

Advanced Oxidation Processes for the Removal of Pesticides from Wastewater: Recent Review and Trends

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Abstract.

Several emerging chemical contaminants may occur in wastewater as a result of human activities. Pesticides is one of the most common groups of pollutants found in wastewater effluents due to their widespread use in agriculture in order to maintain crop quality and quantity [Ternes, 2007; Schwarzenbach *et al.*, 2010]. These micropollutants are usually detected in trace concentrations (ng L^{-1} or $\mu\text{g L}^{-1}$) and are resistant to conventional wastewater treatment systems of urban wastewater treatment plants (WWTP) such as biological processes (secondary treatment). Consequently, the use of advanced oxidation processes (AOPs) is crucial and effective for the removal of these substances to levels that are deemed acceptable. This work studies the application of different types of AOPs as tertiary treatment for removal of different classes of pesticides from polluted water and wastewater.

Keywords: Advanced oxidation processes, pesticides, water treatment, photocatalysis, mineralization

1. Introduction

Aquatic reservoirs receive direct and indirect inputs of organic pesticides that do not always remain in agricultural soils where they are applied for crop protection and fruit tree treatment, but inevitably find their way into aquatic ecosystems through leaching, surface run-off, spray-drift, soil erosion and volatilization. The average agricultural herbicide loss has been estimated to be approximately 1% of the applied volume [Carter, 2000]. Furthermore, pesticides' widespread and steadily increasing use nowadays in intensive agricultural practices to kill unwanted vegetation has resulted in the occurrence of residues of these chemicals and their metabolites in different environmental compartments such as water bodies and soil, being usually at low concentrations.

As a result, surface and groundwater potential pollution from pesticides has become a threat not only for the inhabitants of several environmental compartments, but to human health as well. Fortunately, over the past few decades an enormous emphasis was placed on the section of water quality management and sustainability. Environmental protection agencies in a number of countries, particularly in Europe, North America, Japan,

Southeast Asia and Australia-New Zealand, so as to deal with wastewater discharges and in addition in their efforts to curb aquatic pollution, have recognized the great value of applying water and wastewater treatment procedures to effluents and their component chemicals for the removal of persistent synthetic molecules, such as pesticides. The choice of the methods employed for any wastewater treatment depends on the following criteria: i) the type and concentration of the pollutants present, ii) the level of contaminants allowed in the discharge, iii) the cost of the treatment procedure and iv) the volume of wastewater to be treated. Effluents from chemical and agrochemical industries contain several organic compounds including solvents, pesticides, etc. Pesticides have been classified by scientists according to their target organisms; insecticides, herbicides, defoliants, desiccants, fungicides, nematicides, avicides, and rodenticides are some of the many categories of pesticides. Unfortunately, most of these substances are chemically stable and not easily degradable (via abiotic or/and biotic processes) species and thus belong to the class of persistent organic pollutants (POPs); hence, conventional WWTP are not efficient to remove them to the desired level. Basic water treatment techniques such as flocculation/coagulation, chemical precipitation and biological oxidation are used only for the removal of certain pesticides to a certain extent. However, advanced oxidation processes (AOPs) is a class of oxidation techniques based on the *in situ* generation of highly reactive and oxidizing radical species (mainly powerful hydroxyl radicals, $\cdot\text{OH}$), which interact with the molecules of the organic pollutants and lead to the progressive degradation of the contaminants. According to the available literature, several AOPs have been employed for the oxidation of a variety of pollutants that have resulted at least in the transformation of parent compounds into more innocuous and biodegradable intermediate products, whereas in numerous occasions and under optimized conditions almost complete mineralization of the organic substances to carbon dioxide (CO_2), water and inorganic acids has been achieved [Poyatos *et al.*, 2010]. Extensive research has been conducted on the removal of organic pesticides in water using AOPs. Among the numerous proposed AOPs Fenton process (H_2O_2 and Fe^{2+}), UV treatment, UV/ H_2O_2 process, photo-Fenton, ozonation (O_3)

and heterogeneous photocatalysis using TiO₂ are included [Malato *et al.*, 2009; Poyatos *et al.*, 2010; Ahmed *et al.*, 2011; Dârjan *et al.*, 2013]. The aim of present paper is to highlight the potential of AOPs to degrade pesticides and offer a review of the most promising recent results, with emphasis on the various important parameters applied to enhance the efficiency and applicability of each AOP reported.

2. Advanced Oxidation Processes (AOPs)

As demonstrated in Figure 1, various types of chemical, photochemical, sonochemical and electrochemical reactions have been performed for the degradation and destruction of organic pollutants in aquatic media and the treatment of wastewater. Some selected studies that have employed AOPs for the removal of pesticides from water and wastewater are presented in Table 1.

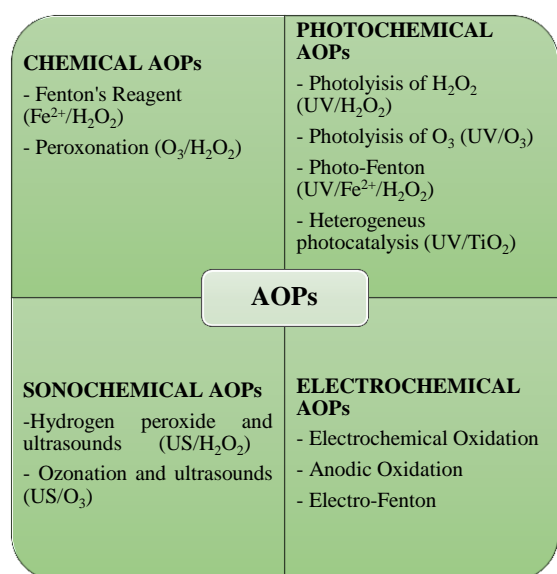
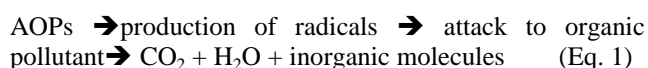


Figure 1. Advanced oxidation processes (AOPs) classification

Despite the fact that AOPs use different reagent systems, however, all procedures in common produce not highly selective, but extremely reactive radical species that can attack most organic molecules via the general scheme described by Equation (1):



AOPs can be classified as photochemical or non-photochemical processes. Examples of the photochemical group are direct photolysis by UV light, UV/H₂O₂, UV/TiO₂, photo-Fenton and photo-Fenton-like processes. Non-photochemical AOPs include ozonation, Fenton process, electrochemical oxidation, hydrodynamic/ultrasonic cavitation and sub/super critical water process. Moreover, AOPs can be categorized either as homogeneous or heterogeneous.

2.1. Homogeneous AOPs

Homogeneous AOPs can be further subdivided into the processes that use energy and the processes that are not using energy [Poyatos *et al.*, 2010].

2.1.1. Homogeneous AOPs using Energy

Homogeneous AOPs using energy in the form of ultraviolet (UV) radiation, ultrasonic (US) energy or electrical energy have been applied for the removal of several pollutants from wastewater. Especially homogeneous treatments employing UV light have generally been used for the degradation of compounds that absorb within the corresponding range of spectrum. UV radiation has been more often applied in the presence of other oxidants such as UV/O₃, UV/H₂O₂, UV/O₃/H₂O₂, UV/Fe²⁺/H₂O₂ (photo-Fenton) etc. [Babuponnusami *et al.*, 2014]. For example, Lau *et al.* (2007) reported the higher efficiency of UV/O₃ treatment achieved for the removal of the carbamate insecticide carbofuran than treatments of direct UV photolysis and ozonation process. The same authors achieved the complete removal of 0.2 mM whereas 24% mineralisation occurred within 30 min [Lau *et al.*, 2007]. Ultrasounds constitute a particular type of AOPs in which the formation of reactive radicals ([•]OH, [•]HO₂, [•]O) can proceed either through a primary physical (direct) mechanism, where sonolysis of water molecules takes place (also known as cavitation consisting of nucleation, growth, and collapse of bubbles), or through chemical (indirect) mechanism, where homolytic fragmentation of water and dioxygen molecules occur [Ghatak, 2014; Oturan *et al.*, 2014]. However, it has been reported that the use of ultrasound in AOPs is not very energy efficient and as much as 50% of the input energy is lost in thermal dissipation [Zouaghi *et al.*, 2011; Ghatak, 2014]. As a consequence, and according to the relevant literature, several sono-chemical and sono-catalytic AOPs have been developed [Ma *et al.*, 2010; Ma, 2012]. Therefore, various combinations of ultrasounds with other oxidants, such as H₂O₂ and dioxygen, as well as with UV irradiation and with various AOPs, including the Fenton's reagent (with different forms of iron: Fe⁰, Fe²⁺ and Fe³⁺) and Fenton-type reactions (called sono-Fenton AOPs) have been applied. Finally, the use of a catalyst has been found to improve the efficiency of the oxidizing AOP system through synergistic effects, as in the case of molinuron [Zouaghi *et al.*, 2011]. Electrochemical AOPs is a form of degradation treatment that is based on the use of electrical energy in order to break up organic pollutants contained in wastewater effluents. This group of homogeneous AOPs is subdivided into electrochemical oxidation, anodic oxidation and electro-Fenton which are all techniques based on the transfer of electrons. That fact makes electrochemical AOPs particularly interesting from the environmental point of view, since they are clean and effective ways for the *in situ* generation of hydroxyl radicals ([•]OH) which are able to destroy a large variety of toxic and POPs, including agrochemicals [Pedrosa *et al.*, 2006].

2.1.2. Homogeneous AOPs without using Energy

Ozonation in alkaline medium and ozonation with hydrogen peroxide are two treatment techniques belonging in the group of homogeneous AOPs that do not use energy [Poyatos *et al.*, 2010].

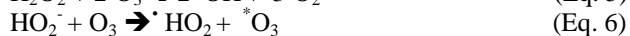
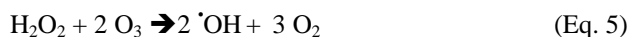
Table 1. Selected studies that employed AOPs for the removal of pesticides from water and wastewater. Reports in chronological order.

Analyte(s) Concentration	& Initial	Experimental set-up		Results		Reference
		Process	Optimum parameters	Degree of removal	Other observations	
Fenitrothion (50 mg L ⁻¹); Diazinon (50 mg L ⁻¹) and Profenifos (50 mg L ⁻¹)		UV; H ₂ O ₂ / Fe ²⁺ ; UV/H ₂ O ₂ ; UV/H ₂ O ₂ / Fe ²⁺ and UV/H ₂ O ₂ / Fe ³⁺	UV illumination:62W medium pressure lamp emitting 100nm< λ <280, corresponding to 1.32 10 ⁻⁵ Einstein s ⁻¹ ; Fenton treatment: pH=3, COD:H ₂ O ₂ = 4.4:1; H ₂ O ₂ :Fe ²⁺ ratio = 100:1. Photo-Fenton treatment: pH=3, COD: H ₂ O ₂ = 2.2:1; H ₂ O ₂ :Fe ²⁺ ratio = 50:1.	Fenton treatment: Within 30min TOC degradation of 86.9%, 56.7% and 89.7% for fenitrothion, diazinon and profenofos, respectively. Photo-Fenton treatment: About 86.9%, 56.7%, 89.7% of TOC degradation of fenitrothion, diazinon and profenofos after 30 min.	The advantages of the photo-assisted Fenton process as an oxidative pre-treatment step over the dark Fenton process are economics, less energy demand, efficiency, low investment and harmless process products.	Badawy <i>et al.</i> , 2006
Carbofuran (20 mg L ⁻¹)		Ultrasound/Fenton	pH=3; [Fe ²⁺] =0.8mmol L ⁻¹ ; [H ₂ O ₂] = 0-300mmol L ⁻¹ at 25°C.	Ultrasonic process: More than 40% of carbofuran was oxidized in 120 min. Decrease in TOC was less than 15% (part of carbofuran was oxidized to intermediates). Combination of the ultrasonic process with Fenton reagents: increased the degradation efficiency to more than 99% with 40% mineralization in 30 min.	Possible degradation pathway for carbofuran is proposed.	Ma <i>et al.</i> , 2010
Fenthion (10mg L ⁻¹)		UV/TiO ₂ and UV/TiO ₂ /H ₂ O ₂	[TiO ₂] = 100mg L ⁻¹ ; [H ₂ O ₂] = 5mmol L ⁻¹ ; UV illumination with 4x18W low pressure Hg lamps emitting irradiation at λ =365 nm (maximum light intensity of the irradiation system was 14.5mW cm ⁻² at a distance of 15cm).	UV-TiO₂ illumination system: after 48h of light exposure 95% of its original concentration was decomposed. UV/TiO₂/H₂O₂ illumination system: total photocatalytic decomposition of target pesticide was accomplished within 5h.	A synergistic effect was observed when the oxidant H ₂ O ₂ was added in the TiO ₂ suspensions increasing the reaction rate of photodegradation of fenthion by a factor of ~18. In all cases the reduction process followed pseudo first order kinetics (Langmuir Hinshelwood model).	Petsas <i>et al.</i> , 2013
2,4-D (1 μ g L ⁻¹); Mecoprop (1 μ g L ⁻¹); 2,4 5-T (1 μ g L ⁻¹); Atrazine (2 μ g L ⁻¹); Terbutryn (2 μ g L ⁻¹) and Metaldehyde (2 μ g L ⁻¹)		UV/H ₂ O ₂ through pilot-scale experiments incorporating microfiltration (MF) and reverse osmosis (RO) (AOP1 and AOP2, respectively)	For both AOPs Treatment capacity: 3 m ³ h ⁻¹ ; Theoretical contact time: ~ 120 s; 12 low-pressure/highoutput amalgam lamps emitting at 254 nm. AOP1: Lamp power set-point: 100%; H ₂ O ₂ dose: 16 mg L ⁻¹ /optimal range: 6–20 mg L ⁻¹ ; AOP2: Lamp power set-point: 600%; H ₂ O ₂ dose: 3 mg L ⁻¹ /optimal range: 1–3 mg L ⁻¹ .	Removed by at least 97% when applying AOP to the reverse osmosis permeate at an H ₂ O ₂ dose of 3 mg L ⁻¹ and an energy demand of 0.62 kWh m ⁻³ .	Application to the MF permeate was much less effective in removing herbicides and pesticides generally, and metaldehyde in particular. Even at very high H ₂ O ₂ doses (16 mg L ⁻¹) with energy demand levels of 0.93 kWh m ⁻³ , metaldehyde removal remained < 50%.	James <i>et al.</i> , 2014
Dimethoate (14.71 mg L ⁻¹); Triazophos (5.87 mg L ⁻¹) and Malathion (24.53 mg L ⁻¹)		Fenton; UV/Fenton and Microwaveelectrodeless Ultraviolet (MWEUV) /Fenton	pH=5; [Fe ²⁺] = 0.8mmol L ⁻¹ ; [H ₂ O ₂] = 100mmol L ⁻¹ at 25±0.5°C; UV emission bands at 254, 313, 365, and 405 nm (U-shaped MWEUV lamp made by quartz tubes filled with 1 mg Hg and 0.66 kPa Ar)	Completely removal by the MWEUV/Fenton process within 120 min.	COD and DOC decreased from 183.2 mg L ⁻¹ to 36.9 mg L ⁻¹ and 43.5 mg L ⁻¹ to 27.8 mg L ⁻¹ , respectively.	Cheng <i>et al.</i> , 2015
Acetamidiprid (100 μ g L ⁻¹)		UV; UV/TiO ₂ ; UV/H ₂ O ₂ /Fe; UV/Na ₂ S ₂ O ₈ and UV/Na ₂ S ₂ O ₈ /Fe	pH=7; 3x30W UV-C low pressure lamps emitting monochromatic light at 254 nm. UV light intensity of the irradiation system: 20 W m ⁻² ; [Fe ²⁺] = 1mg L ⁻¹ ; [H ₂ O ₂] = 50mg L ⁻¹ .	From all of the processes assayed, the UV/H ₂ O ₂ /Fe system was the fastest, reaching complete pesticide removal in 20 min.	Photo-Fenton at natural pH proved to be the most efficient process. The persulfate systems had also shown that they have great potential for micropollutant removal. Humic acids reduced degradation efficiency for UV/H ₂ O ₂ /Fe and UV/Na ₂ S ₂ O ₈ /Fe due to competition with radicals.	Carra <i>et al.</i> , 2016
Atrazine (Not reported)		UV/TiO ₂ and UV/Pt-TiO ₂	Platinized TiO ₂ (Pt-TiO ₂) by coating 1 wt.% of Pt on TiO ₂ surface; UV light irradiation: 352 nm.	The Pt-TiO ₂ -catalyzed atrazine degradation reached 76% in 3 hours without adding H ₂ O ₂ solution or aeration, which was more than 10% higher than the TiO ₂ -catalyzed reaction. The decomposition product of Pt-TiO ₂ -catalyzed atrazine degradation was mainly cyanuric acid.	Pt-TiO ₂ had three main advantages: i) coated Pt could facilitate the generation of appropriate amounts of OH radicals, so it could prevent the formation of over-oxidized TiO ₂ , ii) aeration was not needed, and iii) the excited electrons were mainly unidirectionally transferred to the catalyst surface to avoid recombination of electron-hole pairs.	Chen <i>et al.</i> , 2017

O₃ is unstable in aquatic mediums and especially in pH>7 and therefore its molecules undergo spontaneous degradation to generate hydroxyl radicals (Eqs 2-4), which attack the molecules of the organic contaminant.



Ozonation in the presence of H₂O₂ proceeds through a different set of reactions (Eqs 5-6) in which H₂O₂ is partially dissociated to hydroperoxide anion that reacts with the ozone to produce more radicals.



Both described methods are easily automated and efficient to degrade a large number of pollutants. However, their drawbacks is the high cost of ozone generation and hydroperoxide, respectively.

2.2. Heterogeneous AOPs

Heterogeneous AOPs require the addition of catalysts (metal oxides of Ti, Al, Zn, V, Cr, Mn, etc., or organometal catalysts) for the occurrence of the degradation reactions. Compared with the homogeneous AOPs, the heterogeneous AOPs have the advantage of the easier separation from the product (meaning the treated effluents) [Poyatos *et al.*, 2010]. Catalytic ozonation (Fe²⁺/O₃, TiO₂/O₃), photocatalytic ozonation (UV/TiO₂/O₃), and heterogeneous photocatalysis (UV/TiO₂) are the most commonly used applications [Poyatos *et al.*, 2010].

In our knowledge, the procedure of heterogeneous photocatalysis, has been widely applied in recent years, particularly in the case of organic pollutants refractory to oxidation by the other conventional AOPs [Poyatos *et al.*, 2010]. This type of heterogeneous AOPs involves the irradiation of a semiconducting catalyst that is easily photo-excited with near-UV light. As a result, photo-excited catalyst forms electron-donating and electron-accepting sites that induce oxidation–reduction reactions. In the case that the absorbed UV photons have an energy larger than the energy gap (between the valence and the conducting bands) of the semiconductor, electron-hole pairs are produced, which can either recombine or migrate to the semiconductor surface and then react with chemical species adsorbed on the surface [Oturán *et al.*, 2014].

A variety of semiconductor powders acting as photocatalysts have been used. Among them titanium dioxide (TiO₂) is considered particularly efficient due to the formation of e_{CB}⁻/h⁺ pairs under illumination with near-UV light [Petsas *et al.*, 2013]. Hence, an extend research concerning the use of TiO₂, preferably in its rutile in front anatase form has been conducted [Konstantinou and Albanis, 2003; Petsas *et al.*, 2013]. Numerous heterogeneous TiO₂ photocatalytic degradation and/or mineralization studies have been performed for several organic pollutants, such as pesticides [Konstantinou and Albanis, 2003; Cernigoj *et al.*, 2007; Wu *et al.*, 2009; Hazime *et al.*, 2012; Rivera-Utrilla *et al.*, 2012; Seck *et al.*, 2012; Oturan *et al.*, 2014; Chen *et al.*, 2017].

In most reports, it is observed that the efficiency of oxidation systems employing TiO₂ is higher when combined with hydrogen peroxide and UV radiation

[Poyatos *et al.*, 2010; Petsas *et al.*, 2013]. In general, the addition of an oxidant/electron acceptor, such as H₂O₂, K₂S₂O₈ and KBrO₃, into a semiconductor suspension has been shown to improve the photocatalytic degradation of organic contaminants by removing the e_{CB}⁻/h⁺ recombination, by increasing the hydroxyl radicals (·OH) mass and by generating more radicals and other oxidizing species [Petsas *et al.*, 2013]. Especially when TiO₂ films are used instead of micro-powder formations which is the new tendency, there no need to separate the catalytic particles at the end of the process and furthermore no progressive formation of dark catalytic sludge is observed, that diminishes the efficiency of UV irradiation and reduces the photoreactor performances [Oturán *et al.*, 2014].

3. Conclusions

The various systems of AOPs described in the present review showed that advanced oxidation processes constitute an extremely promising technology tool for the treatment of wastewater to degrade organic pollutants via an efficient and environmental friendly method. According to this revision several and different AOPs have been reported that may be combined in various manners so as to obtain maximum efficiency in the mineralization of organic pesticides.

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