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Advanced Oxidation Processes (AOPs) for Removal of Pesticides from Aqueous Media

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1. Introduction

Advanced oxidation processes (AOPs) are technologies with significant importance in environmental restoration applications (Anipsitakis and Dionysiou, 2003; Bandala et al., 2007). The AOPs concept was established by Glaze et al., (Huang et al., 1993, Glaze, 1987; Glaze et al., 1987) who defined AOPs as processes involving the generation of highly reactive oxidizing species able to attack and degrade organic substances (Bolton, 2001). Nowaday AOPs are considered high efficiency physical-chemical processes due to their thermodynamic viability and capable to produce deep changes in the chemical structure of the contaminants (Domenech et al., 2004) via the participation of free radicals (Domenech et al., 2004). These species, mainly hydroxyl radicals ($HO^{\bullet}$), are of particular interest because their high oxidation capability (Andreozzi et al., 1999; Goswami and Blake, 1996; Huston and Pignatello, 1999; Legrini et al., 1993; Rajeshwar, 1996). However, other studies have suggested that, besides hydroxyl radicals, AOPs can also generate other oxidizing species (Anipsitakis and Dionysiou, 2003; 2004). Generated radicals are able to oxidize organic pollutants mainly by hydrogen abstraction (eq. 1) or by electrophylic addition to double bonds to generate organic free radicals ($R^{\bullet}$) which can react with oxygen molecules forming peroxyradicals and initiate oxidative degradation chain reactions that may lead to the complete mineralization of the organics, as proposed in eq. (1) (Blanco, 2003).

$$RH + HO^{\bullet}\left(or\ SO_4^{\bullet -}\right) \rightarrow HR^{\bullet} + H_2O \quad (1)$$

Free radicals in AOPs, may be produced by photochemical and non-photochemicals procedures. Table 1 list some of the most frequently reported AOPs for application in water restoration.

Among the different approaches for pollutants removal from water, some of them are recognized as mainly efficient for pesticide degradation. Ozonation and ozone related processes (O_3/H_2O_2, UV/O_3), heterogeneous photocatalysis (TiO_2/UV), homogeneous photocatalysis (Fenton and Fenton-like processes) and electrochemical oxidation are considered as the most efficient for pesticide degradation in water (Somich et al., 1990; Scott

Non-photochemical AOPs	Photochemical AOPs
Alkaline media ozonation	Fenton and Fenton-like reactions
O_3/H_2O_2	Heterogeneous photocatalysis
Fenton reaction	UV/H_2O_2
Electrochemical oxidation	UV/O_3
Hydrodynamic/ultrasonic cavitation	
Sub/super critical water	

Table 1. Frequently reported AOPs

and Ollis, 1995; Zepp et al., 1994; Legrini et al. 1993, Bandala et al., 2002a; Arancibia et al., 2002; Masten and Davies, 1994; Chiron et al., 2000; Ikehata and El-Din, 2005; Ikehata and El-Din, 2006, Bandala and Estrada, 2007, Martínez-Huitle et al., 2008). Several different successful laboratory scale applications have been reported for many of these methodologies (Malato et al., 2004; Blanco et al.,2007), however only few full scale development are currently reported, pendent task mostly depending on deep knowledge and analysis of current results and the generation of new approaches to the engineering of the processes (Malato et al., 1999; 2000).

2. Pesticide degradation using photocatalysis

2.1 Heterogeneous photocatalysis (HP)

Photocatalysis have been defined by Kisch (1989) as the acceleration of a photoreaction by a catalyzer. To take place, homogeneous photocatalysis require that the catalyzer (usually a semiconductor) absorbs an energy quantum. After energy absorption, the absorber specie (C) generates energy carriers (e^- and h^+) and excited electrons are transferred to the oxidant (Ox_1). At the same time, the catalyzer accepts electrons from the reducer (Red_2) which fill the holes generated in valence band of the semiconductor. Electron flux in both directions is null and the catalyzer remains unaltered as proposed in reaction sequence (2) (Malato, 1999):

$$\begin{aligned} &C \xrightarrow{hv} C\left(e^- + h^+\right) \\ &h^+ + Red_2 \rightarrow Ox_2 \\ &e^- + Ox_1 \rightarrow Red_1 \end{aligned} \tag{2}$$

The heterogeneous photocatalytic degradation concept involves the use of a solid semiconductor (i.e. TiO_2, ZnO, others) to generate a colloidal suspension stable under radiation for stimulate a reaction in the solid/liquid (or solid/gas) interface. When the semiconductor is in contact with a solution containing a redox pair, charge transference occurs along the interface to balance chemical potentials between the two faces. Metallic oxides and sulfurs are among the most used semiconductor materials available for photocatalytic purposes. Norwadays, titanium dioxide (TiO_2) is the most frequently used semiconductors for heterogeneous photocatalytic processes anytime it has demonstrated to be the most active (Blake, 2000; Blanco et al., 2007). Table 2 depicts some of the semiconductor materials used in photocatalytic reactions along with their band gap energy required for catalyzer activation and the maximal wavelength required for activation.

Degradation of organic pollutants by HP is among the most successful applications of the AOPs as suggested by the wide variety of research groups, installations, references and patents for use of this technology for removing toxic substances in water (Ajona and Vidal,

Material	Band gap energy (eV)	Activation wavelength (nm)
$BaTiO_3$	3.3	375
CdO	2.1	590
CdS	2.5	497
CdSe	1.7	730
Fe_2O_3	2.2	565
GaAs	1.4	887
GaP	2.3	540
SnO_2	3.9	318
$SrTiO_3$	3.4	365
TiO_2	3.2	387
WO_3	2.8	443
ZnO	3.2	390
ZnS	3.7	336

Table 2. Band gap energy and activation wavelength for some semiconductors (Malato, 1999).

2000; Blake, 2000; Bandala and Estrada, 2007). But, the use of heterogeneous photocatalysis for restoration of water contaminated with pesticides has been shown as one of the best fields for application of this technology. It is proposed as an ideal methodology because it can be used for low concentration effluents or complex multicomponent commercial suspensions. Its success application has being recognized by GEF as a promising innovative technology for the destruction and decontamination of Persistent Organic Pollutants (POPs) in developing countries (McDowall et al., 2004). The number of tested pesticides for heterogeneous photocatalytic degradations is wide. Among them, chlorinated, phosphorated, carbamic, thiocarbamic and triazine type pesticides are the most frequently reported. Table 3 shows an actualized reference collection of works published for pesticide degradation using TiO_2 mediated photocatalytic degradation in recent years. This Table shows the importance on the treatment of this type of pollutans, due to the extensive use.

Pesticide	References	Pesticide	References	Pesticide	References
Aldrin	Bandala et al., 2002; Ormad et al., 2010	DMMP	O´Shea,1997.	Permethrin	Chiaranzelli et al., 1995
Acrinatrin	Malato et al., 2000a; Malato et al., 2004	3,4-DPA	Pathirana,1997	Phorate	Chen et al., 1996: Hisanaga et al., 1990
Alachlor	Chiron et al., 1997; Moza et al.,1992;Muszkat et al., 1992, 1995; Wong and Chu, 2003a,b; Hincapié et al., 2005; Ormad et al., 2010; Farre et al., 2005	Endosulfan and derivatives	Ormad et al., 2010	Pyrimethanil	Oller et al., 2006
Aldicarb	Parreño et al., 1994.	Endrin	Ormad et al., 2010	Pirimiphos-methyl	Herrmann et al., 1999
Ametryn	Ormad et al., 2010	EPTC	Mogyoródi et al., 1993. Vidal et al., 1991	Procimidona	Hustert and Moza, 1997

Pesticide	References	Pesticide	References	Pesticide	References
Asulam	Tanaka et al., 1992.	Fenitrothion	Chiron et al., 1997, Tanaka et al., 1992; Herrmann,1999, Hasegawa,1998; Tapalov et al., 2003; Mahmoodi et al., 2008	Prometon	Borio et al., 1998;Herrmann, 1999c;Pelizzetti, 1990b, 1993; Ormad et al., 2010
Atrazine	Parra et al., 2004; Clestur et al., 1993; Lackhoff and Niessner, 2002; McMurray et al., 2006; Campanella and Vitalliano, 2006; Zhang et al., 2006; Bellobono,1995 Chiron et al., 2000; Herrmann,1999; Minero et al., 1996b;Muszkat etal.,1992,1995; Pelizzetti, 1987,1990a,1990b,1991,1992,1993. Sullivan et al., 1994; Texier,1999a, 1999b; Parra et al., 2004; Ormad et al., 2010; Farre et al., 2005	Fenobucarb	Hasegawa, 1998.	Prometryn	Muszkat et al., 1992, 1995; Pelizzetti, 1990b, 1993; Borio et al., 1998; Evgenidou et al., 2007; Ormad et al., 2010
Azinfphos-methyl	Domínguez,1998; Calza et al., 2008	Fenuron	Richard and Bengana, 1996.	Propachlor	Muszkat et al., 1995; Konstantinou et al., 2002; Muneer et al., 2005
Bendiocarb	Hasegawa, 1998.	Imidachloprid	Chiron et al., 1997; Texier et al., 1999a; 1999b; Agüera et al., 1998; Fernández et al., 1999; Sharma et al., 2009	Propanil	Sturini at al., 1997; Konstantinou et al., 2001
Carbaryl	Arancibia et al., 2002; Gelover et al., 2004	HCH and derivatives	Ormad et al., 2010	Propazine	Muszkat et al., 1992, 1995; Pelizzetti, 1992; Ormad et al., 2010
Carbetamid	Brun, 1995; Percherancier et al., 1995.	Heptachlor	Ormad et al., 2010	Propetryne	Herrmann, 1999
Chlorfenvinfos	Farre et al., 2005; Ormad et al., 2010	Iprobenfos	Hasegawa, 1998.	Propoxur	Lu et al., 1995, 1999
Chlorpyrifos	Ormad et al., 2010	Isoprothiolane	Hasegawa et al., 1998.	Propyzamide	Chiarenzelli et al., 1995; Hasegawa, 1998; Torimoto et al., 1996.

Pesticide	References	Pesticide	References	Pesticide	References
Carbofuran	Kuo and Lin, 2000; Mahalakshmi et al., 2006; Mansour, 1997; Tennakone, 1997	Isoproturon	Amorisco et al., 2005. Mansour, 1997; Farre et al., 2005; Sharma et al., 2008a,b,c,d; 2009; Ormad et al., 2010; Haque and Muneer, 2003	Simazine	Hasegawa, 1998.;Pelizzetti et al., 1990b;1992;1993; Ormad et al., 2010
Cyanobenzoate	Muszkat et al., 1995	Lindane	Chiron et al., 1997; Herrmann, 1999c; Sabin , 1992; Guillard et al., 1995; Vidal, 1998; Zaleska et al., 2000.	2,4,5-T	Barbeni et al., 1987; Chiron et al., 1997; Ollis et al., 1991a; Pelizzetti, 1993; Kamble et al., 2006
Cycloate	Vidal et al., 1999; Mogyoródi et al., 1993; Vidal, 1991	Malathion	Muszkat et al., 1995; Mak and Huang, 1992; 1993; Doong and Chang 1997	2,3,6-TBA	Bianco-Prevot et al., 1999
Chloroxynil	Muszkat et al., 1992	Manuron	Herrmann et al., 1999	Terbutylazina	Mansour et al., 1997
Chlorpyriphos	Picaht et al., 2007;Chiarenzelli et al., 1995.	MCC	Tanaka et al., 1999	Terbutryn	Muszkat et al., 1992; Ormad et al., 2010
Chlorsulfuron	Fresno et al., 2005; Maurino et al., 1999	Metamidophos	Doong and Chang, 1997; Hisanaga et al., 1990; Malato et al., 1999	Tetrachlorophenol	Pelizzetti, 1985
2,4-D	Terashima et al., 2006: Sanjay et al., 2004; Singh and Muneer, 2004; Chiron et al., 1997; 2000; D´Oliveira,1993a; Herrmann et al., 1998;1999; Lu et al., 1995,1997; Martin et al., 1995; Müller, 1998;Pichat et al.,1993a;1993b; Trillas et al., 1995;Sun and Pignatello, 1995; Kamble et al., 2006	Metamitron	Mansour ,1997.	Tetrachlorvinphos	Herrmann,1999; Kerzhentsev et al., 1996
DBS	Domínguez et al., 1998;	Metolachlor	Sakkas et al., 2004; Chiron et al., 1997; Ormad et al., 2010	Tetradifon	Chiron et al., 1997; Ormad et al., 2010
DCB	Muszkat et al., 1992.	Metobromuron	Amine et al., 2005; Muszkat et al., 1992.	Thiram	Hasegawa, 1998.
DDT and DDT derivatives	Borello et al., 1989; Chiron et al., 1997; Herrmann,1999c; Pelizzetti, 1985; 1993;Sabin, 1992; Zaleska et al., 2000; Ormad et al., 2010	Methoxychlor	Ormad et al., 2010	Tifensulfuron-methyl	Maurino et al., 1999.

Pesticide	References	Pesticide	References	Pesticide	References
DEMP	O´Shea, 1997a	MIPC	Tanaka et al., 1999	Thiobencarb	Nishida and Ohgaki, 1994.
DEP	Tanaka et al., 1992; Hisanaga et al., 1990; Muneer et al., 1998.	MMPU	Muszkat et al., 1992.	Thiocarbaryl	Nishida and Ohgaki, 1994.
Diazinon	Sakkai et al., 2005; Mahmoodi et al., 2007;Doong and Chang, 1997;Hasegawa, 1998.; Mak,1992; Mansour,1997; Kouloumbos et al., 2003;	Molinate	Mogyoródi et al, 1993; Konstantinou et al., 2001; Ormad et al., 2010;	Triadimefon	Chiarenzelli et al., 1995.
Dichloran	Chiarenzelli et al., 1995.	Monocrotophos	Shankar et al., 2004;Chen et al., 1996	Trifluralin	Ormad et al., 2010
Dichloroaniline	Muszkat et al., 1995.	Monuron	Augliaro, 1993; Pramauro et al., 1993	Trichlorophenol	Barbeni et al., 1986;D´Oliveira et al., 1993; Jardim et al., 1997; Ollis et al., 1991a; Pelizzetti, 1985; 1993; Tseng and Huang, 1991; Tanaka et al., 1992
Dichlorophenol	Bhatkhade et al., 2004; Kim and Choi, 2005; Boyarri et al., 2005; Texier et al., 1999a,b;Jardim et al., 1997; Manilal, 1992	MPMC	Tanaka et al., 1999.	Trichlopyr	Poulius, 1998; Qamar et al., 2006
Dichloropyridine	Kyriacou et al., 1997	MTMC	Tanaka , 1999.	Trietazine	Muszkat et al., 1992, 1995
Dichlorvos	Hasegawa et al., 1998; Chen et al., 1996; Chen, 1997; Lu, 1993, 1995; Mak et al., 1992, Mak and Hung, 1993; Hisanaga et al., 1990; Evgenidou et al., 2005;2006; Oancea and Oncescu, 2008	Oxamil	Texier 1999a.; Malato et al., 2000b; Oller et al., 2006	Vernolate	Mogyoródi et al., 1993; Vidal, 1991.
Dicofol	Chiron et al., 1997; Ormad et al., 2010	Paraquat	Florencio et al., 2004;Moctezuma, 1999.	Vinclozoline	Hustert and Moza, 1997.
Dieldrin	Ormad et al., 2010	Parathion	Zoh et al., 2005, 2006;Chen et al., 1996; Chiron et al.,1997; Herrmann, 1999; Sakkas et al., 2002	Pendimetalin	Mansour, 1997; Moza et al., 1992
Diquat	Florencio et al., 2004; Kinkennon et al., 1995.	Paration-metil	Sakellarides et al., 2004; Zoh et al., 2005,2006;Chiron et	XMC	Tanaka et al. , 1999

Pesticide	References	Pesticide	References	Pesticide	References
			al., 1997, 2000; Evgenidou et al., 2007b; Ormad et al., 2010		
Dimethoate	Oller et al., 2006;Domínguez et al., 1998;Evgenidou et al., 2006; Oller et al., 2006; Ormad et al., 2010	PCDD	Barbeni et al., 1986; Pelizzetti, 1985		
Diuron	Canle et al., 2005; Kinkennon et al.,1995;Muneer et al., 1998; Farre et al., 2005;Katsumata et al., 2009;Macounova et al., 2003;Ormad et al., 2010	PCDF	Barbeni et al., 1986; Pelizzetti, 1985.		

Table 3. References on heterogeneous photocatalytic degradation of pesticides in water using TiO_2.

2.2 Kinetics and reaction mechanisms

For an extended period of time different works analyzing heterogeneous photocatalysis mechanisms have proposed hypotheses on the generation of photoproduced holes (h^+) and surface trapped hydroxyl radicals ($HO^\bullet$) (Romero et al., 1999). Initial steps involved in band-gap irradiation of TiO_2 particles (or any other semiconductor) have been studied in detail by lasser-flash photolysis measurements (Bahnemann et al., 1997; Serpone, 1996). It is well stablished that TiO_2 illumination with radiation of the proper wavelength ($\geq E_g$) generates electron/hole pair which can recombine or dissociate (both reactions are in competition) to produce, in the latter case, a conduction band electron and a valence band hole which are able to migrate to the particle surface. Once in the surface, both charge carriers will be able to interacting with adsorbed electron acceptors and oxidize electron donors. In the heterogenous process in aqueous face, oxygen is often present as electron acceptor and HO^- and H_2O are available as electron donors to yield hydroxyl radicals. It is well documented that these trapping reactions occurs in less than 30 ps (Colombo et al., 1995; Skinner et al., 1995; Serpone et al., 1995).

Considering the importance of mass transference in the process, initial practical approaches to quantitative description of HP kinetics has been commonly carried out using a Langmuir-Hinshelwood (L-H) kinetics model (Al-Ekabi et al., 1988, 1989). This mathematical model assumes that the reaction occurs on the catalyst surface. According to L-H model, the reaction rate (r) is proportional to the fraction of particle surface covered by the pollutant (θ_x). Mathematically,

$$r=-\frac{dC}{dt}=k_r\theta_x=\frac{k_rKC}{1+KC+K_sC_s} \quad (3)$$

where k_r is the reaction rate constant, K is the pollutant adsorption constant, C is the pollutant concentration at any time, K_s is the solvent adsorption constant and C_s is its concentration. During eighties, many authors presented their data using L-H kinetic approach (Chen et al., 1983; Herrmann et al., 1983; Matthews, 1988; Nguyen and Ollis, 1984; Ollis, 1984; Pruden and Ollis, 1983). Nevertheless, despite L-H approach fits properly experimental data, it does not consider the interaction of the radiation field (Bandala et al., 2004; Arancibia et al., 2002).

Other kinetic studies on heterogeneous photocatalysis suggest that reaction rate increases with catalyst concentration to get a maximum value for catalyst concentration between 0.2 and 1 g/L, depending on the compound and the reactor used. Over these concentrations, reaction rate remains unaffected or decreases when catalyst concentration increases (Jimenez et al., 2000; Arancibia et al., 2002; Curco et al., 1996; Gimenez et al., 1999). An interesting problem is the relation between catalyst concentration, reaction rate, radiation absorption and process improvement, because, several studies have suggested important associations depending on the catalyst radiation absorbed (Schiavello et al., 1999; Brandi et al., 1999, Arancibia et al., 2002; Bandala et al., 2004). From these results, several models, most of them based on complex mathematical or static computational approaches, have been developed and proposed in order to predict radiation absorption and scattering as function of catalyst concentration, optical path and catalyst type and its relation to pseudokinetic constants experimentally obtained (Bandala et al., 2004; Arancibia et al., 2002; Curco et al., 2002). Based on the radiation absorbed by the catalyst, some authors, as Cassano's group considered the most representative in the field, have considered that the vital point in this process resides on the *a priori* design of photochemical reactors, that improve of HP reactions and the generation of intrinsic reaction kinetic that may lead to process scaling-up (Alfano et al., 2000; Cassano and Alfano, 2000; Romero et al., 1999; Brandi et al., 2000).

Besides reactor design, heterogeneous photocatalytic degradation reaction can be enhanced by the use of higher active catalyst or inorganic oxidizing species. In the first case, activation of TiO_2 under visible light is a desirable technological approach. In order to utilize visible light for TiO_2 excitation, several dye-synthesized and ion-doped TiO_2 have been developed achieving higher performances in their use for photocatalyzed degradation of different organic substrates (Bae and Choi, 2003; Lin et al., 2006; Xu et al., 2002; Iwasaki et al., 2000; Asah et al., 2001; Irie et al., 2003; Burda et al., 2003) using the band gap narrowing effect produced. However, only few recent reports deals with application of visible light activated TiO_2 to photoassisted pesticide degradation (Senthilnathan and Philip, 2010; Sojicetal, 2010).

2.3 Effect of oxidizing species on the reaction rate

According to reaction sequence 2, production of charge carriers is a fundamental step in degradation processes using HP. Once generated, these species may lead to hydroxyl radicals generation (and the subsequent organic matter degradation) or can recombine to generate the initial state and energy emission. This latter reaction, known as recombination, is a practical problem when using TiO_2 catalyst and it is extremely efficient (reaction rate = 10^{-9} s) when no proper electron acceptor is present in the reaction media (Malato et al., 1998; Hoffman et al., 1995). This side process is energy-wasting and limiting to get high quantum yield (i.e. number of primary chemical reactions per photon absorbed). In most of the cases, dissolved oxygen is used as electron scavenger in these processes and several works have dealed on its efficiency as oxidant agent to complete organic matter mineralization (Li Puma et al., 1993; Martin et al., 1995; Mills et al., 1993; Ollis et al., 1991; Pelizzetti and Minero, 1993). Nevertheless, it has been demonstrated that only low mineralization is reached when dissolved oxygen is used as oxidant agent in, for example, the photoassisted degradation of pesticides (Mills and Morris, 1993; Serra et al., 1994; Minero et al., 1996). Several previous studies have investigated the role of alternative electron acceptors such as peroxide compounds (Wang and Hong., 1999; Wong and Chu, 2003; Dionysiou et al., 2004). Among them, hydrogen peroxide has been identified as widely used to improve photocatalytic processes. This simple peroxide is considered as environmentally friendly and of great interest for "green" chemistry and engineering applications (Ghosh et al., 2001). Hydrogen peroxide has been applied to enhance the rates of TiO_2 photocatalytic reactions (Madden et al., 1997; Pacheco et al., 1993; Malato et al., 1998; Wang and Hong, 1999; Doong and Chang, 1997; Wong and Chu, 2003) using UV radiation (Mengyue et al., 1995; Haarstrick et al., 1996; Pacheco et al., 1993; Malato et al., 1998). The improvement of photocatalytic rates using H_2O_2 has been attributed to many factors, mainly: hydrogen peroxide is better electro acceptor than oxygen (Ollis et al., 1991; Madden et al., 1997; Malato et al., 1998; Peterson et al., 1991; Cornish et al., 2000; Ohno et al., 2001), its potential for reduction is 0.72 V while this value for oxygen reduction is – 0.13 V (Cornish et al., 2000), it is considered able to favor photocatalytic mechanisms by the removal of photogenerated electrons in the conduction band (Dionysios et al., 2004). Nevertheless it has been well documented that, at high concentrations of H_2O_2, it can compete for adsorption with organic matter (Dionysios et al., 2004; Bandala et al., 2002; Sauer et al., 2002; Cornish et al., 2000). Besides hydrogen peroxide, other oxidant agents have been tested for improve photocatalytic reactions (Martin et al., 1995; Pelizzetti et al., 1991; Al-Ekabi et al., 1992; Kenneke et al., 1993). For example, peroxidisulphate ($S_2O_8^{2-}$) has been indicated as an important oxidant, allowing drastical improvements in the TiO_2 photocatalyzed mineralization of pesticides and pesticide mixtures by Malato et al. (1998; 1999; 2000) and they think its use is justified when pesticide mineralization is the major concern.

2.4 Material science implications: slurries or immobilized photocatalyst

Generation of catalyst sludges is among main disadvantages for HP processes in water treatment. This kind of treatment, currently available at pilot-plant level, uses suspended TiO_2 in photoreactors where the semiconductor is recovered after the treatment (Malato et al., 2000; 2002). According to various lab scale research reports (Bideau et al., 1995; Matthews and McEvoy, 1992; Sabate et al., 1992; Chester et al., 1993), the use of TiO_2 in suspensions is more efficient than on its immobilized form. Nevertheless, this latter form posses specific advantages, such as cost reductions, material losses decrease and skipping recovery steps in the process, which make desirable the generation of immobilized titania photocatalyst with higher efficiency as compared with those reported to date (Balasubramanian et al., 2004; Gelover et al., 2004).

Several supporting materials, from sand to quartz optical fiber, have been reported so far for TiO_2 immobilization. In the same way, a wide number of methods for catalyst fixation as reviewed by Pozzo et al., (1997). In last years, the use of *in situ* catalyst generation method seems to be the most promising technology for catalyst immobilization (Rachel et al., 20002; Guillard et al., 2002; Gelover et al., 2004). Other authors (Guillard et al., 2003; Gelover et al., 2004) has demonstrated that, by the use of these *in situ* catalyst generation method, fixed form of titanium dioxide generated present equal efficiency as Degussa P-25 (considered as the most efficient form of titanium dioxide) suspended catalyst for pesticide degradation. However, more scientific research is necessary about the development of this promising idea before it can be considered for future design of efficient photocatalytic plants.

2.5 Homogeneous photocatalysis

Homogeneous photocatalysis refers to those photocatalytic processes in which the catalyst is dissolved in water during the redox process. In general, homogeneous processes can be represented as depicted in reaction sequence (4) (Domenech et al., 2004):

$$\begin{aligned} & C \xrightarrow{h\nu} C^* \\ & C^* + R \rightarrow R^* + C \\ & R^* \rightarrow P \end{aligned} \tag{4}$$

Similarly to heterogeneous photocatalysis, homogeneous processes are based in the generation of hydroxyl radicals but, in difference, some other highly oxidant species can be generated and be responsible of organic contaminant degradation (Anipsitakis and Dionysiou, 2004; Yamazaki and Piette, 1991; Sawyer et al., 1996). Since the well known Fenton's experiments in the latest XIX century, it is documented that hydrogen peroxide/ferrous salts solutions are capable to oxidize organic compounds (Fenton, 1894). Fenton reagent has been reported of high efficiency degrading aliphatic hydrocarbons, halogenated aromatics, polychlorinated byphenils, nitroaromatics, azo-dyes and pesticides (Bigda, 1995) as shown in Table 4.

3. Fenton-like reactions

Besides Fenton reaction, several Fenton-based procedures have been developed, being these reactions, inspired on the Fenton reaction chemistry (so-called Fenton-like processes). It has been demonstrated that, in many of the cases, Fenton-like processes are more efficient than Fenton reaction to water treatment and will, probably, be the next step in the scaling-up of AOPs application to pesticide treatment in water.

When Fenton reaction involves ultraviolet radiation, visible light or both, the reaction is known as the photo-Fenton process. Compared with dark Fenton reaction, photo-Fenton process has numerous advantages such as the increase of degradation rate, minimize in sludge generation and the use of solar energy, among others (Malato et al., 2002; De Laat and Le Troung, 2006; Chacón et al., 2006, Orozco et al., 2008). Photo-Fenton process is among the most efficient methods to generate hydroxyl radicals (Bauer et al., 1999). Even higher than other very well studied and widely applied AOPs such as TiO_2/UV and H_2O_2/UV as shown in comparative studies using 4-chlorophenol as model wastewater contaminant (Krutzler and Bauer, 1999). Many parameters, such as initial concentration of ferric salt and hydrogen peroxide, the ratio of $[H_2O_2]_0/[Fe(II)]_0$, pH, light intensity and temperature influence on the efficiency of photo-Fenton process (Bandala et al., 2007; Lee and Yoon, 2004) are determinants in the efficiency.

Except for Fenton reagent, the potential of generating highly reactive radical species using transition metals coupled with electron acceptors have not been explored completely for water treatment (Anipsitakis and Dionysiou, 2004). Recently, Anipsitakis and Dionysiou (2004) have carried out experiments in order to identify radical generation by the interaction of transition metals with common oxidants. They tested 14 different combinations of metals and oxidant and found that cobalt (II)/potassium peroximonosulfate (Co/PMS) system posses very attractive characteristics for water decontamination (Anipsitakis and Dionysiou, 2004). This homogeneous system have been shown to be able for generate sulfate radicals and demonstrate greater efficiencies when compared with Fenton reagent for the treatment of water containing organic pollutants (Anipsitakis and Dionysiou, 2004).

Pesticide	References	Pesticide	References	Pesticide	References
Abamectin	Fallaman et al., 1999			Metoxichlor	Houston and Pignatello, 1999; Pignatello and Sun, 1995
Acephate	Yu, 2002	Dichlorophenol	Wadley and Waite, 2002; Aaron and Oturan, 2001; Detomaso et al., 2003; Momani et al., 2006; Momani, 2006; Bayarri et al., 2007	Metolachlor	Malato et al., 2002, 2003
Acrinatrin	Fallaman et al., 1999	Dimethoate	Nikolaki et al., 2005; Oller et al., 2005	Metomyl	Wang et al., 2004; Scherer et al., 2004; Muszkat et al., 2002
Alachlor	Houston and Pignatello, 1999; Laperlot et al., 2006; Farre et al., 2007,2005; Wang and Lemley, 2001; Hincapie et al., 2005; Perez et al., 2006	Diuron	Malato et al., 2002; Lapertot et al., 2006; Farre et al., 2007; Hincapié et al., 2005; Perez et al., 2006; Farre et al., 2005; Malato et al., 2003; Edelahi et al., 2004	Metribuzin	Yu, 2002
Aldicarb	Houston and Pignatello, 1999	DMDT	Barbusinski and Filipek, 2001	Metamidophos	Fallaman et al., 1999
Atrazine	Bandala et al., 2007; Houston and Pignatello, 1999; Sun and Pignatello, 1993; Laperlot et al., 2006; Wang et al., 2003; Farre et al., 2007; Ostra et al., 2007; Pignatello, 1993; Arnold et al., 1995; Adams et al., 1990; Ijpelaar et al., 2000; Hincapie et al., 2005; Perez et al., 2006; Farre et al., 2005	3,4-DPA	Saltmiras and Lemley, 2000	Parathion-ethyl	Oturan, 2003
Azinphos-methyl	Houston and Pignatello, 1999	Ethylene thiourea	Fallaman et al., 1999	Paration-methyl	Pignatello and Sun, 1995; Roe and Lemley, 1997; Gutierrez et al., 2007
Bromacil	Muszkat et al., 2002	Endosulfan	Yu, 2002	Pentachlorophenol	Farre et al., 2007
Carbaryl	Kong and Lemley, 2006; Wang et al., 2003	Edifenphos	Barbusinski and Filipek, 2001; Yu, 2002; Badaway et al., 2006	Pyrimethanil	Fallaman et al., 1999

Carptan	Houston and Pignatello, 1999	Fenitrothion	Fallaman et al., 1999; Malato et al., 2002; Malato et al., 2003	Pichloram	Houston and Pignatello, 1999
Carbofuran	Houston and Pignatello, 1999; Wang et al., 2003	Formetanate	Houston and Pignatello, 1999	Profenophos	Badawy et al., 2006
Chlorfenvinphos	Farre et al., 2005; Hincapié et al., 2005; Lapertot et al., 2006; Barbusinski and Filipec, 2001	Glyphosate	Barbusinski and Filipek, 2001	Propamocarb	Fallaman et al., 1999
Chlorophenol	Krutzler et al., 1999; Detomaso et al., 2003	HCH	Yu, 2002	Simazine	Houston and Pignatello, 1999; Adams et al., 1990
Chlorotalonil	Gutierrez et al., 2007	Fenthion	Fallaman et al., 1999; Malato et al., 2002; Malato et al., 2003	2,4,5-T	Pignatello, 1993; Aarón and Oturan, 2001; Pignatello, 1992; Sun and Pignatello, 1993
Chlorpyriphos	Yu, 2002	Imidachloprid	Lapertot et al., 2006; Farre et al., 2007; Hincapie et al., 2005; Farre et al., 2005	Tebuconazole	Faxeira et al., 2005
4-chloro-phenoxia-cetic acid	Sedlak et al., 1992	Isoproturon	Fallman et al., 1999	Tamaron	Faxeira et al., 2005
2,4-D	Oturan et al., 1999; Pignatello, 1992; Sun and Pignatello, 1993; Bandala et al., 2007; Sun and Pignatello, 1992; Sun and Pignatello 1993a,b; Wang et al., 2003; Wang and Lemley, 2001; Aaron and Oturan, 2001; Kong and Lemley, 2006	Luteron	Roe and Lemley, 1997; Oturan, 2003; Houston and Pignatello, 1999	Treflan MTF	Saltmiras and Lemley, 2001
Dicamba	Houston and Pignatello, 1999	Malathion	Houston and Pignatello, 1999	Terbutryn	Adams et al., 1990
Disulfoton	Houston and Pignatello, 1999	MCPP	Aaron and Oturan, 2001	Tetraethyl pyrophosphate	Oturan, 2003
DDT	Barbusinsky and Filipek, 2001; Bousahel et al., 2007	Metamidophos	Gutierrez et al., 2007; Yu, 2002; Fallaman et al., 1999; Faxeira et al., 2005	Trichlorophenol	Aaron and Oturan, 2001
Diazinon	Wang et al., 2003; Badaway et al., 2006; Yu, 2002			Trifluralin	Wang et al., 2003

Table 4. References on homogeneous photocatalytic degradation of pesticides in water

3.1 Effect of metal counterion

An interesting effect that should be take account when applying homogeneous photocatalysis is salt counterion. Inorganic anions (Cl^- , SO_4^{2-} , HPO_4^{2-})in wastewater or added as reagents have a significant effect on the reaction rate in the case of Fenton process. These effects are a) complexation with Fe(II) or Fe(III), affecting iron species reactivity and distribution; b) Precipitation reactions leading to a decrease of the active dissolved Fe(III); c) Scavenging of hydroxyl radicals and d) oxidation reactions involving these inorganic radicals. It have been well documented that cloride ions shows inhibitory effect for oxidation reactions, using both Fe(II) and Fe(III), of phenols (Tang and Huang, 1996), dichlorvos (Lu et al., 1997), atrazine (De Laat et al., 2004) and azo-dyes (Orozco et al., 2008). On the other hand, the effect of inorganic salt counterion in cobalt-mediated Fenton-like processes is not completely clear. It has been shown that precence of chloride ions produce highly chlorinated intermediates during oxidation process probably due to chloride radicals generation (Anipsitakis et al., 2006). The presence of sulfate or nitrate ions did not show any effect on reaction rate. The effect of organic counterion for cobalt salts can be related with the availability to cobalt (II) re-generation during oxidation processes and enhancing of reaction rate by radiation. Currently, we are testing the effect of several organic cobalt salts in the degradation rate of the herbidice 2,4-D and observed that the counterion effect is very important on the global reaction rate.

4. Radiation source

In homogeneous and heterogeneous photocatalysis, radiation is identified as a very important supply to the overall process. Two main radiation sources have been used to promote these processes: artificial radiation and solar radiation. The use of artificial radiation (generally a high pressure mercury or xenon arc lamp) sources has been widely applied for pesticide degradation by mean of different photochemical processes, among them homogeneous or heterogeneous photocatalysis (Chiron et al., 2000). In recent years, application of photocatalytic processes using solar radiation has increased as a cost-effective alternative for these technologies. It is interesting note that, actual industrial/commercial applications developed recently are related to solar enhanced processes (Blanco and Malato, 2003).

Different to solar thermal processes, where large amounts of radiation of any wavelength is collected, in solar photocatalytic processes only high-energy radiation is able to be used to promote photochemical reactions (i.e. $\lambda<600$ nm). This selective wavelength range produce that only very specific solar collection geometries can be useful to be applied for solar driven photocatalytic reactions. Several different solar collector geometries have been tested for application to solar photocatalytic processes (both, homogeneous and heterogeneous) and a wide number of works dealing with the comparison between all these experimental results have been reported (Bandala and Estrada, 2007). From all these information, the actual consense is that low concentration collectors seems to be the best technological option instead of earlier high concentration designs (Blanco et al., 2007; Bandala and Estrada, 2007). In particular, compound parabolic concentrators (CPCs) have been identified as very promising technological approach to industrial application of solar photocatalysis. CPCs combine the characteristics and advantages of high range concentrators and static flat systems. Among their main advantages are use of global solar radiation, absence of tracking systems, low evaporation of volatile compounds, low cost and high optical and quantum efficiencies conditions. Some authors have reported the comparison some solar collection geometries and found that V trough concentator is able to perform solar photocatalytic processes in practically equivalent conditions than widely reported CPCs (Bandala and Estrada, 2007). This solar collection geometry have not being tested enough for solar chemistry applications but, as far as we can see, could be an interesting alternative anytime the actual solar collection geometry design is simpler than CPCs, optical and quantum yields are similar and cost could be considerably lower.

5. Coupled advanced technologies for pesticide degradation

Despite AOPs are cost effective processes for water and mainly wastewater treatment, one of their main problems is their cost when compared with other conventional treatment processes such as biological treatment (Sarria et al., 2003). The treatment of water containing non-biodegradable toxic organic compounds is an environmentally complex issue in several industries such as pulp and paper, textile and petroleum industries. Considering the toxic nature of pesticides, it is clear that these kinds of xenobiotics are, in many cases, low biodegradable and, in most cases, highly refractory organic compounds. Due to this reasons, coupling AOPs and biological processes should be a good alternative to minimize the costs of treatment of water or wastewater containing this kind of pollutants. The strategy of combining chemical and biological processes to degrade contaminants in water has been proposed since middle of 90's (Scott and Ollis, 1995; 1997). Since then several works on the biological treatment of wastewater deal with the combined operation of chemical and biological oxidations (Scott and Ollis; 1995; Beltran et al; 1997; Benitez et al., 2001). Felsot *et al.* (2003), among other authors, have suggested that the combination of physical or chemical methods with biological treatment is likely a feasible option for the treatment of pesticide wastewater. In all these works is demonstrated the beneficial use of chemical oxidation process as a pretreatment or post-treatment of a biological process (Beltran, 2004, Lapertot et al., 2007).

Usually, when coupling chemical and biological processes the aim of the chemical oxidation is not to mineralize the organic contaminants but produce the conversion of high toxic, refractory parent components into biodegradable intermediates capable to be completely removed by biological processes (Esplugas et al., 2004). The possibility of minimal use of the oxidant agent, usually the most expensive component of the chemical process, followed by a low cost biological process (i.e. activated sludge, biofilm reactors) can help to improve the cost efficiency of a high effective process.

The effectivity of the coupled process is usually recorded using time evolution of coarse concentration variables such as total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD) or some of their relationships (Esplugas et al., 2004; Sarria 2003; Pulgarin et al., 1999).

Relatively few works on the application of this kind of coupled methodologies are available in literature. Most of them corresponds to ozonation processes (Marco et al., 1997; Helble et al., 1999; Yeber et al., 1999; Beltran et al., 1999; Benitez et al., 2001; Ledakowicz et al., 2001), H_2O_2/UV (Adams and Kuzhikanni, 2000; Ledakowicz et al., 2001), TiO_2/UV oxidation (Li and Zhang, 1996; Li and Zhao, 1997; Chum and Yizgohon, 1999; Hess et al., 1998; Parra et al., 2002), Fenton and Fenton-like (Pulgarin et al., 1999; Chamarro et al., 2001; Sarria et al., 2003; Rodriguez et al., 2002; Sarria et al., 2001; Sarria et al., 2002) and wet oxidation (Donlagic and Levec, 1998). Table 5 shows some examples of physical-chemical/biological processes, including the treated pesticide, both process and the correspondent reference.

Pesticide(s)	Biological process	Physical-chemical process	References
EPTC, molinate, propazine, atrazine, simazine, prometryn, ametryn, simetryn, pyrazon, tris MEA,	Attached biomass (biofilter)	ozonation	Mezzanote *et al.* (2005)
Tetraconazole, metribuzin	suspended cells	anodic Fenton	Scherer *et al.* (2004)
Atrazine	biomineralization	ozonation	Scherer et al. (2004).
Atrazine/sotriazine	microorganisms	chemical	Scherer et al. (2004).
Atrazine	*Klebsiella terragena* DRS-1	ozone	Ikehata and El-Din, 2005.
Eyanazine, atrazine, metachlor and paraquat	microorganisms	ozone	Ikehata and El-Din, (2005)
Simazine	various microorganisms	oxzone, UV, photolisis or O_3/UV	Ikehata and El-Din, (2005)
Eyanuric acid, amino-S-triazines, chloro-amino-strazines, chloroethyl-S-triazines	microbial culture	ozone	Ikehata and El-Din, (2005).

Table 5. Some examples of coupled biological-physical-chemical process reported in literature

It is clear that pesticide removal from water should be one of the main applications of this coupled methodology. Nevertheless few reports are available in literature dealing with the use of this approach to pesticide remotion (Parra et al., 2000; 2002; Sarria et al., 2002; Lapertot et al., 2007; Al-Momani et al., 2006; Contreras et al., 2003). They had found that most of the tested pesticide effluents, readily determined as non-biodegradable by the Zahn-Wellens test, increased in their biodegradability once the photoassisted process was applied. The actual behavior of toxicity of isoproturon effluent, for example, showed an increase in this parameter during the first reaction minutes followed of sharp decrease. Authors suggest (Parra et al., 2000) that this behavior could be due to formation of intermediate compounds with higher toxicity than the parent pesticide and its further oxidation. For some other cases, effluent biodegradability was not completely reached after photoassisted process. For example, in the case of metobromuron the BOD/COD ratio went from 0.0 (stated as completely non-biodegradable) to 0.1, too low if compared with the BOD/COD ratio considered for municipal biodegradable wastewater, 0.4 (Parra et al., 2000).
As another example, Table 5 shows the partial contribution of the pre- and post treatment using ozone, over the entire coupled ozonation-biological process applied to in streams containing different pesticides, at different concentrations. As observed, preozonation of the stream can be very advantageous for the coupled process, contributing with a 56-98% of the overall pesticide removal. Biological process can contribute (in this specific case) with 1.8-41% of the removal, and finally, post-ozonation process can polish the stream, with additional removals of 0-3%.

6. Pesticide degradation by advanced electrochemical oxidation processes

6.1 General aspects

In the last years, there has been great interest in the development of effective methods of pollutans removal from aqueous solutions based on direct and indirect electrochemical techniques. The most useful direct electrochemical method is anodic oxidation (Kaba et al., 1990; Kotz et al., 1991; Stucki et al., 1991; Comninellis and Pulgarin, 1991, 1993; Murphy et al., 1992; Comninellis and Nerini, 1995; Feng et al., 1995; Johnson et al., 1999; Gandini et al., 2000; Rodrigo et al., 2001; Rodgers and Bunce, 2001; Wu and Zhou, 2001) where organic compounds are essentially degraded by reaction with adsorbed hydroxyl radicals at the anode surface, which are generated from water oxidation:

$$H_2O \rightarrow \bullet OH_{ads} + H^+ + e^- \quad (5)$$

Since the participation of $\bullet OH_{ads}$ radicals in the reaction is the key factor to degrade the pollutan, then the generation efficiency of them should be tightly related to the nature of the anodic material. Thus, although the traditional Pt anodes has been used for this purpose (Kaba et al., 1990; Kotz et al., 1991; Stucki et al., 1991; Comninellis and Pulgarin, 1991, 1993; Murphy et al., 1992; Comninellis and Nerini, 1995), it are less efficient that the oxide-base electrodes such as PbO_2 (Kaba et al., 1990; Feng et al., 1995; Wu and Zhou, 2001), doped PbO_2 (Feng et al., 1995), doped SnO_2 (Kotz et al., 1991; Stucki et al., 1991; Comninellis and Pulgarin, 1991, 1993; Johnson et al., 1999), IrO_2 (Comninellis and Nerini, 1995; Rodgers and Bunce, 2001) or more recently to the boron-doped diamond thin-layer anode, BDD (Gandini et al., 2000; Rodrigo et al., 2001).

On the other hand, the indirect electrochemical methods involves the previous formation of oxidizing agents such as H_2O_2 (Hsiao and Nobe, 1993; Do 1993, 1994; Ponce de Leon and Pletcher, 1995; Brilla et al., 1996; Brillas et al., 1998; Alvarez-Gallegos and Pletcher, 1999; Harrington and Pletcher, 1999; Oturan et al., 1999; Brillas et al., 2000; Oturan et al., 2000, Oturan, 2000; Oturan et al., 2001):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (6)$$

or the well known Fenton's reagent (H_2O_2/Fe^{2+}) (Hsiao and Nobe, 1993; Do 1993, 1994; Ponce de Leon and Pletcher, 1995; Alvarez-Gallegos and Pletcher, 1999; Oturan et al., 1999; Oturan et al., 2000, Oturan, 2000; Oturan et al., 2001):

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + \cdot OH \quad (7)$$

The combination of chemical and electrochemical procedures has also been reported as a good alternative to water treatment. The electro-Fenton and photoelectro-Fenton methods can be considered as advanced electrochemical oxidation processes, AEOPs (Brilla et al., 1996; Brillas et al., 1998; Brillas et al., 2000; Boye, et al., 2002).

6.2 Mechanism of the electrochemical pollutan oxidation

Principal advantages of the electrooxidation method are the case of operations, a wide range of treatment conditions and eliminations of the need to generate, dispense and store treatment reagents, but more important is their capability to induce a very deep oxidation that can result in a virtually complete mineralization of the pollutan (Comninellis C. 1994; Houk et al., 1998; Feng and Li, 2003). It has been shown that the electrode material plays a key role on the evolution of the oxidation process (Martínez-Huitle and Ferro, 2006; Martínez-Huitle et al, 2004; Belhadj and Savall, 1998) and consequently on the by-products of oxidation. According to the mechanism involved in the pollutant oxidation (Martínez-Huitle and Ferro, 2006), the electrode materials have been classified in two main groups: *active* and *non-active* electrode material (Martínez-Huitle and Ferro, 2006; Martínez-Huitle et al, 2004).

The proposed model assumes that the initial reaction in both kind of anodes (generically denoted as M) corresponds to the oxidation of water molecules leading to the formation of physisorbed hydroxyl radical ($M(^{\bullet}OH)$): $M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^-$. Both the electrochemical and chemical reactivity of heterogeneous $M(^{\bullet}OH)$ are dependent on the nature of the electrode material. The surface of *active* anodes interacts strongly with $^{\bullet}OH$ radicals and then (Martínez-Huitle and Ferro, 2006; Martínez-Huitle et al, 2004; Quiroz et al., 2005; Quiroz et al., 2006), a so-called higher oxide or superoxide (MO) may be formed. This may occur when higher oxidation states are available for a metal oxide anode, above the standard potential for oxygen evolution (E^o = 1.23 V vs. SHE): $M(^{\bullet}OH) \rightarrow MO + H^+ + e^-$. The redox couple MO/M acts as a mediator in the oxidation of organics by $MO + R \rightarrow M + RO$; which competes with the side reaction of oxygen evolution via chemical decomposition of the higher oxide species: $MO \rightarrow M + \frac{1}{2} O_2$.

In contrast, the surface of a *non-active* anode interacts so weakly with $^{\bullet}OH$ radicals that allows the direct reaction of organics with $M(^{\bullet}OH)$ to give fully oxidized reaction products such as CO_2 and H_2O ($M(^{\bullet}OH) + R \rightarrow M + m\, CO_2 + n\, H_2O + H^+ + e^-$) where R is an organic compound with *m* carbon atoms and 2*n* hydrogen atoms, without any heteroatom, which needs (2*m* + *n*) oxygen atoms to be totally mineralized to CO_2 and H_2O. This reaction also competes with the side reaction of $M(^{\bullet}OH)$ like direct oxidation to O_2 ($M(^{\bullet}OH) \rightarrow M + \frac{1}{2} O_2 + H^+ + e^-$) or indirect consumption through dimerization to hydrogen peroxide by $2\, M(^{\bullet}OH) \rightarrow 2\, M + H_2O_2$. A *non-active* electrode does not participate in the direct anodic reaction of organics and does not provide any catalytic active site for their adsorption from the aqueous medium (Martínez-Huitle and Ferro, 2006; Quiroz et al., 2006). It only acts as an inert substrate and as a sink for the removal of electrons. In principle, only outer-sphere reactions and water oxidation are possible with this kind of anode. Hydroxyl radical produced from water discharge is subsequently involved in the oxidation process of organics. The model presupposes that the electrochemical activity (related to the overvoltage for O_2 evolution) and chemical reactivity (related to the rate of organics oxidation) of physisorbed $M(^{\bullet}OH)$ are strongly linked to the strength of the M-$^{\bullet}OH$ interaction. As a general rule, the weaker the interaction, the lower the anode reactivity for organics oxidation with faster chemical reaction with $M(^{\bullet}OH)$. The BDD anode is the best non-active electrode verifying this behavior (Martínez-Huitle and Ferro 2006; Belhadj and Savall 1998; Quiroz et al., 2006; Marcelli et al., 2003), then being proposed as the preferable anode for treating organics by electrochemical oxidation.

On the basis of this model, metal oxides such as IrO_2 and RuO_2 (Martínez-Huitle and Ferro 2006; Da Pozzo et al, 2005) known as *active* electrodes, achieving an incomplete oxidation of organic pollutants; whereas *non-active* oxides, such as Ti/SnO_2 and Pb/PbO_2 and their doped analogues are capable to oxidized organics to CO_2 (Martínez-Huitle and Ferro 2006;

Quiroz et al., 2005; Panizza et al., 2001). Within this last group of electrode materials, boron doped diamond (Si/BDD) electrodes have received great attention due to the wide range of their electrochemical properties (Quiroz et al., 2006; Marcelli et al., 2003).

6.3 Application of the direct electrochemical oxidation to removal pesticides from aqueous media

There is a scarce range of studies concerned with direct electrochemical oxidation for removal pesticides from aqueous media. Several reasons can be wielded to explain this little attention given to the study of their degradation, but all seems to indicated that this lack of attention is the risk to form degradation products of pesticides even more toxic than the parent compound that forms the pesticide. This assumption it is addmited if we takes into account the experimental conditions by which various electrooxidation pesticides processes quoted in literature has been performed. However, other important factor of pesticides to be condidered is their unique chemical structure which can associate functional groups with diferent susceptibility to the oxidation. This last characteristic make difficult to determine the degree of pesticide degradation and their corresponding oxidation pathway.

In spite of to be a known fact that the best anode materials to degrade pollutan organic compounds are those based in metallic oxides, the use of Pt electrodes has still been the preferable choise as anode material to degrade pesticides by direct electrochemical oxidation.

6.4 Organophosphates

This is the type of pesticides more reported being the more commonly quoted in literature methidathion, methylparathion, monochrotophos, phosphamidon, demeton-S-methyl, methamidophos, fenthion, and diazinon.

(a) Methylparathion ($C_{10}H_{14}NO_5PS$)

Methylparathion is a sintetic insecticide widely used in farm crops but with a strict control by the Environmental Protection Agency (EPA). The EPA allows 0.002 mg of methylparathion per liter of drinking water, which made justifiable the application of AOPs methods for their destruction from residual waters of agricultural nature. Arapoglou et al. (2003) reported by the first time the application of a direct electrochemical oxidation for the treatment of organophosphoric pesticides. Their electrochemical system was a Ti/Pt anode and a stainless steel 304 as cathode in a brine solution (H_2O + NaCl) under an applied currect of 36 A. After 2h of electrolysis a high reduction of COD and BOD_5 of the oxidized methylparathion as well as a low kWh/COD_r ration were reported. No degradation by-products of this organophosphoric pesticide were identified in any of these experiments.

Vlyssides et al. (2004) reported the electrochemical degradation of methylparathion by using Ti/Pt as anode in an aqueous medium of sodium chloride as electrolyte at 45ºC and an applied current density of 560 mA/cm^2. It was shown that an 8% w/w aqueous suspension of methylparathion and 20 g/L of sodium chloride can be electrolyzed in 2 h of reaction time. Methylparathion is quickly degraded, but a complete mineralization was not observed. Several degradation by-products and intermediates of methylparathion produced by electrochemical oxidation were reported. Formation of paraoxon, p-nitrophenol, benzoquinone, and hydroquinone were identified as primary intermediates of methylparathion degradation. The formation of these type of intermediates originates the formation of carboxylic acids such as oxalic, formic, and acetic acids as final products of the degradation process. Inorganic species were also identified between them nitrate, sulfate, phosphate, as well some oxides such as nitrogen oxides, sulfur dioxide and carbon dioxide. The full chemical analysis of liquid phase as well as of gas phase allows to the author to propose a degradation pathways for methylparathion electrochemical oxidation.

(b) Methidathion ($C_6H_{11}N_2O_4PS_3$)

Hachami et al. (2008) investigated the degradation of 1.4 mM of methidathion in in aqueous solution by anodic oxidation using a boron-doped diamond (BDD) anode. They observed an important reduction of chemical oxygen demand (COD) in the presence of 2-3 % of NaCl, as well as in the pH of electrolyzed solution. From these results the authors has suggested a pseudo first-order kinetics for the COD reduction of methidathion with a rate constant dependent on the applied current and on the electrolysis temperature: k = 0.0073 s^{-1} at 20 mA and 0.0146 s^{-1} at 60 mA, while k = 0.0131 s^{-1} at 298 K and 0.0077 at 363 K. It was concluded that applied current increases the rate of electrochemical oxidation but decreases it with the increases in temperature. The obtained activation energy (- 10.75 kJ) is in agree with the stablished conclusions. No attempt was made to identify the degradation products of methidathion although was suggested that mechanism of electrochemical mineralization can involve some mediators like chlorinated species or other radicals.

(c) Monochrotophos ($C_7H_{14}NO_5P$)

Yatmaz and Uzman (2009) investigated the direct electrochemical oxidation for removal of monochrotophos on Ti electrodes in aqueous solution of sodium salts (chloride or sulphate) as a function of applied current density and initial concentrations of pesticide. At 50 A/m^2 the monochrotophos degradation efficiencies were increased from 40 to 62% with the increase of initial concentration from 50 to 300 mg/L in the first five minutes of electrolysis after which the degradation reaction was stopped The increase in current density from 50 to 100 A/m^2 has a negligible effect on the degradation parameters owing to a poor generation of ·OH radicals on this type of anodes. The use of high concentration of NaCl electrolyte solution increases the electrochemical oxidation efficiency but increases also the risk to formation of chlorined compounds as residuals of degradation. In general, this electrochemical arrangement based on use of Ti as anodes for direct oxidation of monochrotophos was not an efficient method for removal this organophosphorous pesticide from aqueous media.

(d) Phosphamidon ($C_{10}H_{19}ClNO_5P$)

Phosphamidon is also an organophosphate insecticide, considered as an obsolete pesticide but whose disposal provokes serious environmental problems. It is soluble in water and stable in neutral and acid media and for this reason easy to find in aquatic media. This organophosphoric pesticide has been treated by direct electrochemical oxidation using Ti/Pt as anodes. Vlyssides et al. (2005) has reported experimental results from a laboratory scale pilot plant where the achieved reduction was nearly 26%.

Vlyssides et al. (2005) has also reported the electrochemical oxidation of the phosphorothioate pesticides Demeton-S-methyl ($C_6H_{15}O_3PS_2$), Methamidophos ($C_2H_8NO_2PS$), Fenthion ($C_{10}H_{15}O_3PS_2$), and Diazinon ($C_{12}H_{21}N_2O_3PS$). These pesticides were treated by an electrolysis system using Ti/Pt anode and a stainless steel 304 as cathode and also in a laboratory scale pilot plant. They reported that for Fenthion the achieved reduction was over 60%, while for Demeton-S-methyl, Methamidophos and Diazinon was more than 50%.

(e) Methamidophos ($C_2H_8NO_2PS$)

The anodic oxidation of methamidophos was studied by Martínez-Huitle at al. (2008) in a sodium sulphate aqueous solution on Pb/PbO_2, Ti/SnO_2, and Si/BDD (boron doped diamond) electrodes at 30°C. Under galvanostatic conditions, it was observed that the performance of the electrode material is influenced by pH and current density as it was shown by HPLC and ATR-FTIR analyses of methamidophos and its oxidation products along the electrolysis. It was found that methamidophos degradation using Pb/PbO_2 in acid media (pH 2.0 and 5.6) generates formaldehyde as the main product of reaction giving evidence of an indirect mineralization mechanism. Under the same conditions, Ti/SnO_2 showed poor formaldehyde production compared to the Pb/PbO_2 electrode. On Si/BDD electrodes formaldehyde production was not observed, instead the ATR-FTIR results showed the formation of phosphate as the reaction progressed suggesting a complete methamidophos mineralization on this electrode. In addition, HPLC results showed that the electrode efficiency is also dependant on the applied current density. This current density influence is remarkably clear on the Si/BDD electrodes where was evident that the most efficient current density towards a complete methamidophos mineralization was reached with the application of 50 mA/cm^2.

(f) Other pesticides

Until now, electrochemical methods of direct oxidation have seldom been applied to the degradation of other pesticides different to the organophosphorus. However, the electrochemical oxidation of some thiocarbamate (R_1,R_2,$NCOSR_3$, where R's are alkyl, cicloalkyl or aryl groups) herbicides in aqueous NaCl solutions has been investigated (Mogyoródy 2006), as well the oxidation of thiram ($C_6H_{12}N_2S_4$) (Priyantha and Weliwegamage 2008), an organo-sulfur fungicide, and also of the atrazine ($C_8H_{14}ClN_5$) herbicide (Malpass et al. 2006; Mamián et al. 2009). In addition, the electrochemical combustion of mecoprop ($C_{10}H_{11}ClO_3$) (Flox et al. 2006), carbaryl ($C_{12}H_{11}NO_2$) (Miwa et al. 2006, Malpass et al. 2009), and propham ($C_{10}H_{13}NO_2$) (Ozcan et al. 2008) herbicides has also been reported recently.

(g) In conclusion, the application of electrochemical methods by direct oxidation in pesticide removal has scarcely been explored. The complex nature of the molecular structure of pesticides, highly heteroatomic, is a restritive factor to stablish the chemical composition characteristics of solution due to the solubility problems and/or generation of dangerous intermediates. Thus, for instance, pesticides containing N atoms can to form chloramines if the aqueous solution has NaCl as electrolyte (Mogyoródy 2006a, 2006b). However, it is important to point out that presence of NaCl in solution can also confer to the electrodes an enhanced activity. In this case the Cl^- species at the electrode surface act as intermediates in the electron transfer between the pesticide molecule and the electrode (Miwa et al. 2006). The anode material is other important restrictive factor which determinates reaction parameters such as current efficiency, selectivity and product composition. Several works have reported the use of Ti or Pt electrodes (Mamián et al. 2009; Yatmaz and Uzman 2009; Mogyoródy 2006a, 2006b; Vlyssides et al. 2005a, 2005b, 2004; Arapoglou et al. 2003; Pulgarin and Kiwi 1996) with results little adequated for consider its as anodic material for removal of pesticides from aquatic media. The formation of complex mixture of oxidation by-products in solution, no detoxification of solution, or desactivation phenomena of anodes are some of limitations of these type of electrodes for their use in the electrochemical method of direct oxidation. Better results has beeb achieved by using metallic oxides such as

SnO_2, PbO_2, or RuO_2 (Martínez-Huitle et al. 2008; Mogyoródy 2006a, 2006b; Pulgarin and Kiwi 1996), dimensionally stable anodes (Miwa et al. 2006; Malpass G.R.P. et al. 2006, 2009), and more recently boron-doped diamond surfaces (Gao et al. 2009; Ozcan et al. 2008; Flox et al. 2006; Hachami et al. 2008; Martínez-Huitle et al. 2008).

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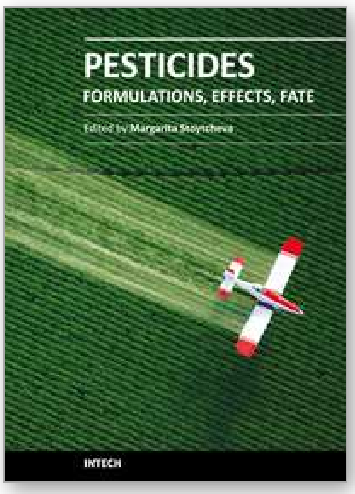

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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.