

# Advanced Oxidation Processes for the Degradation of Emerging Pollutants: Opportunities and Challenges

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**Abstract**— Treatment of waste water containing emerging pollutants is always a challenge as most of the organic water contaminants are resistant to degradation using conventional techniques. Emerging pollutants are a class of compounds in the environment such as endocrinal disruptors resulting from the degradation of some organic compounds or introduction of medicine in the natural environment. One of the potential technologies in the area of removal of organic water pollutants is Advanced Oxidation Process (AOP). Free radical induced degradation is the main process involved in AOP. It is generally observed that the degradation induced by any AOP may not lead to absolute mineralisation. In the present report, various AOPs for the destruction of a number of emerging pollutants are discussed. The advantages and limitations of these technologies are highlighted. Two main AOPs, hydrogen peroxide photolysis and sonolysis, for the destruction of two model pollutants such as fensulfothion and atenolol are presented. Kinetics of the reaction, extent of mineralisation and the details of the products are also presented.

**Keywords**—Emerging pollutants, AOP, degradation reaction, organic contaminants, mineralisation

## Introduction

Emerging pollutants are a class of compounds in the environment such as endocrine disruptors resulting from the degradation of some organic compounds or introduction of medicine in the natural environment. The US EPA (United States – Environmental Protection Agency) defines “emerging pollutants as new chemicals without regulatory status and which impact on environment and human health are poorly understood.” [1-3]. They include drugs of abuse, pharmaceuticals and personal-care products (PPCPs), steroids and hormones, surfactants, perfluorinated compounds (PFCs), flame retardants, industrial additives and agents, gasoline additives, as well as their transformation products (TPs). In addition to these products, nanomaterials, 1,4-dioxane and swimming pool disinfection by-products (DBPs) are also included in this category. These compounds enter into the environment through the disposal of municipal, industrial and agricultural wastes, excretion of pharmaceuticals and accidental spills. They undergo biodegradation, and chemical and photochemical degradation when entering into the environment [3]. Even the trace level of PPCPs can cause chronic toxicity, endocrine disruption and the development of pathogen resistance. Wastewater treatment plants effluents and secondarily terrestrial run-offs (roofs, pavement, roads, and agricultural land) including atmospheric deposition are the major sources of environmentally relevant emerging contaminants. It is not necessary that these chemicals need to

be persistent in the environment to cause harmful effects, but it creates an environmental catastrophe due to its continuous introduction into the environment. For many of these emerging contaminants, risk assessment and ecotoxicological data are not available at the moment and hence it is difficult to predict which health effects they may cause on humans, terrestrial and aquatic organisms, and ecosystems.

The major issue with the removal of these kinds of pollutants is that there is no efficient technology available yet to remove them from natural environment. The conventional surface water treatment process which involves coagulation, flocculation, sedimentation, filtration, and disinfection can only remove some of the contaminants, but they are inefficient to degrade or destroy these chemicals. In this context, Advanced Oxidation Processes are widely experimented for the destruction of these chemicals. AOPs are more environmentally accepted techniques because in many cases it leads to the complete mineralization of the organic pollutants. This technology is based on the production of a highly reactive oxidant such as hydroxyl radical in solution state and utilise its unselective oxidation of organic chemicals to carbon dioxide and water (equation 1).



The production of the hydroxyl radical is the most important part of this technology. Photolysis of hydrogen peroxide, ozone and titanium dioxide, chemical method such as Fenton reaction, sono and electrochemical methods are some of the techniques come under this category [4-6]. The crucial step in this kind of processes is to control the intermediate products of oxidation and finally get all those into carbon dioxide and water. It is however highlighted that most of these technologies are under experimental stage.

In the present report, various AOPs for the destruction of a number of emerging pollutants are discussed. The advantages and limitations of these technologies will be highlighted. Two main AOPs, hydrogen peroxide photolysis and sonolysis, for the destruction of two model pollutants such as fensulfothion and atenolol are presented. Kinetics of the reaction, extend of mineralisation and the details of the products are also presented.

## General Methodologies

The general experimental set up of AOP based experiments is simple and general. The initiator of the

degradation is the hydroxyl radicals ( $\cdot\text{OH}$ ) and hence a radical generating system is required. In the present report, two main hydroxyl radical generating system have been presented. (i) photo-irradiation of  $\text{H}_2\text{O}_2$  using UV light (medium pressure mercury lamp operating in the wavelength range 200-400 nm) and (ii) Ultrasound irradiation using sonoreactor having four variable frequencies (202, 351, 623, and 1003 kHz). The ultrasound was produced using an L3 ELAC Nautik ultrasound generator powered by an Allied Signal R/F generator (T & C power conversion, Model AG 1006). The temperature was maintained at  $25 \pm 1^\circ\text{C}$  by using a water circulator.

The second component of the experiments involve monitoring of the degradation profile by various analytical tools such as UV-VIS, HPLC, TOC, IC, LC-MS, LC-MS/MS and LC-Q-TOF-MS. The degradation profile of the pollutants is generally carried out by HPLC with suitable solvents. The extent of mineralisation is carried out by TOC using UV-persulfate method. IC generally gives an idea about various ionic products (anionic and cationic) formed after the treatment. LC-MS, LC-MS/MS and LC-Q-TOF-MS are very helpful in identifying various trace amounts of organic compounds formed during the treatment.

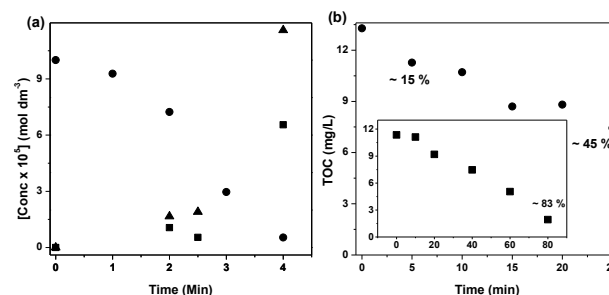
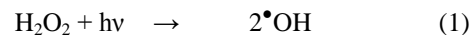
### Degradation studies of fensulfothion induced by the photolysis of hydrogen peroxide

Fensulfothion (Trade name: Dasanit, included in the group of very toxic compounds (T+)), is a typical organophosphorous (OP) compound used against both insects and nematodes. It is a soil insecticide widely used on corn, onions, rutabagas, pineapple, bananas, sugar cane, sugar beets, pea nuts etc. The presence and stability of fensulfothion in soil as well as aquatic environment makes it very important to obtain a proper technology for its destruction.

Both direct UV and hydrogen peroxide/UV photolysis experiments were carried in the initial stage. Direct irradiation was to investigate its photostability. The degradation of fensulfothion was found to be insignificant in the case of direct photolysis and hence it is understood that it is quite stable to direct photolysis. Photodegradation in the presence of hydrogen peroxide ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) was investigated using  $1 \times 10^{-4} \text{ mol dm}^{-3}$  fensulfothion at near neutral pH. At this pH, more than 90% of the parent compound has been disappeared within 4 minutes of irradiation. The degradation profile is presented in Figure 1. TOC measurements were carried out under varying time of irradiation (Figure 1). It is very clear from Figure 1 that there is only a slight reduction in the TOC in the case of low irradiation time scale (5 min) where there is a maximum degradation of the parent compound. The concentration of various ions produced during the treatment was monitored (Fig.1). At longer time scales, a sharp increase in the ions was observed. This is due to the fact that, at lower time scales, the reaction of  $\cdot\text{OH}$  is restricted to parent compound and only the organic intermediates are mainly formed in the solution. This is the main reason why there is only a slight reduction in the

TOC values. But at longer timescales, some of the stable products subsequently undergo reaction with  $\cdot\text{OH}$  and thus results low molecular weight inorganic products [6].

The degradation reaction can be assigned to the direct attack of hydroxyl radical which is produced from the dissociation of hydrogen peroxide as described in Equation 1 [7,8]. The degradation can be accelerated by the presence of oxygen as the experiments are conducted in aerated medium. Although there is no information on the nature of intermediate products formed due to the attack of hydroxyl radical at this stage, it is known that oxygen may facilitate the degradation of reducing intermediate radicals [9].



**Figure 1** (a) Degradation profile of fensulfothion ( $1 \times 10^{-4} \text{ mol dm}^{-3}$ ) in the presence of hydrogen peroxide ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ , pH 5.5) ( $\bullet$ ) and release of sulfate ( $\blacktriangle$ ) and phosphate ( $\blacksquare$ ) ions as a function of irradiation time. (b) TOC removal by  $\text{H}_2\text{O}_2/\text{UV}$  photolysis as a function of time ( $[\text{H}_2\text{O}_2] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ). (Inset) TOC removal by  $\text{H}_2\text{O}_2/\text{UV}$  photolysis ( $[\text{H}_2\text{O}_2] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ ) [6].

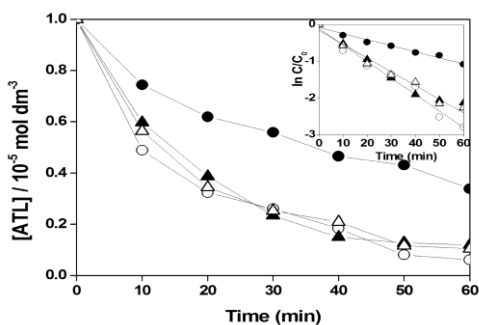
LC-MS/MS analysis have been carried out to investigate the intermediate and stable products after an irradiation time of 3 min when 70% of the fensulfothion was degraded. Nearly 20 products were identified and their structural identity was established. The structural elucidation was based on the analysis of total ion chromatogram (TIC) of the irradiated sample in both positive and negative ion modes.

### Degradation studies of atenolol induced by ultrasound

Atenolol is a beta blocker, a class of drugs mainly used in cardiovascular diseases. It is a selective receptor antagonist drug and is widely used in many countries. Due to its extensive use as a drug, beta blockers are recently identified as an emerging pollutant and are found to exist in the environment, particularly in sewage effluents and surface waters. Among various beta blockers, atenolol have been reported to exist in surface water [10-12]. Sonolysis (ultrasound induced chemical change) is considered as a versatile technique which is used to investigate radical mediated waste water treatment.

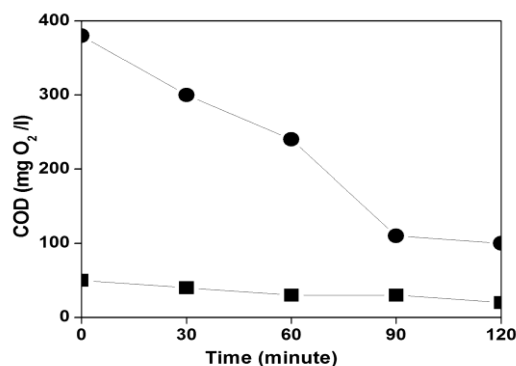
Atenolol (ATL) was exposed to ultra sound of four varying frequencies at a fixed power (50 W) for one hour. The degradation of atenolol with respect to time of sonication is shown in Fig.2. The first order nature of the degradation pattern is also shown in Fig.2. These calculated values of the

first order rate constant are 0.01649, 0.04476, 0.03717 and 0.0372 for 200, 350, 620 kHz and 1 MHz, respectively. It can be seen from these results that when the frequency is increased from 200 kHz to 350 kHz, there is a sharp increase in the rate of degradation as well as efficiency of degradation. However, nearly similar degradation efficiency is observed thereafter for 620 kHz and 1 MHz [13].



**Fig. 2** Effect of frequency on the sonochemical degradation, power = 50 W,  $[ATL] = 10^{-5} \text{ mol dm}^{-3}$ . Inset: First order kinetics of degradation [13]

pH is an important parameter in the water treatment process. The effect of pH on degradation was more pronounced at frequency 350 kHz and power 50 W. The highest rate of degradation is observed at acidic pH ( $k = 0.0634 \text{ min}^{-1}$ ). In order to study the efficiency of this methodology in real system, degradation studies were carried out in river water taken from one of the local rivers. The water quality parameters showed high content of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and relatively high TDS, conductivity and salinity. In the presence of all these ions, ATL showed a degradation of about 83% against 93% in pure water. On the other hand, the COD value got decreased from 380 to 100 mg/l in river water whereas it went down from 50 to 10 mg/l in pure water (Fig.3).



**Fig. 3:** COD reduction of ATL in river water (●) and in pure water (■) during sonolysis [13]

### Advantages and challenges of AOP based degradations

The results from the above two examples clearly spell out the major advantages at the same time the challenges while using AOPs. Using both the techniques, a very efficient degradation of the starting compounds is obtained. However, it is clear that although within a short time of irradiation (4 min), the entire concentration of fensulfothion got disappeared, only about 20% of the mineralisation takes place. Even 40% is obtained only after 25 min. At the same time, nearly about 20 products were formed which may be even toxic. The only option for further degradation is to irradiate much longer period with further addition of  $\text{H}_2\text{O}_2$ . More or less similar situation is observable from the atenolol degradation using ultrasound. However, the high efficiency of degradation in river water is a promising result. The suitability of any AOPs depends on their ability to completely degrade the organic compound to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . However, in majority of cases, we only observe the transformation of the parent compound, but not its complete degradation. In this context, it is very important that one should have a complete understanding of the reaction pathway that ultimately lead to complete mineralisation. Therefore, the area of research in AOP is promising and challenging.

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