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**APPLICATIONS OF SOLAR LIGHT INDUCED AOP IN
DETOXIFICATION OF CONTAMINATED WATER**

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Applications of Solar Light Induced AOP in Detoxification of Contaminated Water

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Abstract – In recent years, there has been a tremendous amount of research and development in the area of photocatalysis, especially heterogeneous photocatalysis. These are Advanced Oxidation Processes (AOPs), characterized by an important feature of production of $\cdot\text{OH}$ radicals. This paper reviews the use of sunlight to produce the $\cdot\text{OH}$ radicals by different photocatalysis and photo-Fenton process. The paper also summarizes the research carried out related to solar photocatalytic degradation of water contaminants such as pesticides.

Keywords: AOP, Pollutants, Solar light, Degradation, Photocatalysis.

INTRODUCTION

Persistent organic chemicals are present as pollutants in wastewater effluent from industrial manufacturers and normal households, and in landfill leachates. They can be found in ground water wells and surface waters. In all cases they have to be removed to protect our water resources or to achieve drinking water quality. Therefore, many processes have been proposed over the years and are currently being employed to destroy these toxins. The so-called photocatalytic detoxification has been discussed as an alternative method for clean-up polluted water in the scientific literature since 1976. [1,2]

Advanced Oxidation Processes (AOPs) may be used for decontamination of water containing organic pollutants. Although there are different reacting systems, all of them are characterized by the same chemical feature: production of hydroxyl radicals ($\cdot\text{OH}$), which are able to oxidize and mineralize almost any organic molecule, yielding CO_2 and inorganic ions. Rate constants (k_{OH} , $r = k_{\text{OH}} [\cdot\text{OH}] C$) for most reactions involving hydroxyl radicals in aqueous solution are usually on the order of 10^6 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$. They are also characterized by their not-selective attack, which is a useful attribute for wastewater treatment and solution of pollution problems. The versatility of the AOPs is also enhanced by the fact there are different ways of producing hydroxyl radicals, facilitating compliance with the specific treatment requirements. Methods based on UV, $\text{H}_2\text{O}_2/\text{UV}$, O_3/UV and $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$ combinations use photolysis of H_2O_2 and ozone to produce the hydroxyl radicals. Other methods, like heterogeneous photocatalysis and homogeneous photo-Fenton, are based on the use of

a wide-band gap semiconductor and addition of H_2O_2 to dissolved iron salts, respectively, and irradiation with UV–vis light. Both processes are of special interest since sunlight can be used for them. [3-5]

The publications regarding the photocatalytic process rose continuously over the last years surpassing meanwhile a total number of more than 1000 peer-reviewed publications per year. Though such a simple search does not necessarily include every single article correctly, it still serves to prove the general trend of an increasing interest of the scientific community. Fig. 1 shows the evolution of these publication activities. Fig. 1 also illustrates that much of the literature takes into account the possibility of driving the process with solar radiation. This fact is due to that a priori the photocatalytic process seems to be the most apt of all AOPs to be driven by sunlight. In this monograph we highlight some of the science and technology being developed to improve the solar photocatalytic disinfection and decontamination of water, as well as efforts to increase water supplies through the safe reuse of wastewater and adequate treatment of industrial wastewater.

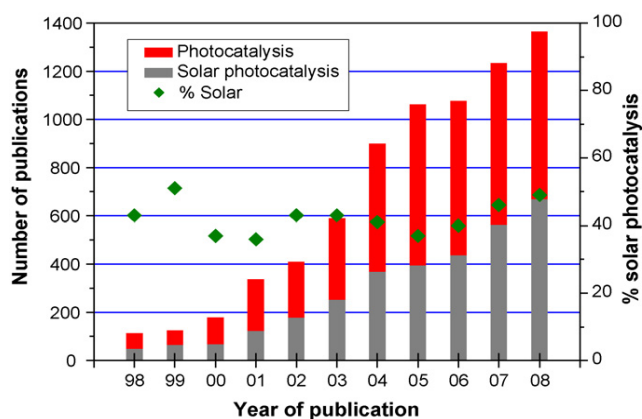


Fig. 1. Publication treating photocatalysis and the share treating solar-driven photocatalysis (source: <http://www.scopus.com>, 2009, search terms "photocatalysis" and "solar" within these results).

REVIEW:

Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO_2 using energy has reported by Malato S., Blanco J., Cáceres J., Fernández-Alba A. R., Agüera A., Rodríguez A. in 2002. They studies four water-soluble pesticides (diuron, imidacloprid, formetanate and methomyl) at pilot scale in heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton using natural-solar UV light. It has been demonstrated that photo-Fenton was more efficient than TiO_2 not only for parent compound degradation but also for TOC mineralisation. TiO_2 and photo-Fenton were found to have equal efficiencies in the case of methomyl, an aliphatic-chain pesticide [10].

Photocatalysis in water environments using artificial and solar light has been examined by Alfano O.M., Bahnemann D., Cassano A. E., Dillert R., Goslich R. in 2002. They reported that photocatalytic technologies for water and wastewater applications, either using artificial or solar light, will advantageously compete in the market, in particular, if more efficient catalysts are developed [11].

Solar photocatalytic degradation of Aldrin has been examined by Bandala E. R., Gelover S., Leal M. T., Arancibia-Bulnes C., Jimenez A., Estrada C. A in 2002. The purpose of this work was to demonstrate the application of concentrated and non-concentrated solar radiation on the photocatalytic degradation of Aldrin in water. Higher accumulated energy is necessary to complete the mineralization of the pesticide [12].

The photocatalytic degradation of dichlorvos under solar irradiation has been studied by Oancea P. and Oncescu T. in 2008. They observed that solar irradiation was a promising procedure for water detoxification, being an unpollutant and an economic method too [13].

Evaluation of operational parameters involved in solar photo-Fenton degradation of a commercial pesticide mixture has been reported by Zapata A., Oller I., Bizani E., Sanchez-Perez J. A., Maldonado M. I., Malato S. in 2009. In this paper photo-Fenton degradation of a mixture of commercial pesticides typically used in greenhouse agriculture, Vydate (10% oxamyl), Metomur (20% methomyl), Couraze (20% imidacloprid), Ditimur-401 (40% dimethoate) and Scala (40% pyrimethanil) has been evaluated. Photo-Fenton efficiency gradually rises with temperature. Nevertheless, at 50°C there was a decrease in efficiency [14].

Photodegradation of methyl parathion and dichlorvos from drinking water with N-doped TiO_2 under solar radiation has been reported by Senthilnathan J. and Philip L. in 2011. In this paper studies for the photodegradation of analytical and commercial grade methyl parathion and dichlorvos were carried out with N-doped TiO_2 and Degussa P-25 TiO_2 under UV, visible and solar radiation using batch reactor. N doped TiO_2 showed higher photocatalytic activity under solar radiation compared to UV and visible light [15].

Removal of ten pesticides from leached water at pilot plant scale by photo-Fenton treatment has been reported by Navarro S., Fenoll J., Vela N., Ruiz E., Navarro G. in 2011. They observed that the photo-assisted Fenton reaction (photo-Fenton treatment) constitutes a very good and rapid method for the reduction and even elimination of the studied pesticides, belonging to different chemical types in leaching water. After only a few minutes of photo-Fenton treatment 90% of the initial pesticide concentration (500 gL^{-1}) was removed. The residual levels at the end of the experiment (60 min) were lower than 31.5 gL^{-1} in all cases [16].

Sunlight photocatalytic degradation of propanil herbicides in aqueous solution determination of degraded products with UV and HPLC has been studied by Dhahir S. A. in the year 2011. In this paper the solar photocatalytic of an aqueous propanil were carried out under natural weathering conditions. They reported that the photocatalysis of $20 \mu\text{g/ml}$ propanil solution degraded 95.0 % of the solution after three hour of solar irradiation, by using 10 mg of zinc oxide as a catalyst [17].

Heterogeneous photocatalytic oxidation of cyprodinil and fludioxonil in leaching water under solar irradiation has been investigated by Fenoll J., Ruiz E., Hellin P., Flores P., Navarro S. in 2011. They found that ZnO appeared to be more effective in cyprodinil and fludioxonil oxidation than TiO_2 probably due to its nonstoichiometry [18].

Konstantinou I. K. and Triantafyllos A. investigated the visible light assisted photocatalytic degradation of azo dye in the presence of TiO_2 irradiated with solar and UV irradiation. They observed that the

mechanism of the photodegradation depends on the type of radiation. Charge injection mechanism takes place under visible radiation whereas charge separation occurred under UV light radiation [19].

In the year 2012, Fatin S.O., Lim H.N., Tan W.T., Huang N.M., have studied comparison of photocatalytic activity and cyclic voltammetry of zinc oxide and titanium dioxide nanoparticles toward degradation of methylene blue. They reported that, on the photocatalytic degradation of methylene blue (MB) solution using commercial ZnO and TiO₂ (P25) photocatalysts, in the form of slurry and immobilized on glass slides, under ultraviolet (UV) and solar irradiations. The average particle sizes of ZnO and P25 were 100 nm and 30 nm, respectively. Under both the irradiations, the photocatalytic activities of ZnO and P25 slurry resulted in better photocatalytic performance than the immobilized photocatalysts. Interestingly, ZnO showed better degradation capability in comparison to P25 under the solar irradiation. This result revealed that solar light provided a good source of energy to degrade MB in the presence of ZnO [20].

Jeni J., Kanmani S. have studied solar nanophotocatalytic decolorisation of reactive dyes using titanium dioxide in the year 2011. They found that, the complete color removal was achieved at optimum conditions of catalyst dose of 160 mg/l, pH=5.5 and contact time = 95 min for dye sample h-e7b and catalyst dose of 500 mg/l, pH = 7.4 and contact time = 150 min for dye sample h-e6g, respectively. at optimum conditions, COD reduced from 120 mg/l to 23 mg/l and from 108 mg/l to 17 mg/l for the two types of dye respectively[21].

In the year 2011, Yogendra. K., Naik S., Mahadevan K. M., Madhusudhana. N., have studied a comparative study of photocatalytic activities of two different synthesized ZnO composites against Coralene Red F3BS dye in presence of natural solar light. The photocatalytic decolorizing efficiencies of two synthesized ZnO composites (ZnO composite-I and ZnO composite -II) against Coralene Red F3BS dye in aqueous solution was investigated. The ZnO composites were synthesized by simple solution combustion method using hydrazine hydrate as a combustion agent and characterized by Scanning Electron Micrograph (SEM) and X-Ray Diffraction (XRD). All the photocatalytic experiments were carried out in presence of natural sunlight. By varying catalyst concentrations and pH of dye solutions, the influence of these parameters on decolorization were studied. Among the synthesized ZnO composite particles, ZnO composite-II proved to be very efficient by achieving a rapid 98% decolorization of the dye at highly alkaline condition [22].

In the year 2010, Hussein F. H. and Thekra A. have studied, solar photolysis and photocatalytic treatment of textile industrial wastewater. they have reported that, under optimal conditions, the extent of decolorization was 100% after different periods of time ranging from 10 to 100 minutes. The decolorization percentages differ with the difference in type of dye used in textile industry. The results indicate clearly that titanium dioxide and zinc oxide could be used efficiently in photocatalytic treatments of textile industrial wastewater. However, the activity fell in the sequence: ZnO > TiO₂ (Anatase) > TiO₂ (Rutile)[23].

Neppolian B., Choi H.C., Sakthivel S., Arabindoo B., Murugesan V., have studied Solar/UV-induced photocatalytic degradation of three commercial textile dyes in the year 2002. They found that the degradation efficiency of the three dyes is as follows: Reactive Yellow 17 (RY17) > Reactive Red 2 (RR2) > Reactive Blue 4 (RB4), respectively. The experimental results indicate that TiO₂ (Degussa P25) is the best catalyst in comparison with other commercial photocatalysts such as, TiO₂ (Merck), ZnO, ZrO₂, WO₃ and CdS. Though the UV irradiation can efficiently degrade the dyes, naturally abundant solar irradiation is also very effective in the mineralisation of dyes. The comparison between thin-film coating and aqueous slurry method reveals that slurry method is more efficient than coating but the problems of leaching and the requirement of separation can be avoided by using coating technique. These observations indicate that all the three dyes could be degraded completely at different time intervals. Hence, it may be a viable technique for the safe disposal of textile wastewater into the water streams [24].

CONCLUSION:

APOs are nowadays, a promising as well as a powerful tool for degradation of hazardous chemicals. Several researchers have already been using various AOPs approaches to explain optimization process. This review article explicates the theory of APOs, and provides several applications to highlight the importance of AOPs in the field of photocatalytic processes. APOs are of special interest since sunlight can be used for them. At last we can sum up that, AOPs are the most promising green technique in use.

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