiency in the treatment of low pollutant concentration effluents. This reactor is an effective combination of the two reactors types described above (Bahnemamm, 1999; Malato et al., 2002).

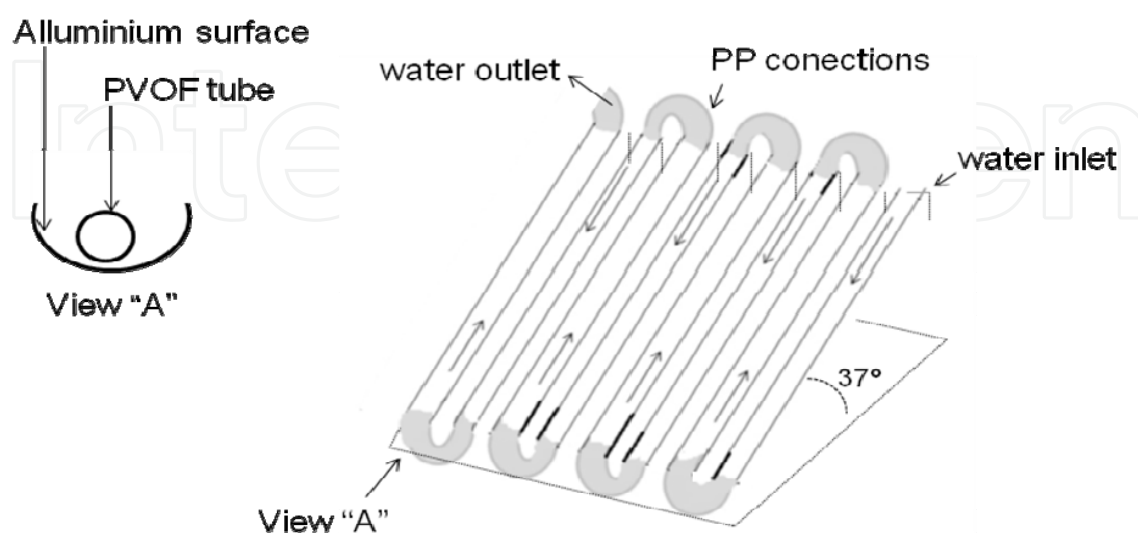


Fig. 7. Simplified diagram of a compound parabolic collecting reactor.

4.2.4 Double skin sheet reactor

This type of reactor without concentration consists of a transparent box with an internal structure similar to that shown in Figure 8, through which is pumped the suspension containing the pollutant and the photocatalyst. It has the advantage of using the total radiation and be very simple to operate (Bahnemamm, 1999; Malato et al., 2002).

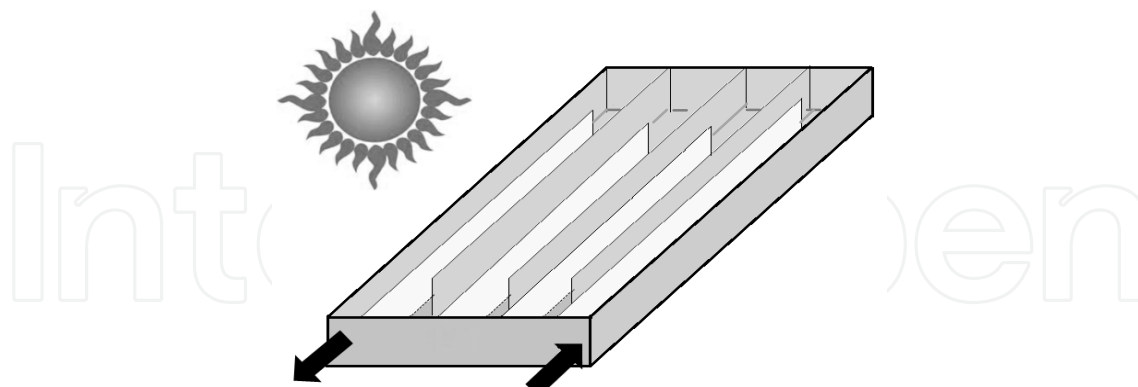


Fig. 8. Simplified diagram of a double sheet reactor.

4.3 Industrial units

Figure 9 shows a diagram of a photocatalytic installation that can be alternatively used for heterogeneous TiO_2 photocatalysis or for homogeneous photo-Fenton photocatalysis (or any other of the treatments previously described). In both cases the catalyst (TiO_2 or iron) must be separated at end of treatment to be recycled and reused.

The surface area of the solar collector depends essentially on the effluent to be treated, mandatorily of the type and concentration of the contaminant, and on solar irradiation conditions and the location where treatment plant will be installed. The lifetime of the catalysts depends on the type of effluent to be treated and of the desired treatment final quality. In the end, the toxicity of the treated effluent must always be evaluated.

The project of an industrial effluent decontamination plant by photocatalysis requires a careful selection of the type of reactor to use, the arrangement of the reactor at the installation (series or parallel), the operation mode of the photocatalyst (fixed or suspended), the system for recycling catalysts and flow velocity, among others. The concentration of photocatalyst is also a key parameter and must be adjusted according to the following basic principles: for suspensions of TiO_2 , the speed of reaction is maximum for concentrations among 1 to 2 grams of TiO_2 per liter of effluent to be treated, when the optical path is small (1-2 cm maximum). When the optical path is substantially higher, the appropriate concentration of photocatalyst is several hundred milligrams per liter. Anyway, when TiO_2 concentrations is too high there is an internal filter effect and the rate of photodegradation decreases due to excessive opacity of the solution, which itself inhibits the illumination of the photocatalyst.

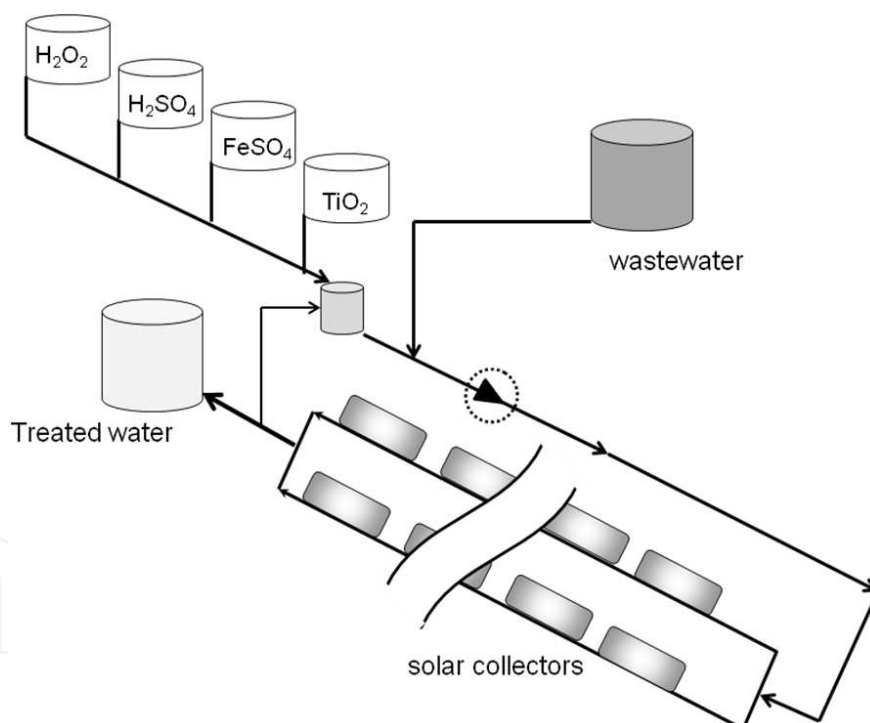


Fig. 9. Simplified diagram of a photocatalytic effluent treatment plant.

If the treatment plant is intended for treatment of a specific effluent, it does not need to be versatile and will be very similar to that shown in Figure 10. On the other hand, if an installation needs to treat various types of wastes, it must have the versatility to adapt to the optimal photodegradation conditions of the various types of effluents, e.g., having different types of solar collectors and reactors (as is the case of Almeria solar platform) and the project will be much more complicated.

5. Applications of photocatalysis on the treatment of industrial effluents

Solar driven AOPs proved to be an excellent environmental remediation method to destroy persistent organic compounds not treatable by biological processes. In many cases, they allow the degradation of several persistent organic toxic pollutants decreasing the toxicity of the effluents released into the environment. These methods are particularly suitable for treating recalcitrant substances including those requiring special attention (hazardous or controlled ones). Several organochlorinated substances (dioxins, PCBs, etc) are persistent and sufficient toxic to disturb the environmental health and must be degraded prior to their environmental release. Without being exhaustive on the list of applications and systems to be treated, we will refer some examples that we consider most significant.

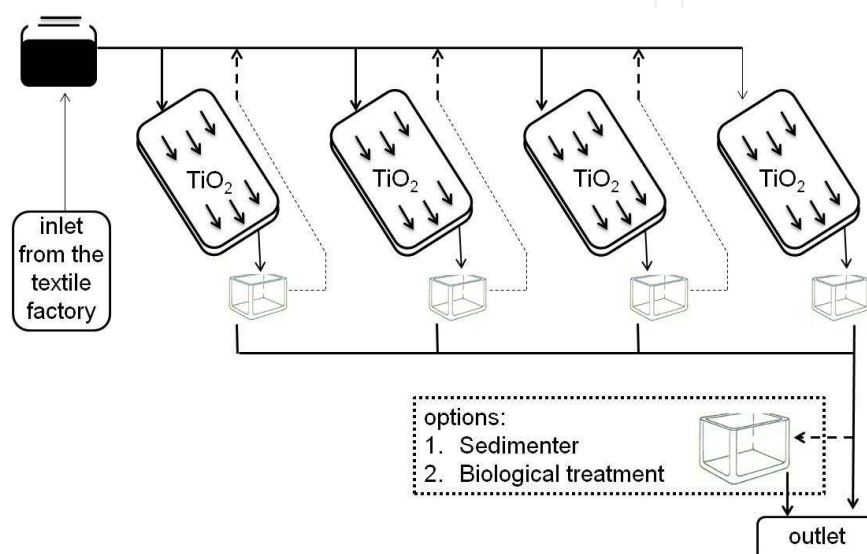


Fig. 10. Simplified diagram of a unit for dyes degradation with thin film fixed reactors.

Water is essential for life and therefore a key resource for humanity. Although it may seem that the water is very handy on our planet that is not true. Of the entire planet's water, 97.5% of the water is salty, among the remaining 2.5%, 70% is frozen and the rest is largely inaccessible in underground aquifers or as soil moisture. In fact, less than 1% of world potable water is available for immediate human consumption and even that is not uniformly distributed around the globe. For this reason, methodologies such as advanced oxidation processes that allow the maintenance of water quality are essential (Andreozzi et al., 1999; Chong et al., 2010; Comninellis et al., 2008; Matilainen & Sillanpaa, 2010). The problematic of water treatment and industrial wastewater treatment are inseparable issues since these industrial effluents constitute a major source of water contamination and are usually discharged into the environment in aqueous media.

The classical treatment processes of drinking water include treatment with ozone and filtration through granular activated carbon beds. Photocatalysis emerged as a promising tool for the treatment of water (and for the degradation of persistent substances even when they are present in low concentrations or complex matrices). So the advanced oxidation processes have been widely reported as an appropriate remediation methodology of all kinds of biorecalcitrants pollutants in water and industrial wastewater and their application to large-scale treatment facility is already being implemented, as discussed in section 4.

Typical examples of water pollutants that were efficiently mineralized by photocatalysis are effluents from industries containing dyes (Guillard et al., 2003), pesticides (Burrows et al., 2002; Marinas et al., 2001) and the effluents from the paper industry (Peiro et al., 2001). Various applications are also known for the decontamination of waste gases (Fu et al., 1996; Hay & Obee, 1999) including those involving self-cleaning surfaces (Hashimoto & Watanabe, 1999).

5.1 Industrial effluents containing dyes

The dyes are common industrial residues present in wastewaters of different industries, ordinarily in textile dyeing process, inks, and photographic industries, among others. The environmental aspects of the use of dyes, including their degradation mechanisms in various environment compartments, have been a target of increasingly interest. It is estimated that nearly 15% of world production of dyes is lost during synthesis and dyeing process. Concomitantly, the major problem related with dyes is the removal of their colour from effluents. The non treated effluents frequently are highly colored and then particularly susceptible to public objection when disposed in water bodies. The dye concentration in residual waters can be smaller than others contaminants, but because of its high molar absorption coefficients they are visible even in very low concentrations. So, methodologies of effluents discoloration became very relevant. The oxidation processes are very much used in treatment of dye containing effluents (Khataee & Kasiri, 2010; Oliveira et al., 2008, 2011; Rauf & Ashraf, 2009; Saggiaro et al., 2011; Soon & Hameed, 2011). Figure 10 presents a pilot unit commonly used on the degradation of dyes with thin film fixed bed (Guillard et al., 2003).

5.2 Effluents containing pesticides and pharmaceuticals

The photodegradation and mineralization of pesticides and pharmaceuticals has been widely studied because of the danger they represent to the environment and also due to the highly recalcitrant nature of some of these compounds. For a comprehensive review of pesticide degradation see Blake, 1999 or some of the reviews listed here (Atheba et al., 2009; Bae & Choi, 2003; Felsot et al., 2003). Either titanium photocatalysis or Fenton parent methodologies usually promote rapid destruction of persistent pesticides.

Municipal water recycling for industrial, agricultural, and non-potable municipal may contain several different pharmaceuticals including antibiotics, hormones and other endocrine disruptors, sulphonamides, antipyretics, etc. Those are present in municipal sewage, largely as a result of human use and/or excretion. Much of the concern regarding the presence of these substances in wastewater and their persistence through wastewater treatment processes is because they may contribute to directly or indirectly affect the environmental and human health (Exall, 2004; Vigneswaran & Sundaravadivel, 2004).

In spite of the variable removal of antibiotics during conventional waste water treatment processes, many of these chemicals are often observed in secondary treated effluents. Conventional water and wastewater treatment are inefficient for substantially removing many of these compounds. While there appears to be no standard treatment for removal of all residual pharmaceuticals under conventional treatment processes, there is a strong opinion that advanced oxidation processes can be used for the effective removal of these

compounds (Auriol et al., 2006; Dalrymple et al., 2007; Gueltekin & Ince, 2007; Homem & Santos, 2011; Khetan & Collins, 2007; Santos et al., 2009) . Research has show that advanced oxidative processes, which generate very active oxidative species such as the hydroxyl radicals, are promising tools for the destruction of pharmaceuticals compounds (Gültekin, et al., 2007; Le-Minh et al., 2010).

6. Conclusion

Advanced oxidation processes offer a consistent path to the treatment of recalcitrant substances that can not be treated by conventional effluents treatments. Either TiO₂ mediated photocatalysis or Fenton related methodologies offer feasible alternatives for the treatment of dyes, organochlorinated substances (pesticides, dioxines, furanes, PCBs, etc.) and pharmaceutical products, enabling the decomposition of such substances. Those methods, which are very attractive from the point of view of sustainable and green chemistry because they can use solar light as energy source, are being increasingly tested in several treatment plants (some of them pilot plans) with the help of solar collecting technology.

7. Acknowledgements

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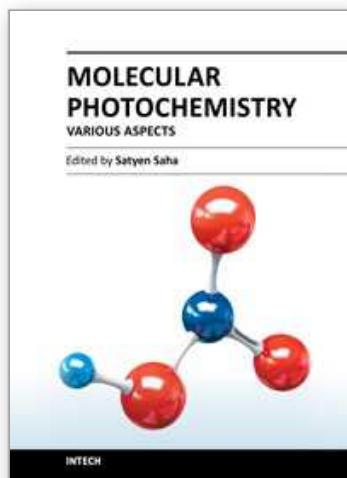
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There have been various comprehensive and stand-alone text books on the introduction to Molecular Photochemistry which provide crystal clear concepts on fundamental issues. This book entitled "Molecular Photochemistry - Various Aspects" presents various advanced topics that inherently utilizes those core concepts/techniques to various advanced fields of photochemistry and are generally not available. The purpose of publication of this book is actually an effort to bring many such important topics clubbed together. The goal of this book is to familiarize both research scholars and post graduate students with recent advancement in various fields related to Photochemistry. The book is broadly divided in five parts: the photochemistry I) in solution, II) of metal oxides, III) in biology, IV) the computational aspects and V) applications. Each part provides unique aspect of photochemistry. These exciting chapters clearly indicate that the future of photochemistry like in any other burgeoning field is more exciting than the past.

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