

## **A REVIEW OF SOLAR PHOTOCATALYTIC DEGRADATION OF WASTEWATER USING ADVANCED OXIDATION PROCESSES**

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### **ABSTRACT**

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**In the 21<sup>st</sup> Century, Majority of water pollution is caused due to incorrect discharge of waste products into the water bodies. These pollutants can be categorized as dyes, textiles, pesticides and hydrocarbons. This review paper deals with a comprehensive analysis of various methods for degradation of these pollutants in water. Due to the efficient mineralization of organic compounds; advanced oxidation process is gaining relevance in the industries. The Photochemical AOP is the predominant way of degradation amongst various oxidation processes.**

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### **INTRODUCTION**

In Post-industrial era the effluent waste water released from factories are toxic endocrine disrupting, mutagenic or potentially carcinogenic to humans, animals and aquatic life in general.

There are various ways for the treatment of wastewater, which are categorized as Physical which includes treatment by screening, sedimentation, floation and filtration of the contaminants present in the H<sub>2</sub>O; The chemical method which comprises of precipitation, coagulation, carbon filtering and disinfection. The most widely used technique is a combination of physical and chemical processes which include activated carbon adsorption, multiple oxidation and reduction reactions, and ion exchange and membrane

processes. One such emerging physio-chemical technique is the Advanced Oxidation Processes or the (AOP's).

Advanced Oxidation Processes (AOPs) have been proposed as of late as an appealing option for the medication of polluted ground, surface, and wastewater holding pesticides or natural effluents. The most frequently utilized AOPs uses hydrogen peroxide, dissolved oxygen as their oxidant. Amongst AOPs, the combination of (ultra violet / titanium dioxide / hydrogen peroxide) and (ultra violet / hydrogen peroxide) are acknowledged as the most guaranteeing for the remediation of polluted waters. (Babuponnusami *et al.*, 2015)

The advantage of AOP is that they provide many ways for the production of intermediate transitory

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radicals & thus increases the flexibility for specific chemical treatments. AOPs are classified according to the reactive phase (homogeneous and heterogeneous) or by formation of transient radical methods (chemical, electro-chemical, sono-chemical and photochemical). Generally Homogeneous catalysis utilizes Photo-Fenton technology while Heterogeneous catalysis comprises TiO<sub>2</sub> and Hydrogen Peroxide.

It is to be noted that abundant solar energy is present to generate free radicals at no cost. Hence, Photochemical advanced oxidation process is preferred over other methods. This review paper gives a summary of the understanding of the mechanism of heterogeneous, homogeneous Photocatalysis and equipment's used in the process of photocatalysis i.e. (through photochemical AOP). The paper also analyses the demerits of the aforementioned process and the alternatives used to overcome them.

### Photocatalysis Mechanism

#### Heterogeneous photo catalysis Mechanism

The semiconductor titanium dioxide has been widely used as a photocatalyst for starting a chain of redox reactions on its exterior. The catalyst behaves as if it has a single e- in its ultimate orbital. The mechanism of this type of photocatalysis can be summarized as below:

When sunlight having sufficient energy falls on the surface of titanium dioxide ( $\lambda < 400$  nm) the e- gets excited and fills the conduction band in nanoseconds which in turn generates an electron hole pair (Bahnemann *et al.*, 2004)

The electron scavenger like dissolved oxygen gets reduced to O<sup>2-</sup> in the conduction band and the pollutant (P) gets consecutively gets oxidized to (P<sup>+</sup>). It was also seen that in the absence of H<sub>2</sub>O, hydroxyl radicals couldn't be created and hence slowed down the process of photocatalytic degradation. This also confirms the reports from few papers that the heterogeneous photocatalytic reaction couldn't start without the presence of H<sub>2</sub>O.

The reduced superoxide ion (O<sup>2-</sup>) and the hydroxyl radical formed after the hydrolyzing of water help in the degradation of the effluent (P<sup>+</sup>) to convert it into carbon dioxide and water. In case of aromatic pollutant compounds first hydroxylation by electrophilic aromatic substitution mechanism takes place. Further oxidation leads to ring opening which in turn converts itself into carboxylic acids and aldehydes. In certain cases these carboxylic acids undergo decarboxylation reaction to form harmless carbon dioxide

and water. It is also worthwhile to note that the amount of successive oxidation of pollutant depends on the time for which reaction takes place as more reaction time leads to more surface activation of semiconductors which in turn forms more radical species which facilitate the degradation of the pollutant.

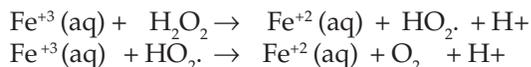
The physical mechanism of any heterogeneous photocatalytic process follows that of adsorption. Firstly the mass transfer of the effluent from the bulk phase (liquid) to that of the semiconductors surface takes place. In the second step the pollutant gets adsorbed to the photon activated surface of the semiconductor. Then photocatalytic reactants convert the initial pollutant to that of a secondary pollutant which may be more or less toxic depending upon the semiconductor. Then desorption of the secondary pollutant from the catalysts surface takes place. After that the final product gets transferred from the semiconductors surface to the liquid (bulk phase).

#### Homogeneous photocatalysis Mechanism (Photo Fenton reaction)

It was first discovered in the 1970s and remains one of the most useful AOPs for its mineralizing of biorefractory organic mixtures in highly acidic environments (Chong *et al.*, 2010). When the reaction is carried out in darkness the hydrogen peroxide very slowly oxidizes ferrous to ferric ion which helps in the creation of hydroxyl radicals. In the presence of sunlight this reaction is expedited as H<sub>2</sub>O<sub>2</sub> breaks down very quickly for the generation of hydroxyl radicals. Then hydroxyl radicals help in oxidation of effluents to further transitory particles. The mechanism is described as:



The recovery of Fe<sup>+2</sup> from Fe<sup>+3</sup> can be explained via 2 different mechanisms



All these soluble ironhydroxy compounds can absorb the entire spectrum of light. In the presence of sunlight the rate of Fenton reaction is exponentially greater than when it is used in dark. The underlying cause is due to formation of ferrous ions from the photochemical effect of light and the simultaneous production of the OH radicals in the process.

The continuous cycle of Fe<sup>+2</sup> to Fe<sup>+3</sup> and back to Fe<sup>+2</sup> generates hydroxyl radicals, provided that the concentration of peroxide in the process is significant.

If the concentration of Fe is less; then this regeneration step is rate determining step for the reaction.

The addition of  $H_2O_2$  in enhances both the homogeneous photocatalysis and  $TiO_2$  photocatalysis. The  $H_2O_2$  can hinder the generation of  $e^-h$  pair but creates additional Hydroxyl radicals. Although  $H_2O_2$  may be generated via the  $TiO_2$  photocatalysis, the amount of hydroxyl radicals formed by  $TiO_2$  may be inadequate to drive the Fenton reaction.

### Merits and demerits of the above processes

#### Merits

Variety of characteristics for the  $TiO_2$  photocatalysis has broadened their feasibility in water medication, such as their operation in room temperature and pressure. Turbulent flow of  $H_2O$  is ensured so that appropriate mixing takes place without increase in pressure; else the costs will increase as a pump will be required. Also complete degradation of the pollutant and its transitory compounds without creating further toxicity into non-toxic substances such as  $CO_2$ , HCl and water. One of the salient features is that  $TiO_2$  can be operated at low costs. It is seen that for photo Fenton reaction low pH from 2.5 - 3 is to be maintained during the reaction time which often increases the expenditure of the process. So in terms of cost efficiency the heterogeneous photocatalytic degradation stands apart than that of Fenton reaction.

However the major advantage of Homogeneous Fenton reaction is that it uses the bandwidth upto 600 nm whereas  $TiO_2$  can utilize till 400 nm, thereby maximizing the usage of the bandwidth of sunlight.

#### Demerits

One of the major disadvantages is that  $TiO_2$  which is frequently used for photocatalytic degradation can only absorb light which has wavelengths in near UV region due to which the remaining part of the visible spectra remains to be unutilized. Also one major drawback of  $TiO_2$  is that the powder form which is most efficient in degradation cannot be separated easily after the water treatment process. This is detrimental for the recycling ability of the catalyst. The  $TiO_2$  catalyst agglomeration reduces the surface area and hence the effectiveness of the catalyst.

### Treatment of effluents using photocatalyst by solar energy

The Homogenous photocatalytic reaction has better degradation rate than the heterogeneous photocatalysis, but for its best (optimized) operation, it is largely

reliant on various  $H_2O$  quality constraints:-

- Homogeneous Fenton reaction is highly pH sensitive. An ideal pH of 2.5 is required to be maintained otherwise, the reaction cannot sustain. Low pH often detracts the formation of precipitates and also at low pH in this case the predominant species in  $H_2O$  is  $[Fe(OH)]^{2+}$ . However low pH is costly and requires constant pH alteration.
- Ions such as  $CO_3^{2-}$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$  and  $Cl^-$  also disturb the equilibrium of Fe in  $H_2O$ . These ions reduce the acidity of water and reduce the homogenous Fenton reaction rate.  $CO_3^{2-}$  and  $PO_4^{3-}$  reacts with the iron to form Iron carbonate and iron phosphates. These ions also hunt hydroxyl radicals. Due to these reasons the search for alternative semiconductors for photocatalytic degradation has started.
- The UV energy obtained from the sunlight source is much less compared to the UV energy from the lamp itself, thereby making the sunlight ineffective for pollutant degradation.

The effluents degraded by both  $TiO_2$  and  $H_2O_2/TiO_2$  for wastewater treatments using solar energy are enumerated and compared in detail and same is tabulated in Table 1.

### Pesticides

One of the most problematic concerns, in places where agricultural fields exist, is of the contamination of the water of the rivers and lakes nearby with pesticides. These pesticides are highly soluble in water and are very toxic, making it an important issue to be addressed. In addition to the washing of fields, pollutants from agro industries also contribute to the contamination of the waste water. The most efficient and effective way of degrading these pesticides were found to be using solar photo-catalysis. In an experiment conducted for 19 different pesticides, using solar compound parabolic concentrating (CPC) pilot plant, the Photo-Fenton reaction gave better results than the other solar AOP's. S-Metolachlor, 2, 4-D, MCPA, Imidacloprid, Alachlor and Terbutylazine were some of the pesticides that were tested. In a separate experiment, the degradation was carried out only for Vydine-Triadimenol pesticide. Both the methods, solar and UV, were tested on this pesticide yielding high degradation rates up to 98% for UV at 254nm using  $TiO_2$  as catalyst. Moreover 59% and 60% degradation was achieved by solar irradiation in the month of June, using  $H_2O_2$  oxidation and ferric ion oxidation respectively. Alternatively, a similar experiment on Diuron and 2,4-D pesticides that resulted from wash-

Table 1. Treatment of effluents using photocatalyst by solar energy

Ref. no.	Effluents	Source & details	Reagents	Exp Setup details	Results
[4-6]	Pesticides	Sunlight	19 Pesticides were quantified. (TiO <sub>2</sub> /UV and TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> /UV, both with and without acidification) and homogeneous (UV, H <sub>2</sub> O <sub>2</sub> /UV, Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /UV and Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> )  Diuron and 2,4-D pesticides and real wastewater effluents from sugarcane plantation Iron sulphate heptahydrate (FeSO <sub>4</sub> •7H <sub>2</sub> O), Hydrogen peroxide (30%), sulphuric acid and NaOH. Vydine-Triadimienol (C <sub>14</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>2</sub> ) UV, UV/H <sub>2</sub> O <sub>2</sub> , UV/Fe(III) as well as photo-Fenton and heterogeneous photo-catalysis with TiO <sub>2</sub> .	The solar collectors are made-up of four borosilicate tubes (cut-off at 280 nm) connected by polypropylene junctions.  CPCs with 8 Pyrex glass tubes and a total illuminated area of 3.6m <sup>2</sup>	The photo-Fenton reaction, performed with an initial iron concentration of 140 mg Fe <sup>2+</sup> L <sup>-1</sup> , leading to an average dissolved iron concentration of 14 mg L <sup>-1</sup> after FePO <sub>4</sub> precipitation, proved to be the most efficient process. After 120min of normalized time photo treatment, the Diuron and 2,4-D herbicides degraded.
[8,9]	Dyes	Sunlight and 8 W lamps, (UV254 or UV350).  9W Radium lamp, 400w high press Hg lamp, Simulated Solar Radiation 150 w solar simulator sys sunlight.  Sunlight with the mean UV-light intensity (290-390 nm)	Remazol Black B dye and Aqueous mixture of 16 dyes Titanium dioxide, particle size 21 nm, 50±15 m <sup>2</sup> /g specific surface area.  Methyl Orange(MO) Slurry of P-25 TiO <sub>2</sub> , AgNO <sub>3</sub>	Reactor1: Jacketed continuous stirred tank photo-reactor - 1.5 L capacity - with UV-lamp. Reactor 2: Solar CPC reactor - 6 quartz tubes -1.5 L capacity  Batch-type laboratory scale photo-reactor. Covered with glass to minimize evaporation. Between 11:00 and 16:00. Average intensity 1.36x10 <sup>4</sup> Einstein s <sup>-1</sup>  Solar photo catalytic reactor with support catalyst, which contained 10 glass tubes (18 cm in length, 1 cm in diameter) with TiO <sub>2</sub> or Ag/TiO <sub>2</sub> film, coated on inside wall. Open cylindrical borosilicate glass reactors with suspensions containing TiO <sub>2</sub> and H <sub>2</sub> O <sub>2</sub> .	UV <sub>254</sub> > Sol-Jun > Sol-Mar > UV350. The degradation rate of pesticide was strongly accelerated by photo-Fenton and TiO <sub>2</sub> processes regardless of the illumination source.  Photo catalytic performance is sufficiently higher in the presence of UVA radiation since TiO <sub>2</sub> activates at wavelength below 385 nm. Sunlight better than artificial solar radiation.  Ag/TiO <sub>2</sub> exhibited much higher MO degradation rate (99.0%) than pure TiO <sub>2</sub> (35.2%), and the MO degradation could be negligible under single sunlight condition.
[17]	Effluent	Sunlight with magnetic stirring. Average temperature 30 °C.	Real textile effluents TiO <sub>2</sub> (P-25, 80% anatase, 20% rutile with a specific surface of 50 m <sup>2</sup> g <sup>-1</sup> ). H <sub>2</sub> O <sub>2</sub> (30%, analytical grade).	250.0 mg L <sup>-1</sup> of TiO <sub>2</sub> associated with 1.0 x 10 <sup>2</sup> mol L <sup>-1</sup> of hydrogen peroxide increases decolorization rates and mineralization levels due to the increase in the	

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				number of possible formation mechanisms of hydroxyl radicals. Optimum concentration of $H_2O_2$ : 0.3M with pH 6 Color removal: $TiO_2$ with $H_2O_2$ : 84%, $TiO_2$ only: 45%, $H_2O_2$ only: 70%
	Sunlight for 4 hours, in May-June	Distillery Effluent Hydrogen peroxide, sodium hydroxide, sulphuric acid, potassium dichromate, ferrous ammonium sulphate, titanium dioxide	Batch reactor: glass of 500mL with magnetic stirrer. Side wall covered with aluminum foil. Daily average global radiation = 5.2 kW h/m <sup>2</sup>	
[10-14] Hydrocarbons	Sunlight	Phenol p-benzoquinone, hydroquinone, phenol, maleic, malonic, succinic, and oxalic acids, sodium oxalate, methanol, and $FeCl_3 \cdot 6H_2O$ , Ammonium Metavanadate.	Two reactor types A and B, built with borosilicate glass tubing Type A reactor - batch CPC photo treatment system with no flow and a 20 mL capacity Reactor B - CPC closed flow type photo reactor with 1200 mL capacity. Reflectors covered with adherent aluminized plastic film.	To reach efficient destruction and COD reduction of phenol contaminated waters in the range of 184-733 mg/L with the $FeOx-H_2O_2$ solar assisted system at natural pH, as mentioned before, the best conditions and reactants mass ratios obtained and proven in batch and closed flow CPC reactors in this research were: $H_2O_2$ /phenol = 5.5, oxalate/phenol = 1.5 and oxalate/ $Fe^{3+}$ = 15, with a maximum reaction time of 90-120 min and an accumulated radiation energy of 1200-1600 kJ/L.
		p-Nitro aniline PNA, Hydrogen peroxide (30%), ferrous sulfate ( $FeSO_4 \cdot 7H_2O$ ), sulfuric acid, sodium hydroxide and Deionized water. Chip Board Production waste Formaldehyde, melamine, urea, wood extractives, lignin, urea/formaldehyde and melamine/formaldehyde resin fragments. Iron salts, Hydrogen peroxide (30%), diluted aqueous solutions of sulphuric acid.	200mL double glass cylindrical jacket reactor, thermostat, and a magnetic stirrer (@280 rpm).  CPC reactor with an aperture of about 1.62 m <sup>2</sup> and a capacity of up to 150 L. The system consisted in a module containing 10 borosilicate glass tubes (external dia 32 mm, wall thickness of 1.4 mm, and L = 1500 mm).  CPC with total collection surface of 0.1m <sup>2</sup> And 2L	pH value at 3.0, 10 mmol/L $H_2O_2$ , 0.05 mmol/L $Fe^{2+}$ , at 20°C. Degradation efficiency more than 98% within 30 min reaction.  The best results are achieved using a combination of $Fe^{2+}$ and $Fe^{3+}$ salts adding hydrogen peroxide at an effluent temperature of 313K, which is favourable for the thermal Fenton's reaction, and a controlled pH of below 3 during the treatment.  63% of SDS degradation was achieved in the absence of solar

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	<p>sulphate heptahydrate (<math>\text{FeSO}_4 \bullet</math> removal was obtained in the hydrogen peroxide (50% stabilized) and sodium peroxymonosulphate (PMS).</p> <p>Bisphenol-A Indium-Tin Oxide, Acetic Acid, Ethanol and Titanium tetraoxide</p> <p>Synthetic Wastewater containing apple juice Ferrous Sulfate (<math>\text{FeSO}_4 \cdot 7\text{H}_2\text{O}</math>), Oxalic Acid (<math>\text{COOH}</math>)<sub>2</sub> <math>\cdot 2\text{H}_2\text{O}</math> and 30% <math>\text{H}_2\text{O}_2</math>, <math>\text{H}_2\text{SO}_4</math>, NaOH.</p> <p>Soil washing wastewater and synthetic samples Ferrous sulfate heptahydrate (<math>\text{FeSO}_4 \bullet 7\text{H}_2\text{O}</math>), cobalt acetate (<math>\text{CoAcO}_2</math>), hydrogen peroxide (50% stabilized) and sodium peroxymonosulfate (PMS). Real and simulated winery wastewaters Titanium Dioxide, Hydrogen Peroxide (50% w/v), Iron Sulfate Heptahydrate and Sulfuric acid.</p> <p>1,10-phenanthroline laboratory wastewater Potassium ferrioxalate (<math>\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \bullet 3\text{H}_2\text{O}</math>), potassium</p>	<p>Erlenmeyer flask covered (<math>7\text{H}_2\text{O}</math>), cobalt acetate (<math>\text{CoAcO}_2</math>),</p> <p>Xenon lamp in an open cylindrical pyrex cell under continuous stirring. Current applied using galvanostat. Anode- Indium Tin Oxide Film Cathode-Zirconium plate CPC with 50 L CSTR, centrifugal recirculation pump, a solar collector unit with an area of 2 m<sup>2</sup> in an aluminum frame, 16 borosilicate glass tubes (OD 32 mm, transmissivity 50% -90% at 300-350 nm)</p> <p>CPC with total collection surface of 0.1m<sup>2</sup></p> <p>CPC with illuminated area</p> <p>Open dark glass vessels exposed to sunlight during</p>	<p>radiation whereas a 79% of SDS with aluminum foil.</p> <p>CPC reactor. •99% of SDS degradation using cobalt/PMS versus 60% using photo-Fenton Photo-electro-catalytic: complete degradation in 1 hour. Photocatalysis:25% degradation Electrochemical oxidation:30 %.</p> <p>The OH radicals are the main species responsible for the degradation of wastewater containing apple juice and the radical pathway is pathway for the degradation (79%).</p> <p>10mM <math>\text{Fe}^{2+}</math>, 60 mM <math>\text{H}_2\text{O}_2</math>, Time: 60 min. 48% of SDS degraded in real soil washing wastewater and 63% in synthetic samples.</p> <p>• Solar radiation- removal of 4.16m<sup>2</sup> of only 8%. • The photo-Fenton reaction gives 2.5 times higher degradation than the heterogeneous photocatalysis combined with <math>\text{H}_2\text{O}_2</math>. • Biological oxidation combined with photo-Fenton reaction is not adequate for winery wastewater.</p> <p>Total degradation of phenanthroline and 25% TOC removal</p>
[18-21] Waste waters			
[16,30] Sunlight			

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<p>ferrioxalate (FeOx) <math>\text{FeSO}_4</math>, <math>\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}</math>, <math>\text{H}_2\text{O}_2</math> 30% (w/w), Ammonium metavanadate, <math>\text{H}_2\text{SO}_4</math> and 1,10-phenanthroline (<math>\text{C}_{12}\text{H}_8\text{N}_2</math>) Municipal Waste Water with 66 micropollutants Titanium dioxide, Iron sulphate (<math>\text{FeSO}_4 \cdot 7\text{H}_2\text{O}</math>) hydrogen peroxide (30%, w/v), sulphuric acid. Pulp mill waste water Ferrous Iron sulphate (<math>\text{FeSO}_4 \cdot 7\text{H}_2\text{O}</math>) hydrogen peroxide (30%, w/w), sulphuric acid and NaOH.</p>	<p>autumn and winter.</p>	<p>after 150min</p>
<p>Soil washing waste water Ferrous sulfate heptahydrate (<math>\text{FeSO}_4 \cdot 7\text{H}_2\text{O}</math>), cobalt acetate (<math>\text{CoAcO}_2</math>), hydrogen peroxide &amp; sodium peroxymonosulfate (PMS) Simulated and real waste water with <i>E. coli</i> <i>E. coli</i>, hydrogen peroxide, <math>\text{NaHCO}_3</math> (96 mg <math>\text{L}^{-1}</math>), NaCl (7 mg <math>\text{L}^{-1}</math>), <math>\text{CaSO}_4 \cdot 2\text{H}_2\text{O}</math> (60 mg <math>\text{L}^{-1}</math>), urea (6 mg <math>\text{L}^{-1}</math>), <math>\text{MgSO}_4</math> (60 mg <math>\text{L}^{-1}</math>), KCl (4 mg <math>\text{L}^{-1}</math>), <math>\text{CaCl}_2 \cdot 2\text{H}_2\text{O}</math> (4 mg <math>\text{L}^{-1}</math>), peptone (32 mg <math>\text{L}^{-1}</math>), <math>\text{MgSO}_4 \cdot 7\text{H}_2\text{O}</math> (2 mg <math>\text{L}^{-1}</math>), meat extract (22 mg <math>\text{L}^{-1}</math>).</p>	<p>Tubular pyrex glass reactor in the focus of CPC with total collection area of 0.1 <math>\text{m}^2</math>.</p>	<p>Photo-Fenton reaction : 69% Co/PMS/UV process : 51%</p>
<p>[22] <i>E. coli</i> Disinfection</p>	<p>CPC and PET bottles.</p>	<p>Bacterial concentrations of <i>E. coli</i> can be reduced to less than 2 CFU/mL.</p>

ing of sugarcane plantation. The initial concentration of Diuron and 2,4-D which were between 860-930 mg/L and 21-600 mg/L completely degraded after 120 minutes of solar photocatalytic activity (Moreira *et al.*, 2012; Shawaqfeh *et al.*, 2010; Mendoza-Marín *et al.*, 2010).

### Textile Dye

The most noticeable contaminants in the water receiving body are the effluent from textile industries because of their evident color. The high amount of organic compounds that are present in these effluents even in the diluted form may have a mutagenic action. In an experiment conducted on real textile effluents, it was observed that the H<sub>2</sub>O<sub>2</sub> degraded completely when added with an initial concentration of 0.01 mol/L with titanium dioxide of 250 mg/L. The degradation completed in 6 hours with an average solar radiation of 2.85 MJ/m<sup>2</sup> (Carla *et al.*, 2009).

Remazol Black B dye, when tested with solar radiation, completely decolorized after 120 minutes in the presence of 2 g/L of TiO<sub>2</sub>. Similarly an aqueous solution was made from 16 dyes consisting of Remazol Black B dye as the major component (44%), the decolonization occurred only after 5 hours with a catalyst concentration of 4 g/L. These two experiments were also conducted under different illumination sources; it was observed that photocatalytic performance was better in the presence of UVA radiation (Chatzisymeon *et al.*, 2013).

In a separate experiment methyl orange was taken into consideration. Under sunlight for 120 minutes, the combination of silver with titanium dioxide yielded better degradation than pure TiO<sub>2</sub>. The beauty of the experiment lied in the CPC which was coated with the film on the inside wall (Liu *et al.*, 2013).

### Hydrocarbons

Phenols are subjected to various constraints as per the EPA 2002 as it was ranked in the 183<sup>rd</sup> position amongst the 275 toxic substances. Even a small concentration of 1-8 mg/L produces an unpleasant odor and taste. An experiment was carried out on phenol effluent in two different CPC's namely no flow and closed flow. The ratios that were obtained from the batch process were utilized in the closed flow and the ideal conditions and reactants mass ratios achieved as follows:

The mass ratio between Hydrogen peroxide and phenol was found to be 5.5. That of the oxalate ions and phenol was 1.5. Also the mass ratio between

oxalate ions and ferric ions was found to be 15. Approximately 1200-1600 KJ/Liter radiation was collected in the process. The reaction was carried out for 1.5 to 2 hours. A transformation efficiency of phenol was obtained to be 100% when 200mg/L was degraded using Photo-Fenton within the first hour of treatment for both the reactors (Prato-Garcia *et al.*, 2009).

p-Nitro aniline is enumerated as a priority contaminant in H<sub>2</sub>O because of its carcinogenic and toxicity, due to which its has been studied by various methods. It is used as an intermediate in the manufacture of organic compounds such as azo dyes and pesticides; these were found to be efficiently destructible by Fenton processes, using a double glass cylindrical jacket reactor. It was found that under optimum conditions of pH at 3.0 with 10 mmol/L of H<sub>2</sub>O<sub>2</sub> and 0.05 mmol/L Fe<sup>2+</sup>, the degradation efficiency of 0.072-0.217 mmol/L of PNA was more than 98% within 30 min reaction (Sun *et al.*, 2008).

Common surfactants are normally non-toxic and harmless, but recently it was found that they pose health and environmental effect. Sodium Dodecyl Sulphate (SDS) is a common representative of these surfactants. In an experiment, a comparative observation was made on solar radiation and CPC. It was found that 63% was degraded in the absence of solar radiation with initial conditions of 10mM FeSO<sub>4</sub> and 60mM of H<sub>2</sub>O<sub>2</sub>. On the other hand, an increment of 17% was obtained using CPC reactor. Further improvement was made by decreasing the pH value from 5 to 2. In addition to this, another technique was carried out using cobalt/peroxymonosulfate as the catalyst, 99% degradation of SDS was achieved compared to only 60% using Fenton (Bandala *et al.*, 2008).

A similar experiment was carried out on SDS and resulted in 28% degradation using around 18 KJ/L of energy, whereas using the same amount of energy, 52% was degraded using PMS. Complete degradation was achieved with 12 KJ/L by photo-Fenton reaction and cobalt/PMS gave the same result using 2.7 KJ/L of accumulated energy (Bandala *et al.*, 2008).

Learning disabilities, brain development disorders and endocrine disruption, these are some of the adverse effects of endocrine disrupting compounds such as Bisphenol-A. Out of the many treatment methods like biological, sonochemical, electrochemical and photochemical processes, the latter two were chosen along with photo-electrochemical for further investigation. It was conducted in an open

cylindrical pyrex cell with anode as the titanium dioxide/ indium tin oxide film and boron doped diamond/ zirconium serving as the cathode. After one hour of simulated solar radiation by an 150W xenon lamp, electrochemical oxidation resulted in 30% degradation, photochemical yielded 25% degradation, whereas, photo-electrochemical degraded completely. It was also inferred that degradation was favored in the presence of sodium chloride and at lower pH values. Moreover it was observed that irrespective of the starting concentration of Bisphenol-A, 85% conversion could be achieved within 90 min of reaction time (Daskalaki *et al.*, 2013).

Wastes arising from chipboard production were also tested for degradation using advanced oxidation process. These effluents comprise of Formaldehyde, melamine, urea, lignin and melamine/formaldehyde resin fragments. The process was carried out using CPC reactor with an aperture of 1.62 m<sup>2</sup> and a capacity of 150 L in the presence of sunlight. The optimum results were achieved using Fenton reagent at an effluent temperature of 313 K and controlled pH of 3 during treatment process (Eduardo *et al.*, 2004).

### Waste Water effluents

During the advent of 20<sup>th</sup> Century almost all the industries used to dump their waste materials into the surrounding environment to increase their profits. Water often gets polluted directly by release of harmful chemicals into it. The dumping of waste materials in the soil near water bodies often caused indirect pollution through soil erosion. Hence it is important to check the feasibility of photocatalytic degradation in reducing the pollutants released from industries.

An experiment was conducted to degrade synthetic waste water containing apple juice in the presence of sunlight as the source. A CPC plant with 2m<sup>2</sup> capacity using 16 borosilicate glass tubes with transitivity 50 – 90% at (300-350 nm) was used. It was observed that the hydroxyl radical was the main species responsible for the degradation of apple juice. Using Fe<sup>+2</sup> oxidation 79% of degradation was achieved (Durañ *et al.*, 2012).

Similarly, Distillery effluent was degraded in the presence of sunlight for 4 hours in the period of May and June. Homogeneous Fenton, TiO<sub>2</sub> and combination of them were used for mineralization of the effluent. A glass reactor with 500 ml capacity was used for the batch process. The optimum concentration of H<sub>2</sub>O<sub>2</sub> was noted at 0.3M with a pH of 6. Maximum color

removal of effluent (84%) was noticed with combination of TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>. Fenton reaction and Heterogeneous photo catalysis decolorized on 70% and 45% of the effluent respectively (Vineetha *et al.*, 2013).

In yet another experiment, municipal waste water with 66 micropollutants was degraded using sunlight as the source. A pilot CPC plant was used which had the capacity of 3m<sup>2</sup>. Solar photo Fenton process efficiently removed micropollutants which were followed by ozonation process. Solar heterogeneous photocatalysis coupled with TiO<sub>2</sub> was found to be least efficient to eliminate micropollutants (Prieto-Rodri'guez *et al.*, 2013).

A similar experiment was conducted on real and simulated winery waste water using sunlight as the source. The experiment was conducted on CPC plant which had illumination area of 4.16 m<sup>2</sup>. The solar radiation could remove 8% of winery wastes from this process. It was noted that Homogeneous Fenton gave 2.5 times better degradation than heterogeneous photocatalysis coupled with H<sub>2</sub>O<sub>2</sub>. Also inadequate degradation of winery waste water was observed when biological oxidation was combined with photo Fenton process (Souza *et al.*, 2013).

Also laboratory waste waters containing 1, 10-phenanthroline was degraded using sunlight. Open dark glass vessel was used as equipment for testing. The apparatus was exposed to sunlight during autumn and winter. Total degradation of 1, 10-phenanthroline was observed after 150 min and 25% removal of Total Organic Content (TOC) was also achieved in the same time (Silva *et al.*, 2007).

A similar experiment was conducted to degrade pulp mill effluents using sunlight and CPC with collection area was 3.02 m<sup>2</sup>. It was observed that using 50 mg/L of Fenton reagent 36% of waste water was degraded using solar photo Fenton method and 90% of effluents were degraded using 10 mg/L of Fe<sup>+2</sup> and 50 mM of H<sub>2</sub>O<sub>2</sub> (Malato *et al.*, 2012).

### E- Coli

In another experiment using CPC and PET bottles, both real and simulated e-coli bacteria was brought down to levels less than 2 CFU/mL (Bichai *et al.*, 2012).

### Emerging Catalysts

Many alternative catalysts have emerged for Photocatalytic degradation. One of the reasons is due to large electron band width of TiO<sub>2</sub> (3.2 eV) only near UV light is able to be absorbed. The following factors are taken into account before considering it as an

alternative (Di Paola *et al.*, 2012).

The band gap of the semiconductor should be small so that it can accommodate larger wavelengths. Secondly, the intermediates or the end products should be less toxic than that of the reactants. Post operation recovery of the Catalyst should also be simple and it could be reused effectively for more number of times and the pollutant should be degraded efficiently. These catalysts like behave like a single electron characteristics in the outer orbital have lesser bandwidth than  $\text{TiO}_2$ , some of which are tabulated in Table 2.

Studies have shown that certain zinc oxides, CdS and GaP have also shown promising photocatalytic effect but it has been shown that the end products which have been degraded are highly toxic. However a vast number of these photo catalysts have shown satisfying degradation effect in the visible region, a detailed description of which is tabulated in Table 3.

**Table 2.** Emerging photo catalyst with its band gap

Photo Catalyst	Band Gap
$\text{NaBiO}_3$	2.14579 eV
BiOI	1.8 eV
BiOBr	2.31
$\text{Bi}_3\text{O}_4\text{Br}$	2.17 eV
$\text{TiO}_2$ doped with 0.5 wt.% of $\text{Sm}^{3+}$	2.80 eV
Chitosan (bio polymer) embedded with $\text{TiO}_2$ & Pd	2.60 eV

### Bismuth oxy halides

Bismuth oxyhalides ( $\text{BiOX}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ )) are other ternary semi-conductors that have been studied as potential candidates for photocatalytic applications. All  $\text{BiOX}$  compounds crystallize in the tetragonal matlockite structure, a layer structure characterized by  $[\text{Bi}_2\text{O}_2]$  slabs interleaved by double slabs of halogen atoms.

Pentachlorophenol (PCP) and its salts, most notably sodium pentachlorophenate (PCP-Na), are widely used as biocides for the protection of timber and textiles all over the world. PCP and its salts have attracted great attention worldwide owing to the toxicity, endocrine disturbing effect, mutagenicity, carcinogenicity, and bioaccumulation. PCP has been listed as a priority pollutant by the U.S. Environmental Protection Agency. This pollutant could not be degraded by Titanium dioxide. However 0.1 g of bismuth oxyiodide nanosheets in a 250 mL solution containing 50 ppm of sodium penta chloro phenate (PCP-Na) was able to degrade 90.3% of PCP-Na in an hour. Also when a set of bismuth oxy bromides ( $\text{BiOBr}$  &  $\text{Bi}_3\text{O}_4\text{Br}$ ) were used as photo catalysts, PCP-Na was degraded efficiently. A 50 mL solution was taken containing 40 mg/L of PCP-Na. After 15 minutes of reaction time it was found that 10% and 92.5% of PCP-Na was degraded by 50 mg of  $\text{BiOBr}$  and  $\text{Bi}_3\text{O}_4\text{Br}$  respectively.

In yet another experiment 100 mg of Nano- $\text{NaBiO}_3$  crystals was used in 150 mL of waste water solution containing 50 ppm of PCP-Na. In a reaction time of 1 hour, 90.5% of PCP-Na was degraded. In all of the

**Table 3.** Treatment of effluents using emerging photocatalyst by solar energy

Ref. No.	New Catalyst	Source for photo catalysis	Effluents	Percentage Degradation
[30]	$\text{Al}_2\text{O}_3$ -supported Fe(III)-5-sulfo-salicylic acid (SSAL) catalyst	Sunlight	Di Nitro Butyl phenol (DNPB)	99.5
[27]	Bi doped $\text{TiO}_2$		Isoproturon	89.5
[28]	$\text{TiO}_2$ doped with $\text{Sm}^{3+}$ by sol-gel method		Diuron	0.3 wt% $\text{Sm}^{3+}$ - 80% , 0.5 wt% $\text{Sm}^{3+}$ - 42%
[24]	BiOI Bismuth oxyiodide	Virtual Sunlight	PCP-Na	90.3
[25]	$\text{NaBiO}_3$	with 500 W Xe lamp	PCP-Na	90.5
[26]	$\text{BiOBr}$ and $\text{Bi}_3\text{O}_4\text{Br}$		PCP-Na	$\text{BiOBr}$ - 10%, $\text{Bi}_3\text{O}_4\text{Br}$ - 92.5%
[31]	Pd/ $\text{TiO}_2$ -CS (chitosan-a bio polymer) using sol gel method	Virtual Sunlight with 300 W Xe lamp	Methylene blue dye	92.25
[29]	Layered double hydroxides	Virtual Sunlight with 150W halogen lamp	Rhodamine B dye	Zn/Al- $\text{NO}_3$ -LDHs - (96.5%) Zn/Al- $\text{NO}_3$ -LDHs and Zn/Fe- $\text{NO}_3$ -LDHs Zn/Fe- $\text{NO}_3$ -LDHs- (72.4%).

experiments conducted above virtual sunlight was simulated using 500 W Xe lamp as a source for degrading the effluent (PCP-Na) (Chang *et al.*, 2009; Ji *et al.*, 2009; Wang *et al.*, 2013).

### Doped Catalysts

Due to the inherent relatively large band gap characteristic of  $\text{TiO}_2$ , a lot of research has focused on lowering the threshold energy for excitation in order to utilize a larger fraction of solar energy. Many studies have revealed that anion doping of  $\text{TiO}_2$  such as N, S, C, I, Br and Cl shifts the optical absorption edge of  $\text{TiO}_2$  to lower energies, thereby increasing the photoactivity of the catalysts. In addition,  $\text{TiO}_2$  doping with transition metal cations that include Cr, Sm, Fe and several others have been reported. Recently, several Bi-based photocatalysts are synthesized and their activities are exploited under UV as well as visible light irradiation.

In an experiment  $\text{TiO}_2$  was doped with Bi with different Weight % from 0.5 to 5% [Bi to  $\text{TiO}_2$  ratio]. Sunlight was used as a source to degrade 50 mL of solution of 114 ppm Isoproturon. The photocatalytic activity was found to be maximum in 2 wt. % doping of Bi. In a reaction time of 120 minutes and using 1 g/L of the aforementioned sample, upto 89.5% of degradation was achieved.

The reduced efficiency at dopant concentration (>2%) is due to the formation of  $\text{Bi}^{3+}$  clusters. The presence of  $\text{Bi}^{3+}$  clusters which are detrimental to the photocatalytic activity. Similarly Samarium ( $\text{Sm}^{+3}$ ) was doped with  $\text{TiO}_2$  to increase its photocatalytic activity by sol-gel method. Two samples of 0.3 wt. % and 0.5 wt. % of doped catalysts were used. 0.5 g of catalyst was used to degrade 70 mL of solution containing 40 ppm of Diuron, a pesticide. The reaction time was for 3 hours and sunlight was used as a source for degradation. The 0.3 wt%  $\text{Sm}^{+3}$  were able to degrade 82% of diuron which was significantly higher than 0.5 wt% of  $\text{Sm}^{+3}$  which degraded 42% of the effluent (Subrahmanyam *et al.*, 2011; de la Cruz *et al.*, 2011).

Higher  $\text{Sm}^{3+}$  content the Sm would be present at surface of particles and form clusters which do not favor the degradation processes that must be carried out at surface. For  $\text{Sm}^{3+}$  doping with 0.5 wt% degradation decreased to 42%, which is even lower than the activity shown by pure  $\text{TiO}_2$  calcined at  $500^\circ\text{C}$ , which confirms the fact that there exists a type of surface modification that is detrimental for photocatalytic activity.

### Layered Doubled Hydroxide (LDH)

Layered double hydroxides (LDHs), also known as hydrotalcite like- compounds (HTLcs) or anionic clays, are a class of host-guest layered solids with the general formula  $[\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2]^{x+} \text{A}^{n-}_{x/n}$  where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are di- and trivalent metal cations,  $\text{A}^{n-}$  denotes exchangeable organic or inorganic anion with negative charge n, m is the number of interlayer water, and  $x = (\text{M}^{3+} / (\text{M}^{2+} + \text{M}^{3+}))$  is the layer charge density of LDHs (Xia *et al.*, 2013). With the consideration that LDHs have two or three different metals and that the proportion between these metals can be controlled, LDHs can be as doped as semiconductors, which could influence the layered-structure LDH materials possessing semiconductor properties and facilitates the transfer of the photogenerated electrons to the surface of photocatalysts, and this might provide great potential for their application in dye degradation. Two types of LDH namely Zn/Al- $\text{NO}_3$ -LDH & Zn/Fe- $\text{NO}_3$ -LDH were used in an experiment in which simulated sunlight (150 W He lamp) was being used to degrade a textile dye (Rhodamine B). Promising degradation was observed when 150 mL of solution containing 100 mg/L of effluent was under reaction for 2 hours. The Zn/Al- $\text{NO}_3$  LDH & Zn/Fe- $\text{NO}_3$  LDH degraded 96.5% and 72.4% of the Rhodamine B dye respectively.

### $\text{Al}_2\text{O}_3$ -supported Fe (III)-5 (ssal) catalysts

To enhance the photo catalytic activity of  $\text{Al}_2\text{O}_3$ , an acid Fe (III)-5-sulphosalicylic acid (ssal) is added to support the oxide during the Fenton reaction. An experiment was conducted using sunlight as the source and 40 mg/L of Di nitro butyl phenol (DNBP) in 100 mL solution. In 100 minutes with 1 g of the catalyst along with  $\text{H}_2\text{O}_2$  about 99.5% of DNBP was degraded (Zhang *et al.*, 2010).

### Pd/ $\text{TiO}_2$ -CS (chitosan) – bio polymer catalyst

Also like other nanocomposite materials chitosan (biopolymer) when embedded with  $\text{TiO}_2$  is proven to be an effective photocatalyst. This Pd/ $\text{TiO}_2$ -CS nano composite catalyst was prepared by sol-gel method. 0.75 g of the above catalyst was able to degrade 99.75% of methylene blue in 30 minutes. In the experiment 100 ppm of Methylene blue was prepared in 500 mL water. Also sunlight was simulated using a 300 W Xenon lamp (Abdelaal *et al.*, 2013).

## Solar collectors

### Concentrating Solar Reactor

Concentrating Solar Collector are systems in which sunlight needs to be focused for effective water treatment. Its reflective surface is reinforced by a structure. This structure is controlled by motors on the axes and automatic tracking devices in such a way that the reflective surface is always perpendicular to the rays. This structure was created on the following principles of optics that when a ray moves parallel to the axis of parabola and touches its surface, the ray gets reflected and passes through its geometric focus. A Pyrex glass tube is placed in the geometric foci which act as an absorber. The contaminated water is allowed to flow through the tube where the degradation takes place.

The advantages of concentrating Solar reactors is that It has higher energy density (energy per unit volume) because of which less amount of water can be treated in a specific amount of time. Solar energy collected could be used simultaneously for other purposes. The flow is turbulent in this equipment and Volatile Compounds do not evaporate. The use of this type of reactor is not widespread as the operation of this type of collector due to the presence of tracking devices has proved to be costly. Only direct radiation is being utilized resulting in Low optical efficiency (45-50%). Water overheating is a constant problem because of which machine cannot be operated continuously (Malato *et al.*, 2007).

### Non-concentrating solar reactor

One-sun (non-concentrating) collectors are static systems as they have no moving parts or solar tracking devices. The apparatus consists of a rectangular stainless-steel staircase vessel having 20-25 steps. The photoreactor is provided with a Pyrex glass (UV-transparent) cover to limit water evaporation. The photoreactor, with a solar radiation-collecting surface of 1 m<sup>2</sup>, is mounted on a fixed rack tilted at the same angle as the latitude of the site.

Amongst many advantages the Manufacturing costs are cheaper because their components are simpler, which also means easy, low-cost maintenance. They are able to make use of the diffuse as well as the solar UV-A. The support structures are easier and cheaper to install and the surface required for their installation is smaller, because, since they are static, they do not project shadows on the others. They do not concentrate radiation, so that efficiency is not reduced by factors associated with concentration and solar tracking. As there is no concentrating system

(with its inherent reflectivity), the optical efficiency is higher than for PTCs (Malato *et al.*, 2007).

Some of the cons while using this collector is that only Laminar flow is achieved during the treatment of wastewater because of which low mass transfer takes place. The reactor lacks in Weather resistance, Chemical inertness and ultraviolet transmission. Vaporization of reactants in this equipment is also observed.

### Compound parabolic collector (CPC)

The sunrays need to be concentrated to achieve maximum radiation. A Compound Parabolic Collector serves this purpose. As the name suggests, it comprises of two parabolic mirror segments with different focal points. One focal point lies on the parabola of the other. With respect to reflection through the axis, the parabolic surfaces are symmetrical. A basic CPC, consists of a cylindrical reactor tube with a reflective surface. They have been found to provide the best optics for low concentration systems and can be designed with a concentrating ratio close to one (Tanveer *et al.*, 2013).

CPC has the capacity to capture both direct and diffuse UV-sunlight. Of the numerous advantages the notables ones includes its intrinsic simplicity, cost-effectiveness, easy to use, low capital investment. The reflector design enables almost all the UV-radiation arriving at the CPC aperture (not only direct, but also diffuse) to be collected and available to the process in the reactor. The light reflected by the CPC is distributed around the back of the tubular photo reactor so that most of the reactor tube circumference is illuminated.

## CONCLUSION

Advanced Oxidation process has gained a tremendous role in degrading the industrial effluents in the previous decade. The applications of photochemical AOP which comprises of heterogeneous TiO<sub>2</sub> catalysis and homogeneous Fenton reaction are widespread as the source required for degradation is sunlight. The Compound parabolic collector is the best apparatus for degradation as it uses both direct and diffuse radiation. Many emerging catalysts like bismuth oxyhalides are being used in order to overcome the challenges faced by heterogeneous photocatalytic degradation. However their toxicity with respect to aquatic life needs to be checked before any conclusion is drawn.

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