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SOLAR ENERGY UTILIZATION IN INDUSTRIAL EFFLUENT TREATMENT

Leena V Bora[1], Rajubhai K. Mewada[2]

[1]*Department of Chemical Engineering, Nirma University*
[2]*Department of Chemical Engineering, Nirma University*

Abstract —Solar energy is a vital source for the treatment of hazardous wastes which are eliminated by the industries. There are equipments like parabolic trough collectors (PTR), flat plate collectors, etc. Used for concentrating the solar energy. Various catalysts such as TiO2 are used for the treatment of waste water by the process called photo catalysis i.e. such catalyst gets activated in the presence of sunlight. Other process like Fenton oxidation, Fenton degradation, and other photochemical methods are useful for the treatment of industrial effluents. Fenton process is well known in all the industries like chemical, pharmaceutical, textile, food, sugar industry for the waste water treatment. Solar drying is an important process for solid waste treatment in which exposure to sunlight can kill various harmful bacterias and other pesticides. Such process is widespread in agriculture sector, cement industry and also food industry. In this paper, we have discussed about the processes which can be helpful to treat industrial wastes by using solar energy.

Keywords- Advanced oxidation process; Fenton process; photo-fenton; photocatalysis

I. INTRODUCTION

Industries discharge a large amount of waste and contaminate water, land and hence affect the health of the people. Therefore these effluents must be treated before its disposal. Due to increase in the demand and the cost of non renewable resources such as fuel, it is recommended to use non conventional sources such as solar energy for the treatment. Solar energy enables the industry to modify their energy requirements, improve their energy stability, and increase energy sustainability which lead to improvement in system efficiency. The use of solar radiation in the treatment of industrial effluent is a shift of artificial UV light to sustainable and renewable solar source and thus reducing the cost. [1]

The main causes of surface and groundwater contamination are industrial effluents (even in small amounts), excessive use of pesticides, fertilizers (agrochemicals) and domestic waste landfills. Wastewater treatment (WW) is usually based on physical and biological processes. After elimination of particles in suspension, the usual process is biological treatment (natural decontamination). Unfortunately, some organic pollutants, classified as bio-recalcitrant, are not biodegradable. In the near future, Advanced Oxidation Processes (AOPs) may become the most widely used water treatment technologies for organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability.

These processes involve generation and subsequent reaction of hydroxyl radicals (•OH), which are one of the most powerful oxidizing species. Many oxidation processes, such as TiO2/UV, H2O2/UV, Photo-Fenton and ozone (O3, O3/UV, O3/H2O2) are currently employed for this purpose. Their attack is not very selective, which is a useful attribute for use in pollution treatment. The versatility of AOPs is also enhanced by the fact that there are different •OH radical production possibilities, so they can be adapted to specific treatment requirements. Their main disadvantage is their high cost. The use of AOPs for WW treatment has been studied extensively, but UV radiation generation by lamps or ozone production is expensive .So future applications of these processes could be improved through the use of catalysis and solar energy. Therefore, research is focusing more and more on those AOPs which can be driven by solar irradiation, photo-Fenton and heterogeneous catalysis with UV/TiO2.[6]

II. SOLAR COLLECTORS FOR PHOTOCATALYTIC APPLICATIONS

2.1 Concentrating collectors

Contrary to solar thermal processes, which collect large amounts of photons at any wavelength to reach a specific temperature range, solar photochemical processes use only high-energy short-wavelength photons. TiO_2photocatalysis uses UV or near-UV sunlight (300 to 400 nm) and photo-Fenton heterogeneous photocatalysis uses sunlight up to 580 nm. Sunlight at wavelengths over 600 nm is normally not useful. Nevertheless, the specific hardware needed for solar photocatalytic applications has much in common with those used for thermal applications. As a result, both photochemical systems and reactors have followed conventional solar thermal collector designs, such as parabolic troughs and non-concentrating collectors [7].

The original solar photoreactor designs [8] for photochemical applications were based on line-focusing parabolic-trough concentrators (PTCs). The parabolic-trough collector consists of a structure that supports a reflective

concentrating parabolic surface (Figure 1). This structure has one or two motors controlled by a solar tracking system on one or two axes respectively that keep the collector aperture plane perpendicular to the solar rays. In this situation, all the solar radiation available on the aperture plane is reflected and concentratedon the absorber tube that is located at the geometric focal line of the parabolic trough.[6]

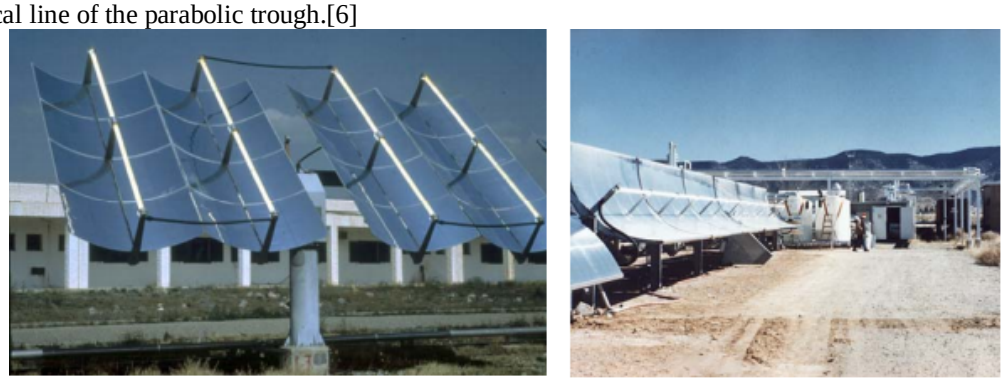

Figure 1.Parabolic-troughs with two-axis solar tracking (left) and single-axis solar tracking (right).

The solar radiation that reaches ground level without being absorbed or scattered, is called direct radiation, while radiation which has been dispersed before reaching the ground is called diffuse radiation, and the sum of both is called global radiation. Figure 2 shows the path of direct solar radiation (ID) until it arrives inside the absorber tube. It must arrive at the surface and be reflected (part is lost due to mirror reflectivity, $\eta R_{,\lambda}$) in the right direction (here 2affected by accurate sun tracking, ηs) by the mirror, before penetrating (part is lost due to glass transmissivity, $\eta T_{,\lambda}$) in the tube. Furthermore, the parabolic trough concentration factor must also be considered (ratio of surface area of the parabola capturing the radiation and surface area of the tube, Sp/S_T). Global radiation (IG) is also collected by the PTCs, but global radiation is collected directly by the transparent absorber tube without intervention the collector and is only affected by the transmissivity of the glass, $\eta T,\lambda$

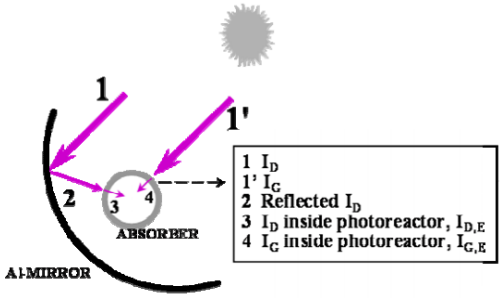

Figure 2: Concentration of solar radiation

2.2 Non-concentrating collectors

One-sun (non-concentrating) collectors are, in principle, cheaper than PTCs, as they have no moving parts or solar tracking devices. They do not concentrate radiation, so efficiency is not reduced by factors associated with concentration and solar tracking. Manufacturing costs are cheaper because their components are simpler, which also means easy, low-cost maintenance. Non-concentrating collector support structures are easier and cheaper to install as well, and the surface required for their installation is smaller, because, since they are stationary, there is no shading. They are able to make use of the diffuse as well as the direct solar UV-A. Extensive effort in the design and testing of small non-tracking collectors has resulted in several different non-concentrating solar reactor prototypes.

One example of a non-concentrating collector is shown in Figure 3. It consists of a rectangular stainless steel staircase vessel having 21 steps. The photoreactor is provided by a pyrex glass (UV transparent) to prevent water evaporation. The photoreactor, with a solar radiation collecting surface of $1m^2$ is mounted on the same rack tilted at the same angle as the latitude of the site.

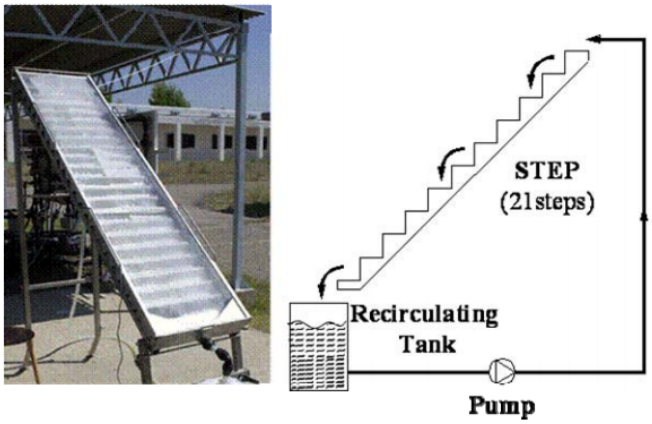

Figure 3: Non-Concentrating Photoreactors

	ADVANTAGES	DISADVANTAGES
Concentrating collectors	- Turbulent flow - No vaporization of compounds - More practical use of a supported catalyst - Smaller reactor tube area	- Only direct radiation - High cost (sun tracking) - Low optical efficiency - Low quantum efficiency ($r = k\ I^{<1}$ with TiO_2) - Water overheating
Non concentrating photoreactors	- Direct and diffuse radiation - No heating - Low cost - High optical efficiency - High quantum efficiency ($r = k\ I$ with TiO_2)	- Laminar flow (low mass transfer) - Vaporization of reactants - Reactant contamination -Weather resistance, chemical inertness and ultraviolet transmission

Table 1: Comparison between concentrating and non-concentrating photoreactors

2.3 Compound parabolic collector (CPC)

CPC is made of two halves of parabola with closely located focal points and their axes inclined to each other. Incident rays within the angle between the two axes (acceptance angle of the CPC) are reflected with single or multiple reflections towards the region between the two focal points and get concentrated in that region. Thus, CPCs can accept incoming radiation over a relatively wider range of angles. By using multiple internal reflections, any radiation that is entering the aperture, within the collector acceptance angle, finds its way to the absorber surface located at the bottom of the collector [2].

Between parabolic concentrators and flat stationary systems, they combine the characteristics of both. While they concentrate solar radiation, they retain the stationary and diffuse-radiation collection properties of flat plate collectors. They have therefore been chosen as a good option for solar photochemical applications by various research groups. Summarizing, the advantages of CPCs are their turbulent flow conditions, no vaporization of volatile compounds, no tracking, no overheating, they can make use of both direct and diffuse solar radiation, are low-cost, weatherproof, reactants are not contaminated, and they have both high optical and high quantum efficiency, since there is a lower e-/h+ density than in a concentrating system (as the photonic density is lower) and therefore recombination is also lower. Having the advantages of both non-concentrating and concentrating systems and none of the disadvantages, CPCs seem to be the best option for solar photocatalytic processes.

The reason for this is that they illuminate the complete perimeter of the receiver, rather than just the "front" of it, as in conventional flat plates or tubes laid side by side (very often used as non-concentrating collectors in solar photocatalysis). The concentration factor (C_{CPC}) of a two-dimensional CPC collector is given by the following equation.

$$C_{CPC} = \frac{1}{\sin \theta_a} = \frac{a}{2\pi r}$$

The semi-angle of acceptance (θa) for photocatalytic applications is usually between 60 and 90 degrees. A special case is the one in which θa = 90º, whereby C_{CPC} = 1 and each CPC curve is an ordinary involute (Figure 4). When this occurs, all the UV radiation that reaches the aperture area of the CPC (direct and diffuse) can be collected and redirected to the reactor. If the CPC is designed for an acceptance angle of +90º to -90º, all of the diffuse solar radiation incident on the

collector plane also impinges directly or indirectly on the photoreactor tube. The light reflected by the CPC is distributed all around the tubular receiver (Figure 4) so that almost the entire circumference of the receiver tube is illuminated and the light incident on the photoreactor is the same as would impinge on a flat plate.

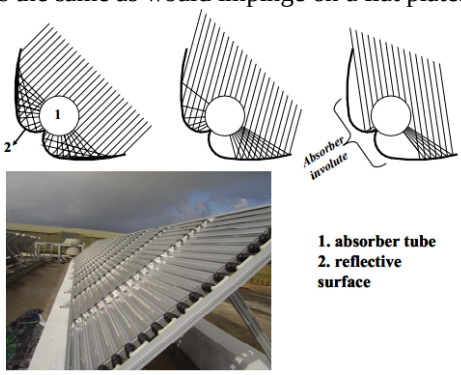

Figure 4: Schematic drawing and photograph of a compound parabolic concentrator

On the basis of geometric configuration of absorber tubes, CPCs have been divided into four types: tabular, flat, fin and inverted vee. Fin or tabular absorber is illuminated on all sides, thereby requiring only half as much absorber material. This result in lower material costs, smaller conductive losses to the back, and gains in
performance since the transient response is improved. While in case of flat receiver configuration has a higher optical transmission due to its shape factor. The benefit of CPC is intrinsic simplicity; cost effectiveness, easy to use and low capital investment. Reflector designs for CPC have ability to collect all direct and diffused UV radiation, resulting in more efficient UV based wastewater treatment. The design of conventional CPC has two disadvantages: (i) its height increases rapidly with aperture, making the structure unwieldy to handle and (ii) a sizable percentage of radiation incident within the acceptance angle suffers multiple reflections before reaching the receiver, resulting into a drop in its optical efficiency. These limitations can be captured by placing the focal points close to aperture. Reflected light on the back of absorber tubes is efficiently used by the pollutants inside the tubes to proceed photochemical reaction. CPCs have been widely studied at pilot plant scale but there are not many evidences regading commercial scale level. Factors inhibiting its performance at commercial level are slow overall rates, low quantum yields, low-order dependence of rates on light intensity, poisoning and fouling of the catalyst, and scavenging of active oxidizing agents by spectator species. Also, solar energy experiences diurnal and annual cycles and varies with weather patterns. The water being treated can contain chemicals that block the critical wavelengths necessary for photo activity and may require pre or post treatment.

Reactor type	Name of reactor	Absorber type	Concentration ratio	Temperature range (°C)
Non-concentrating collector	(i). Compound parabolic collector (CPC)	Tabular	1–5	60–240
	(ii) Evacuated tube collector (ETC)	Flat	1	50–200
	(iii) Flat plate collector (FPC)			30–80

Table 2: Different types of non-concentrating reactors

Role of absorbing tubes and reflecting material is very important in working with CPCs. Absorbing tubes are the major platform which will ensure the compatibility of solar irradiation for the pollutant degradation and excitation of photochemical reaction. Intensity of irradiation reaching at the absorbing tubes depends upon the reflecting material. The higher the reflective behaviour of material, the higher radiations prevail on the tubes and as a result efficiency of photochemical reaction increases. Other auxiliary parts are tank, mixer, circulating pump and temperature controller. Mixer not only ensures uniform composition of reagents but also plays important role in reaction efficiency and uniform mass transfer. Temperature controller keeps the reactor temperature under controlled conditions. In high temperature areas where temperature can have severe affect on reaction kinetics and raise water evaporation issues, controller provides a safe working environment. Flow rate which is adjusted by a simple flow metre, ensures appropriate residence time of fluid in tubes. In order to prevent suspended particles introduction to system a simple filtering media is used to prevent damage in pump and tubes.
Fluid is introduced in the tank and stirrer is started to mix and achieve uniformity. With the help of pump fluid is introduced in the tubes. Reflected radiations by reflector are absorbed by the tubes and photochemical reaction proceeds inside the tubes. In the presence of required conditions (oxidant, catalyst, pH etc.) solar irradiation generates high

oxidizing species which attack on the target pollutant and degrade it into simple and easily removable compounds. Processed fluid leaves the tubes and goes back to tank by completing circle. Samples are collected at the end of tubes after specified time intervals. [13]

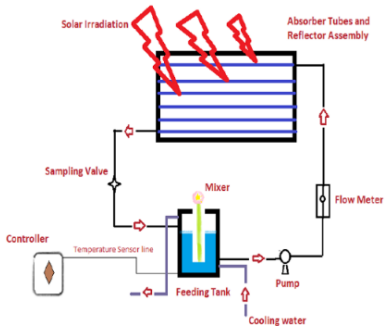

Figure 5: Working of CPCs

III. SOLAR PHOTO REACTOR

In the treatment of industrial waste water, a flat solar energy collector was used which concentrated the solar energy. A catalyst such as TiO2 is used for the treatment which is initiated by the photons.[3]

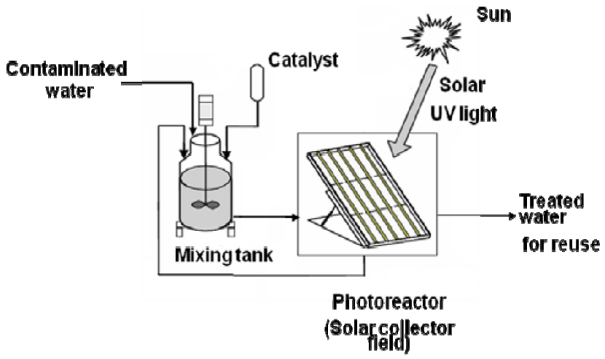

Figure 6: Solar Photo reactor

IV. ADVANCED OXIDATION PROCESSES

AOP are specific chemical reactions characterized by the generation of chemical oxidizing agents capable of oxidizing or degrading the pollutant of interest. The efficiency of the AOP is generally maximized by the use of an appropriate catalyst and/or ultraviolet light. In most AOP, the objective is to use systems that produce the hydroxyl radical (HO•) or another species of similar reactivity such as sulfate radical anion ($SO_4^{\bullet-}$). These radicals react with the majority of organic substances at rates often approaching the diffusion-controlled limit (unit reaction efficiency per encounter). Both of these species are thus highly reactive and only modestly selective in their capacity to degrade toxic organic compounds present in aqueous solution. The principal reaction pathways of HO• with organic compounds include hydrogen abstraction from aliphatic carbon, addition to double bonds and aromatic rings, and electron transfer [4]. These reactions generate organic radicals as transient intermediates, which then undergo further reactions, eventually resulting in final products corresponding to the net oxidative degradation of the starting molecule [5].

The AOP are of two main types: homogeneous and heterogeneous processes, both of which can be conducted with or without the use of UV radiation. Thus, for example, the homogeneous process based on the reaction of Fe^{2+} with H_2O_2, known as the thermal-Fenton reaction process typically becomes more efficient for the mineralization of organic material present in the effluent when it is photocatalysed. This latter process ($Fe^{2+}/Fe^{3+,}$ H2O2, UV-Vis) is commonly referred to as the photo-Fenton reaction. Among the heterogeneous AOP, processes using some form of the semiconductor TiO_2 stand out because UV irradiation of TiO2 results in the generation of hydroxyl radicals, promoting the oxidation of organic species [9].

4.1 Fenton reaction

The thermal Fenton reaction is chemically very efficient for the removal of organic pollutants. The overall reaction is a simple redox reaction in which Fe(II) is oxidized to Fe(III) and H_2O_2 is reduced to the hydroxide ion plus the hydroxyl radical.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$$

The ferric ion produced in can in principle be reduced back to ferrous ion by a second molecule of hydrogen peroxide. However, this thermal reduction is much slower than the initial step and the addition of relatively large, essentially stoichiometric amounts of Fe(II) may be required in order to degrade the pollutant of interest [7]. Another important limitation of the Fenton reaction is the formation of recalcitrant intermediates that can inhibit complete mineralization. Despite these potential limitations, the conventional Fenton reaction has been widely used for the treatment of effluents.

For the degradation of organic molecules, the optimum pH for the Fenton reaction is typically in the range of pH 3-4 and the optimum mass ratio of catalyst (as iron) to hydrogen peroxideis 1:5 respectively. One way of accelerating the Fenton reaction is via the addition of catalysts, in general from certain classes of organic molecules such as benzoquinones ordihydroxybenzene (DHB) derivatives. It is also possible to accelerate the Fenton reaction via irradiation with ultraviolet light or sunlight, a process generally known as the photo-assisted Fenton or photo-Fenton reaction.

4.2 Photo-fenton Process

One of the most efficient AOP is the photo-Fenton reaction ($Fe^{2+/}Fe^{3+,}$ H_2O_2, UV light), which successfully oxidizes a wide range of organic and inorganic compounds. The irradiation of Fenton reaction systems with UV/Vis light (250-400 nm) strongly accelerates the rate of degradation. This behavior is due principally to the photochemical reduction of Fe(III) back to Fe(II), for which the overall process can be written as:

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^{+}$$

Studies of the pH dependence of the photo-Fenton reaction have shown that the optimum Ph range is 3. Studies of the photochemistry of $Fe(OH)^{2+,}$ which is the predominant species in solution at this pH and that is formed by deprotonation of hexaaquairon(III), have shown that $Fe(OH)^{2+}$ undergoes a relatively efficient photoreaction upon excitation with UV light to produce Fe(II) and the hydroxyl radical. Therefore, irradiation of Fenton reaction systems not only regenerates Fe(II), the crucial catalytic species in the Fenton reaction, but also produces an additional hydroxyl radical, the species responsible for provoking the degradation of organic material. As a consequence of these two effects, the photo-Fenton process is faster than the conventional thermal Fenton process. The efficiency of the photo-Fenton process can be further enhanced by using certain organic acids to complex Fe(III). Thus, for example, oxalic acid forms species such as $[Fe(C_2O_4)]^{+}$, which absorbs light as far out as 570 nm, i.e., well into the visible region of the spectrum. This species makes the photo-Fenton reaction more efficient because it absorbs a much broader range of wavelengths of light and because, upon irradiation, it efficiently decomposes (quantum yield of the order of unity) to Fe(II) and CO_2

$$2[Fe(C_2O_4)]^{+} + h\nu \rightarrow 2Fe^{2+} + 2CO_2 + C_2O_4^{2-}$$

The use of photo-Fenton reaction has considerable advantages in practical applications. It generally produces oxidation products of low toxic, requires only small quantities of iron salt (which can be either Fe^{3+} or Fe^{2+}) and offers the possibility of using solar radiation as the source of light in the reaction process sunlight constitutes an inexpensive, environmentally friendly, renewable source of ultraviolet photons for use in photochemical processes.

4.3 Ozone

Ozone is a powerful oxidizing agent with a high reduction potential (2.07V) that can react with many organic substrates. Using ozone, the oxidation of the organic matrix can occur via either direct or indirect routes. In the direct oxidation route, ozone molecules can react directly with other organic or inorganic molecules via electrophilic addition. The electrophilic attack of ozone occurs on atoms with a negative charge (N, P, O, or nucleophilic carbons) or on carbon-carbon, carbon-nitrogen and nitrogen-nitrogen pi-bonds.Indirectly, ozone can react via radical pathways (mainly involving HO•) initiated by the decomposition of ozone. A process that employs ozone is only characterized as an AOP when the ozone decomposes to generate hydroxyl radicals, a reaction that is catalyzed by hydroxide ions (OH-) in alkaline medium or by transition metal cations

$$2O_3 + 2H_2O \rightarrow 2HO^{\bullet} + O_2 + 2HO_2^{\bullet}$$

The efficiency of ozone in degrading organic compounds is improved when combined with H_2O_2, UV radiation or ultrasound. The initial step in the UV photolysis of ozone is dissociation to molecular oxygen and an oxygen atom, which then reacts with water to produce H_2O_2

$$O_3 + h\nu \rightarrow O_2 + O^{\bullet}$$

$$H_2O + O^{\bullet} \rightarrow H_2O_2$$

In a second photochemical step, H_2O_2 photodissociates into the active species, two hydroxyl radicals

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet}$$

The O_3/UV process has been employed commercially to treat ground water contaminated with chlorinated hydrocarbons, but cannot compete economically with the H_2O_2/UV process. A major problem with the use of ozone for water treatment is bromine formation in waters containing bromide ion. Strategies such as addition of H_2O_2 (O_3/H_2O_2) can reduce bromine formation and assure the suitability of ozone for treating drinking and wastewater.

4.4 Heterogeneous AOP

Another important class of AOP is based on the use of solid semiconductors as heterogeneous catalysts for the mineralization of organic compounds. In this type of photocatalysis, an electron in the valence band of the semiconductor (CdS, TiO_2, ZnO, WO_3, etc.) is promoted into the conduction band upon excitation. The electron in the conduction band typically reacts with O_2, while the hole in the valence band can react with an adsorbed pollutant or oxidize water to produce a surface-bound HO• radical.

The anatase form of titanium dioxide (TiO_2) is the material most indicated for use in photocatalytic water treatment, considering aspects such as toxicity, resistance to photocorrosion, availability, catalytic efficiency and cost. Using TiO_2 as the semiconductor, the photocatalysis is based on the activation of anatase by light . The band gap or energy difference between the valence and conduction bands of anatase is 3.2 eV. Thus, UV light of wavelength shorter than 390 nm is capable of exciting an electron (e-) from the valence to the conduction band.

$$TiO_2 + h\nu \rightarrow e^- + h^+$$

An important feature of TiO_2 photocatalysis is the very high oxidation potential of the holes left in the valence band (3.1 eV at pH 0), making it possible for photoexcited TiO_2 to oxidize most organic molecules.[9]

CONCLUSION

This review deals with the (i) industrial wastewater treatment and (ii) water disinfection applications via sunlight induced advanced oxidation processes (AOPs). While potentially effective, most of the UV light induced AOPs have drawbacks in terms of high operational costs, which is mainly a result of high energy consumption. The use of sunlight enables to move towards natural and unlimited source of UV light which is a key agent in photo based AOPs. Solar reactors replace the artificial UV resources and provide inexpensive, renewable, and sustainable solution for wastewater treatment and water disinfection.

CPC is the most mature reactor type of non-concentrating solar reactors that show better performance compared to concentrating solar reactors. Reflective surface and absorbing tubes has key role in operation, therefore material selection and construction of these components needs special attention.

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