# Solar photo catalytic degradation of environmental contaminants

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## Abstract
Solar energy has been proved as an innovative and promising route for the treatment of industrial effluents, waste water and for the purification of water. The solar detoxification process has challenged the effectiveness of conventional treatment processes for the degradation of environmental contaminants. The literature review of scientific and technological aspects on solar photo catalytic degradation and detoxification process has been conducted and briefly represented in the present paper.

**Key words:** Solar detoxification, effluent, metal oxide, photo-catalysis, spent wash.

## Introduction:
The major environmental problem faced today is the continuous discharge of industrial effluents and sewage into inland surface water. At present, unit treatment processes and unit operations are grouped under primary, secondary and tertiary treatments. These processes are energy intensive treat the effluent partially. Therefore, tertiary treatments involving physical, chemical and biological process are employed. The photo-chemical treatment is most advisable among these.

## Photochemical Reactions:
The photochemical processes are useful for industrial units like effluents from distilleries, pesticide industries, paper mills, pharmaceutical companies and chemical industries, but are in developing stage. The oxidation and reduction reactions are the basic mechanisms in photo catalytic treatment of water/air in their remediation and photo catalytic hydrogen production. A simplified mechanism for photo catalytic process on a semiconductor is presented in equation 1.

$$\text{Photo catalyst (e.g., } TiO_2\text{)} + hv = eCB + hVB \text{ ----------------------------- (1)}$$

For photo catalytic water/air remediation as an environmental application, valence band (VB) holes are the important elements. These induce the oxidative decomposition of environmental pollutants in which the positive hole can oxidize pollutants directly, but mostly reacting with water constituent like hydroxide ion, ($OH^-$) to produce the hydroxyl radical (•OH), which is the very powerful oxidant with the oxidation potential of 2.8 V. This •OH rapidly attacks pollutants at the surface of semi-conducting material and in solution as well and can mineralize them into $CO_2$, $H_2O$, etc. The photo catalysts have a potential to completely oxidize a variety of organic compounds, including many highly persistent organic pollutants. The reducing conduction band (CB) electrons are more important when photo catalytic reaction is applied for hydrogen production in water splitting. In order to initiate hydrogen production, the conduction band level must be more negative than the hydrogen production level. These reactions are as follows:

$$2H_2O \rightarrow 2H_2 + O_2 \quad \text{------------------------------------------------------(2)}$$

$$H_2O \leftrightarrow H^+ + OH^- \quad \text{------------------------------------------------------(3)}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{-----------------------------------------------(4)}$$

$$2H_2O \rightarrow O_2 + 4H+ + 4e^- \quad \text{-----------------------------------------------(5)}$$

Theoretical redox potential for overall reaction (eq. 2) at pH 7 is EH = -1.23 V, with the corresponding half-reactions of -0.41 V (eq 4) and 0.82 V (eq 5). It, gives a Gibbs energy ($G_o$) = +237 kJ/mole (Li et al., 2000). A large number of metal oxides and sulfides are primarily active under UV irradiation having wavelength < 385 nm or electron band gap ($E_{bg}$) energy =3.0 eV which is present in only a small portion of solar light (Vinodgopal et al., 1994; Li et al., 2000). For example, $TiO_2$ has a wide band-gap energy of 3.0 ~ 3.2 eV. It prevents the utilization of visible-light that accounts for most of solar energy. More recently, significant efforts have also been made to develop new or modified semiconductor photo catalysts which are capable of using visible-light (wavelength 400–700 nm) including metal ion doping, nonmetallic element doping, and sensitization with organic dyes or small band-gap semiconductors like CdS, MgO and CaO. There is no general rule at all, each case being completely different (Goslich et al., 1997, Malato et al., 2002).

**Solar photo catalytic degradation of contaminants**

In general, the types of polluting compounds that have been degraded include alkanes, halo alkanes, aliphatic alcohols, carboxylic acids, aromatics, halo aromatics, polymers, surfactants, herbicides, pesticides, and dyes (Malato et al., 2003).

The photo catalysis mineralizing the contaminants into carbon dioxide, water, and inorganic, practical applications of solar technologies have been studied and developed most intensively for heterogeneous $TiO_2$ or ZnO photo catalysis. There is no general rule at all, each case being completely different than another (Goslich et al., 1997, Malato et al., 2002). In general, the types of compounds or contaminants that have been degraded include alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, halo aromatics, polymers, surfactants, herbicides, pesticides, and dyes (Malato et al., 2003). The review of literature (Bahnemann et al., 1991; Chiou et al., 2008; Okamoto et al., 1985; Rincn and Pulgarin, 2003; Topalov et al., 2000) reveals that much work appears on the photo-catalytic activity of $TiO_2$ for the removal of salts, color and other organic and inorganic impurities and almost no systematic work is conducted on the other photo-catalytic materials like MgO, ZnO and CaO.

**Potential application of solar detoxification:**

Since 1972, when Fujishima and Honda discovered the photo-catalytic splitting of water molecules using $TiO_2$ electrodes, research on the heterogeneous photo-catalysis started growing rapidly. The applications have been directed towards environmental cleanup. The other applications of the technique have been implemented in many fields such as, drinking water treatments, industrial effluent treatments or health applications. Some of these are as follows:

**1. Destruction of organics:**

Photo-catalysis has been used for the destruction of variety of organic compounds such as alcohols, carboxylic acids, phenol derivatives or chlorinated aromatic into harmless or least harmful products like $CO_2$, $H_2O$ and simple minerals acids (Balasaraswathy, 2004; Huang, 1991; Mehos and Turchi, 1992; Turchi et al., 1993; Wyness, 1994). Water contaminated by oil can be treated efficiently by photo-catalytic reactions (Canela, 1999). Herbicides and pesticides such as 2, 4, 5trichlorophenol, 5-triazine herbicides and DDT which contaminate the water can be also mineralized (Alfano et al., 2000).

**2. Removing trace metals:**

Trace metal such as (Hg), chromium (Cr), lead (Pb) and others metals and metallic compounds are considered to be highly health hazardous. These find their way through the water. The environmental application of heterogeneous photo-catalysis includes removal of heavy metals such as Hg, Cr, Pb, Cd, As, Ni, Cu (Alfano et al., 2000; Hofl et al., 1997). Removals of these toxic metals are essentially important for human health and water quality. The photo reducing ability of photo-catalysis has been used to recover expensive metals from industrial effluent such as gold, platinum and silver (Alfano et al., 2000).

**3. Removing inorganic compounds:**

The organic compounds are sensitive to photochemical transformation on the catalyst surfaces. Inorganic species such as bromated or chlorated azide, halide ions, nitric oxide, palladium and rhodium species and sulfur species can be decomposed (Balasaraswathy, 2004; Blanco and Malato, 2001). The metal salts such as $AgNo_3$, HgCl and organometallic compounds (ex.$CH_3HgCl$) as well as cyanide, thio-cyanide, ammonia, nitrate and nitrites can be removed from water or waste water (Hofl et al., 1997; Wyness et al., 1994).

**4. Water disinfections:**

Photo-catalysis can also be used to destroy bacteria and viruses. *Streptococcus mutants, Streptococcus natuss, Streptococcus cricetus, Escherichia coli, Lactobacillus acidophilus, Scaccharomyces cerevisisas*, poliovirus were destructed effectively using heterogeneous photo catalysis (Priya et al., 2008).

**5. Degradation of natural organic matter:**

Humic substances (HS) are known to affect the behavior of some pollutants significantly in naural environments, such as traces of metal speciation and toxicity (Davis et al., 1994) solubilization and adsorption of hydrophobic pollutant (Blake et al., 1991) and aqueous photochemistry (Topalov et al., 2000).

Advanced oxidation process has been applied to decrease the organic content in water including humic acids (Kim et al., 1998; Matthews, 1990; Muneer and Bahnemann, 2001; Obee, 1996). It has the advantage of not leaving any toxic byproducts, residue or sludge. The first pioneer work in this field carried out by Bekbolet in 1996 who studied the effectiveness of photo-catalytic of humic acid (Li et al., 2000).

**6. Photo-catalysis and waste water treatment:**

The emphasis on treatment technology, including advance oxidation process (AOPs), and solar irradiation, was placed on their basic principles, applications, and new technological developments. Merits and demerits of these technologies are compared to highlight their current limitations and future research needs [Ollis et al., 1991]. The major applications investigated for this technology are for the removal of colour [March et. al.,1995; Vinodgopal et al., 1994], reduction of chemical oxygen demand [Mills, 2002; Nogueira and Jardim, 1996], degradation of harmful fungicides, herbicides, and pesticides [Klausner et al., 1994;Zou et al., 2005], destruction of hazardous inorganic such as cyanides [Pare, 2008], treatment of heavy metals [Chiou et al., 2008; Sharma et al., 2008], mineralization of hazardous organic wastes [Al-Ekabi, 1989; Turchi and Ollis, 1990], purification and disinfection of water [Al-Ekabi and Serpone, 1988], destruction of malodorous compounds [Canela et al., 1999], decontamination of soil [Hamerski et al., 1999], decontamination of indoor air [Jacoby, 1995; Obee, 1996] and destruction of cancer cells [Blake et al., 1999; Okamoto et al., 1985]. The efficiency of $TiO_2$, photo-fenton and the modified photo-fenton (ferrioxalate) reagent in the presence of solar irradiation was evaluated for the organic content reduction in terms of dissolved organic carbon of a municipal or the industrial wastewater [Ahmad and Olli's, 1984].

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