

## 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.

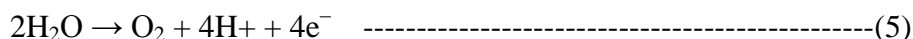
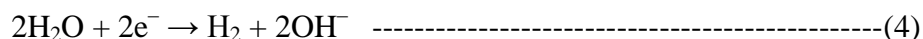
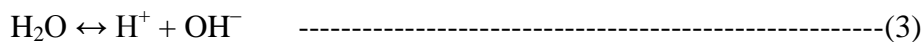
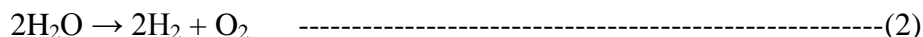
### Photochemical Reactions:

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.



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, ( $\text{OH}^-$ ) to produce the hydroxyl radical ( $\bullet\text{OH}$ ), which is the very powerful oxidant with the oxidation potential of 2.8 V. This  $\bullet\text{OH}$  rapidly attacks pollutants at the surface of semi-conducting material and in solution as well and can mineralize them into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , 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:



Theoretical redox potential for overall reaction (eq. 2) at pH 7 is  $E_H = -1.23$  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,  $\text{TiO}_2$  has a wide band-gap energy of  $3.0 \sim 3.2$  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  $400\text{--}700$  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  $\text{TiO}_2$  or  $\text{ZnO}$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  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<sub>2</sub>, H<sub>2</sub>O 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, 5-trichlorophenol, 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<sub>3</sub>, HgCl and organometallic compounds (ex.CH<sub>3</sub>HgCl) 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<sub>2</sub>, 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].

### References:

- Ahmed, S. Ollis, D. F., (1984). "Solar Photoassisted catalytic decomposition of the chlorinated hydrocarbons Trichloroethylene and Trichloromethane," *Solar Energy*, Vol.32 (5), pp.597-601.
- Al-Ekabi, H., Serpone, N., (1988). "Kinetic studies in Heterogeneous Photocatalysis: 1. Photocatalytic Degradation of Chlorinated Phenols in Aerated Aqueous Solutions over TiO<sub>2</sub> Supported on a Glass Matrix," *Journal of Physical Chemistry*, Vol. 92, pp.5726-5731.
- Al-Ekabi, H., Serpone, N., (1989). "Kinetic studies in Heterogeneous Photocatalysis", *Langmuir*, Vol.5, pp. 250-255.
- Alfano, O.M., Bahnenabb, D., Cassano, A. E., Dillert, R. Goslich, R., (2000). Photocatalysis in water environments using artificial and solar light, *Catal. Today*. 58, 199-230.
- Bahnemann, D., Bockelmann, D. Goslich, R., (1991). Mechanistic studies of water detoxification in illuminated TiO<sub>2</sub> suspensions, *Solar Energy Materials*. 24, pp. 564-583.
- Balasaraswathy, P., (2004). Paper presented in National Conference of Indian Association of Dermatology. *Sunlight in India*.
- Blake, D. M., Maness, P., Huang, Z., Wolfrum, E. J., Huang, J., (1999). Application of the Photocatalytic Chemistry of Titanium Dioxide to Disinfection and the Killing of Cancer Cells in Separation and Purification Methods, *Environ. Sci. Technol.* 28, pp. 1-50.
- Blake, D.M., Webb, J., Turchi, C. Magrini, K., (1991). Kinetic and Mechanistic Overview of TiO<sub>2</sub>- Photocatalyzed Oxidation Reactions in Aqueous Solution, *Sol. Energy Mater.* 24, pp. 584- 593.
- Blanco, J., Malato, S. (2001). *Solar detoxification technology*, Part B, Chapter 6, UNESCO Publication.

Canela, M.C., Alberici, R.M., Sofia, R.C.R., Eberlin, M.N., Jardim, W.F., (1999). Destruction of Malodorous Compounds Using Heterogeneous Photocatalysis, *Environ. Sci. Technol.* 33 pp. 2788-2792.

Chiou, C.H., Wu, C.Y. Juang, R.S., (2008). "Photocatalytic degradation of phenol and m-nitrophenol using irradiated TiO<sub>2</sub> in aqueous solutions" *Separation and Purification Technology*, Vol. 62(3), pp. 559-564.

Goslich, R., Dillert, G. Bahnemann, (1997). Solar Water Treatment: Principal and Reactors, *Wat. Sci. Tech.* 35, pp. 137-148.

Hamerski, M., Grzechulska, J. Morawski, A.W., (1999). Photo-catalytic purification of soil contaminated with oil using modified TiO<sub>2</sub> powders, *Sol. Energy.* 66, pp. 395-399.

Hofl, C., Sigl, G., Specht, O., urdack, I. Wabner, D., (1997). Oxidative degradation of AO<sub>x</sub> and COD by different advanced oxidation processes: A comparative study with two samples of a pharmaceutical wastewater, *Water Sci. Technol.* 35 pp. 257-264.

Jacoby, W.A., Blake, D.M., Noble, R.D., Koval, C.A., (1995). Kinetics of the Oxidation of Trichloroethylene in Air via Hetero-geneous Photocatalysis, *J. Catal.* 157, pp. 87 -86.

Kim, B.R., Podsiadlik, D.H., Kalis, E.M., Hartlund, J.L., Gaines, W. A., (1998). Photochemical Destruction of Cyanide in Landfill Leachate, *J. Environ. Eng.* 124, pp. 1108-1113.

Klausner, J.F., Martin, A. R., Goswami, D.Y., Schanze, K.S., (1994). "On the accurate determination of reaction rate constants in batch type solar photocatalytic oxidation facilities," *Journal of Solar Energy Engineering*, Vol.116 (1), pp.19-24.

Li, X.Z., Yue, P.T., Mak, C.L., (2000). Photooxidation of wool dyeand TCP in aqueous solution using an innovative TiO<sub>2</sub> mesh electrode, *Water Sci. Technol.* 42, pp. 181-188.

Malato, S., Blanco, J., Caceres, J., Fernandez, A.R., Aguera, A., Rodriguez, A., (2002). Photocatalytic treatment of water-soluble pesticides by photo-fenton and TiO<sub>2</sub> using solar energy, *Catal. Today.* pp. 209-220.

Malato, S., Blanco, J., Vidal, A., Alarcon, D., Maldonado, M. I., Caceres, J., Gernjak, W., (2003). Applied Studies in Solar Photocatalytic Detoxification: An Overview, *Sol. Energy.* 75, pp. 329-336.

- March, M., Martin, A., Saltiel, C., (1995). "Performance Modeling of Nonconcentrating Solar Detoxification systems", *Solar Energy*, Vol.54 (3), pp. 143-151.
- Matthews, R.W., (1990). Purification of water with near UV illuminated suspensions of titanium dioxide, *Water Res.* 24, pp. 653-660.
- Mehos, M., Turchi, C., (1992). Measurement and analysis of near ultraviolet solar radiation, *Solar Eng.* pp. 51-55.
- Mills, A., Elliott, S. N., Parkin, I. P., O'Neill, S.A., Clark, R.J., (2002). "Novel TiO<sub>2</sub> CVD films for semiconductor photocatalysis" *Journal of Photochemistry Photobiology A: Chemistry*. Vol.151, pp.171-179.
- Muneer, M. Bahnemann, D., (2001). Semiconductor-Mediated Photocatalysed Degradation of Two Selected Pesticide Derivatives, Terbacil and 2, 4, 5-Tribromoimidazole, in Aqueous Suspension, *Water Sci. Technol.* 44, pp. 331-338.
- Obee, T.N., (1996). Photooxidation of Sub-Parts-per-Million Toluene and Formaldehyde Levels on Titania Using a Glass-Plate reactor, *Environ. Sci. Technol.* 30, pp. 3578-3580.
- Okamoto, K., Yamamoto, Y., Tanaka, H., Tanaka, M., Itaya, A., (1985). Heterogeneous photocatalytic decomposition of phenol over TiO<sub>2</sub> powder, *Chem. Soc. Jpn.* 58, pp. 2015-2022.
- Ollis, D. F., Pelizzetti, E., Serpone, N., (1991). "Photo-catalyzed destruction of water contaminants." *Environmental Science and Technology*, Vol. 35, pp. 971-976.
- Pare, B., Jonnalagadda, S.B., Tomar, H., Singh, P., Bhagwat, V.W., (2008). "ZnO assisted photocatalytic degradation of cridine orange in aqueous solution using visible irradiation", *Desalination*, Vol. 232(1-3), pp. 80-90.
- Priya, S.S., Premalatha, M., Anantharaman N., (2008). Solar Photocatalytic Treatment of Phenol Wastewater Potential, challenges and opportunities, *International J. App. Eng. Res.* 3 pp. 36-41.
- Rincn, A. G. Pulgarin, C., (2003). Photocatalytical inactivation of E. coli: effect of (continuous/intermittent) light intensity and of (suspended-fixed) TiO<sub>2</sub> concentration, *Applied Catalysis B: Environmental.* 44 pp. 263-284.

Sharma, S. D., Saini, K.K., Kant, C., Sharma, C.P., Jain, S.C., (2008). "Photodegradation of dye pollutant under UV light by nano-catalyst doped titania thin films" *Applied Catalysis B: Environmental*, Vol.84 (1- 2), pp. 233-240.

Topalov, A., Molnar-Gabor, D., Kosanic M., Abramovic, B., (2000). Photomineralization of the Herbicide Mecoprop Dissolved in Water Sensitized by TiO<sub>2</sub>, *Water Res.* 34 pp. 1473-1478.

Tseng, J. M. Huang, C.P., (1991). Removal of chlorophenols from water by Photocatalytic Oxidation, *Water Sci. Technol.* 23 pp. 377-387.

Turchi, C. S. Ollis, D.F., (1990). "Photocatalytic Degradation of organic water contaminants: mechanisms involving hydroxyl radical attack, *Journal of Catalysis*. Vol.122, pp. 178-192.

Turchi. C.S.,Klausner J.F., and Marchand, E., (1993). Field test results for the solar photocatalysis detoxification of fuel-contaminated ground water, *Chemical Oxidation: technology for the Nineties, 3rd International Symposium*.

Vinodgopal, K., Bedja, I., Hotchandani, S., Kamat, P. V., (1994). "A photocatalytic approach for the decolorization of textile azo dyes in colloidal semiconductor suspensions." *Langmuir*, Vol.10 (6), pp.1767- 1771.

Wyness, P., Klausner, J. F., Goswami, D. Y., Schanze, K. S., (1994). "Performance of concentrating solar photocatalytic oxidation reactors, part 1: flat-plate configuration." *Journal of Solar Energy Engineering*, Vol.116, pp. 2-7.

Zou, L., Li, Y., Hu, E., (2005). "Photocatalytic Decolorization of Lanazol Blue CE Dye Solution Using a Flat Plate reactor" *Journal of Environmental Engineering* , Vol. 131(1), pp.102-107.

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