

## A REVIEW OF HETEROGENEOUS SEMICONDUCTOR PHOTOCATALYSIS OF ORGANIC CONTAMINANTS

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### ABSTRACT

Photocatalysis is a rapidly expanding technology for effluent treatment. In this review, an insight into the theoretical aspects involved in the treatment is discussed. The effects of adsorption, intensity of light, pH, presence of anions and mechanistic pathway for pollutants removal have been specifically covered. An analysis of the available literature data has been made and general conclusions have been drawn on the above mentioned effects.

**KEYWORDS :** Photocatalysis, Semiconductor, Industrial effluents

### I. INTRODUCTION

Industrial effluents comprises a large number of toxic, refractory compounds ranging from aliphatics, aromatics, metals, alkalis, cyanides, high concentration of suspended matter, gases which have deleterious effects on the receiving environment. To reduce the impact of these pollutants on receivers, it is necessary to find a treatment process which is cost effective and environmentally friendly. At present several methods have been developed to treat these pollutants with certain limitations. The physicochemical treatment like coagulation, flocculation, floatation, membrane processes, includes nano- filtration, reverse osmosis or activated carbon results in phase transfer of pollutants without abating them. The biological methods are not suitable for treating industrial effluents as the microbes loses its activity in these effluents. In this direction, destructive treatment methods like advanced oxidation processes (AOP's) are currently employed for the complete abatement of pollutants in the environment. AOP's are based on the generation of highly reactive, non selective transient hydroxyl radical ( $\text{OH} \cdot$ ,  $E_0 = 2.8 \text{ V vs NHE}$ ) act as an oxidant for degrading the pollutants. The hydroxyl radicals are generated by combining either the oxidants like  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  or semiconductor with UV/Solar light. The generation and utilization of these oxidants in treating the pollutants is costlier which therefore restricts its commercial applicability.

### II. MATERIALS AND METHODS

On the other hand, semiconductor photocatalysis is gaining importance over other competing AOP's due to (1) its complete mineralization of refractory organic compounds (2) no waste disposal (3) low cost and (4) operated at ambient temperature and pressure. In this

process, semiconductors that promote reactions in the presence of light are not consumed in the overall reaction and are regarded as photocatalyst. The characteristics of the photocatalyst are (1) photoactive (2) able to utilize UV/Solar light (3) chemically and biologically inert (4) not prone to corrosion (5) inexpensive and (6) non toxic. The semiconductor photocatalyst includes Si,  $\text{TiO}_2$ , ZnO,  $\text{WO}_3$ , CdS, ZnS,  $\text{SrTiO}_3$ ,  $\text{SnO}_2$ ,  $\text{WSe}_2$ ,  $\text{Fe}_2\text{O}_3$ . The band gap energies for the photocatalyst is given in Table I. (Rajeshwar 1995)

**Table-1. Band Gap energies**

| Photocatalyst           | Band gap energy (eV) | Photocatalyst             | Band gap energy(eV) |
|-------------------------|----------------------|---------------------------|---------------------|
| Si                      | 1.1                  | ZnO                       | 3.2                 |
| $\text{TiO}_2$ rutile   | 3.0                  | $\text{TiO}_2$ anatase    | 3.2                 |
| $\text{WO}_3$           | 2.7                  | CdS                       | 2.4                 |
| ZnS                     | 3.7                  | $\text{SrTiO}_3$          | 3.4                 |
| $\text{SnO}_2$          | 3.5                  | $\text{WSe}_2$            | 1.2                 |
| $\text{Fe}_2\text{O}_3$ | 2.2                  | $\text{A Fe}_2\text{O}_3$ | 3.1                 |

The photocatalyst act as a sensitizer for the light induced redox processes due to their electronic structure which are characterized by filled valence band (VB) and an empty conduction band (CB). The minimum wavelength required to promote an electron depends on the band gap energy of the photocatalyst and is given by  $E_{bg} = 1240/\lambda_{\min}$  when a photon with an energy of  $h\nu$  matches or exceeds the band gap energy of the photocatalyst or with an ' $\lambda$ ' either equal to or greater than  $\lambda_{\min}$  is applied on the photocatalyst, an electron ( $e^-$ ) from VB is promoted to the CB leaving behind a hole ( $h^+$ ). The excited state CB electrons and VB holes can react with electron donors and acceptors adsorbed on the photocatalyst surface and a subsequent redox reaction occurs. In the absence of electron and hole scavengers, the input energy is dissipated as heat within a few nanoseconds by

recombination. The redox potential of the VB holes must be sufficiently positive (+1.0 to +3.5 V vs NHE) to generate  $\cdot\text{OH}$  radicals which are responsible for the degradation of the pollutants. The redox potential of the CB electrons must be sufficiently negative (+0.5 to -1.5V vs NHE) to act as good reductants in order to reduce the adsorbed  $\text{O}_2$  to superoxide. The schematic representation of the process taking place at the catalyst surface is shown in Fig 1 (Legrini 1993)

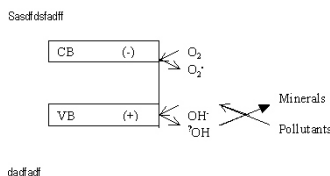


Fig. 1 Schematic representation of the processes taking place at the catalyst surface.

### Photocatalyst

To oxidize organic pollutants, the valence band location at the semiconductor electrolyte interface has to be positive potential as symbolized by the semiconductors  $\text{TiO}_2$ ,  $\text{ZnO}$  and  $\text{CdS}$ . Some of the semiconductors listed above suffer from its photodegradation applicability. For example n-Si photocatalyst are poor in photooxidation kinetics. Metal sulphides are unstable as they undergo photoanodic corrosion while  $\alpha\text{-Fe}_2\text{O}_3$  undergoes photocathodic corrosion. Hence  $\text{TiO}_2$  and  $\text{ZnO}$  appear to be preferred photocatalyst in degrading the organics. A lot of research work is available on photocatalysis in terms of mineralization of the pollutants, reaction mechanism, degradation of individual compounds, comparison of different photocatalysts etc., (Ollis *et al*), Hoffmann *et al*; Mills *et al* (1993). Mills *et al* (1997) reviewed the semiconductor sensitized photosynthetic and photocatalytic processes for the removal of organics, destruction of cancer cells, bacteria and viruses. The objective of this review paper is to assess the current status of the technology available for the commercial implementation of the process. The chemical parameters that affect the photocatalysis process like nature of light, nature of photocatalyst, pH, presence of other anions, degradation schemes are also reviewed in this paper.

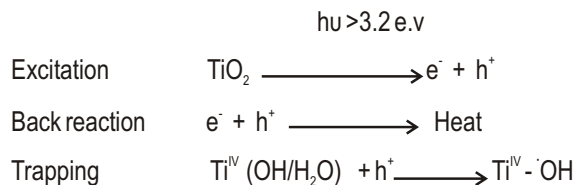
Generally if the pollutant is organic in nature, the preferred photocatalyst is  $\text{TiO}_2$ . The range of organics that can be mineralized using  $\text{TiO}_2$  as photocatalyst includes aliphatics, aromatics, dyes, detergents, pesticides and herbicides. The photoreactivity of  $\text{TiO}_2$  varies with varying % of anatase and rutile. Mills *et al* (1993) and Martin *et al* concluded that rutile form of  $\text{TiO}_2$  is inactive or much less

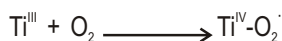
active in photodegradation while  $\text{TiO}_2$  in anatase form appears to be efficient in mineralizing the organics. Apart from  $\text{TiO}_2$  in anatase form, two commercial  $\text{TiO}_2$ , Degussa P-25 and Hombikat UV 100 are also used in treatment processes. Degussa P-25 is a non porous 70:30% (anatase to rutile) mixture with a BET surface area of  $55 \pm 15 \text{ m}^2 \text{ g}^{-1}$  and has a crystalline size of 30 nm in  $0.1 \mu\text{m}$  diameter aggregates. In recent years, Degussa P-25 has been set as the standard for photooxidation of many pollutants like phenols, pesticides, VOC's and also in gas phase purifications. Kirchnuova *et al* has compared the efficiency of Degussa P-25 and Hombikat UV 100 on photomineralization of n-butanol which showed that Degussa P-25 performed better than Hombikat UV100. Instead of using bare  $\text{TiO}_2$  powders, researchers have investigated the effect of  $\text{TiO}_2$  immobilized on various supports like activated carbon (Alana *et al*), porous silica (Marugan *et al*), Pt modified porous membrane (Tsuruchi *et al*) for the degradation of alcohols.

After  $\text{TiO}_2$  the photocatalyst which is extensively used in photooxidation of organics is  $\text{ZnO}$ . The degradation of individual compounds, diazinon, methyloange were studied by Daneshwar *et al* and Wang *et al* using  $\text{ZnO}$  as a photocatalyst. Kansal *et al* compared the photodegradation efficiency of lignin using  $\text{TiO}_2$  and  $\text{ZnO}$ . It has been found that  $\text{ZnO}$  had better catalytic activity in the presence of solar light than  $\text{TiO}_2$ . But the work of Ergenidou *et al* on dichlorovos suggests that in the presence of UV light  $\text{TiO}_2$  resulted in complete mineralization while  $\text{ZnO}$  resulted in the disappearance of pollutants. Even though, several researches reported that photodegradation of organics using  $\text{ZnO}$  as an alternative to  $\text{TiO}_2$ , at high pH it is unstable, undergoes dissociation to  $\text{Zn}(\text{OH})_2$  on the  $\text{ZnO}$  particle surface leading to deactivation of the catalyst which makes  $\text{TiO}_2$  as a suitable catalyst for degradation.

### Reaction scheme for photocatalysis

The first step in the photocatalysis reaction is the excitation of  $\text{TiO}_2$  by radiating sufficiently energetic photons ( $\lambda < \lambda_{\text{min}}$ ) to produce an  $e^-/h^+$  pair. When water dissociates on pure  $\text{TiO}_2$  surface, two distinctive hydroxyl groups are formed. These hydroxyl groups will react with holes generated to produce  $\cdot\text{OH}$  radicals (Turchi and Ollis) and its reactions are given below.





The organic pollutants (S) are adsorbed on  $\text{TiO}_2$  surface site



The hydroxyl radicals attack the organic pollutant resulting in the formation of intermediates (Q)



Hydroxyl radicals attack the intermediates (Q) till they are completely mineralized or to further degraded products (R) which are dependent on the concentration of  $\cdot\text{OH}$  radicals and the nature of products (Q and R) formed.



Other reactions includes



The above mechanism suggests that hydroxyl radicals are formed not only via hole but also by  $\text{H}_2\text{O}_2$  through superoxide radical (Okamoto et al). Tunesi and Anderson suggests that  $\text{H}_2\text{O}_2$  produced by the above mechanism undergoes decomposition to  $\cdot\text{OH}$  radicals which further reacts with degraded products resulting in almost complete mineralizing of the pollutant.

### III. RESULTS AND DISCUSSION

#### Effect of light

The UV light provides the photons required for the electron transfer from VB to CB of the photocatalyst. The energy of a photon is related to its wavelength ( $\lambda$ ) and the overall energy input of the photocatalytic processes. Mathews and McEvoy showed that the presence of shorter wavelength (254 nm) is more effective than radiation at 354 nm due to the fact that shorter wavelength is associated with greater photon energy during their degradation study on salicylic acid. Hofstalter also reported that shorter wavelength resulted in higher degradation rate of 4-chlorophenol with smaller amount of intermediates formed.

The nature of light source also affects the degradation due to emission of either different wavelength or range of wavelengths. Chapius et al studied the oxidation of VOC's in indoor air quality using fluorescent

visible light and UV light and found that fluorescent visible light is less efficient than UV Black light. Benoit Marque et al observed that the degradation rate was higher in  $\text{TiO}_2$  irradiated from XeCl excimer than radiation from mercury arc lamp for butanol and butylamine compounds. Ollis et al stated at low intensities the degradation rate increased linearly while at intermediate intensity the degradation rate dependent on the square root of intensity. At higher intensity, the rate is independent of the intensity.

#### Effect of adsorption

As seen in the reaction schemes discussed above, the degradation of pollutants occurs on the surface of the photocatalysts. The substrates which are adsorbed strongly degrades faster which indicates that photocatalysis is a surface reaction. Several investigators also observed a close relationship between surface adsorbability and degradation rate. Subramanian et al and Tanaka et al showed as the adsorption of the substrate/pollutant increases the degradation rate is also increased during their study on p-hydroxy benzoic acid and dyes respectively.

#### Effect of pH

The pH of the solution may affect the surface change of the photocatalyst and the ionization state of the pollutant which ultimately determines its adsorbability to the catalyst. Adsorption is maximum at zero point charge ( $pZ_{\text{pc}}$ ) the pH at which degradation rate is maximum. If the pollutant is weakly acidic, the degradation rate increases at low pH due to increase in adsorption. If the pollutant undergoes hydrolysis at alkaline pH, there will be rise in degradation rate at higher pH. Moreover, the concentration of  $\cdot\text{OH}$  radicals is relatively higher which in turn increases the degradation rate at alkaline pH (Trillas et al). If the pollutant dissociates or form radicals at a certain pH range, the increase in degradation rate is specific to the nature of the substrate which is observed in the findings reported by Tanaka and Saha for TCP photocatalysis.

#### Effect of other ions

Effluents, surface waters, ground waters may contain apart from the pollutants, different salts of varying concentration. The salts are in ionized state in the solution which affects the adsorption of target pollutants and act as scavengers of  $\cdot\text{OH}$  radicals and UV light. Abdullah et al studied the effect of inorganic anions on photocatalytic oxidation of organic carbon. The presence of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  retards the photocatalysis reaction while nitrates, perchlorate ions had a negligible effect on photocatalysis. Haarstrick et al also observed the negative effect of chloride and bicarbonate ions on the degradation of 4-chloro phenol and p-toluene sulphonic acid. The detrimental effect of various anions was suggested by Yawalkar et al during the degradation of the phenol and the

order is as follows:  $\text{SO}_4^{2-} < \text{CO}_3^{2-} < \text{Cl}^- < \text{HCO}_3^-$ . In general,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{Cl}^-$  have a greater negative effect on degradation rate due to adsorption of these ions as well as their reaction with  $\cdot\text{OH}$  radicals.

#### Degradation Schemes

The nature of organic compounds, aliphatic, aromatic and the functional group attached play a vital role in the degradation rate. The degradation of organics is also dependent on the adsorption of substrate on  $\text{TiO}_2$  surface. Degradation schemes for aliphatic alcohols, ketones, amines were studied by Hatipoglu, Vincent et al; and Blake and Griffin respectively. In case of aliphatics, the  $\cdot\text{OH}$  radicals generated abstracts the 'α' hydrogen atom via meta thesis reaction resulted in a 'C' centered radicals. These radicals formed undergoes reaction with molecular oxygen to form hydroxylated peroxy radical as in the case of alcohols or undergoes β scission to form methyl radical and ketene in case of ketones. The ketenes formed undergo further oxidation to form peroxy radicals. The peroxy radicals formed undergoes oxidation to form either degraded products or to complete mineralization.

In case of aromatics, the  $\cdot\text{OH}$  radicals attack at different positions on the aromatic ring depending upon the directing effect of the functional group. The functional group containing lone pair of e<sup>-</sup>s like O<sup>-</sup>,  $\text{NR}_2$ , OH, OR,  $\text{NHCOR}$ ,  $\text{OCOR}$ , SR, X<sup>-</sup> are electron donating (+I) groups. These groups on photocatalysis yield ortho/para directing hydroxylated intermediates. The benzene derivative with functional group of O<sup>-</sup> will have highest degradation rate and the rate decreases in the above order mentioned. In the case of electron withdrawing groups (-I) like  $\text{NR}_3^+$ ,  $\text{NO}_2$ , CN,  $\text{SO}_3\text{H}$ , CHO, COR, COOH, COOR,  $\text{CONH}_2$ ,  $\text{NH}_3^+$  the benzene derivative with  $\text{NR}_3^+$  functional group shows the highest degradation rate and the rate decreases in the order mentioned (Bhatkande, Pangakar et al). The hydroxylated intermediates undergo further reaction with  $\cdot\text{OH}$  radicals with a cleavage of aromatic ring resulting in the formation of short chain aliphatic compounds. On further oxidation, these compounds are either completely mineralized or forms highly oxygenated compounds.

#### IV. CONCLUSION

In this review paper, the chemical (reaction) parameters which affect the degradation processes have been discussed. The effect of adsorption has been analyzed and found that the pollutants which are readily adsorbed are degraded at a faster rate indicating that the process is a surface phenomenon. The effect of various anions and pH has been discussed and observed that knowledge of dissolved salts is essential for the application of the photocatalysis to actual industrial effluents. It has been found that the nature of light source and catalyst (immobilized or powdered photocatalyst) also affects the operation of the photocatalysis process.

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