Photoreactors for Heterogeneous Photocatalysis for Wastewater Treatment

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Abstract - ***Heterogeneous photocatalysis is a science of chemical engineering which finds its applications in various field, especially, hydrogen production through water splitting and degradation of organic contaminants in wastewater. A lot of research is being carried out in synthesizing a suitable catalyst as well as developing a suitable photoreactor where the application can be carried out. Design of a proper reactor involves a proper study of reaction kinetics of the involved reactions, study of solid-fluid interactions, and solar energy utilisation. This paper briefly discusses some of the types of photoreactors that have been designed so far for the purpose of wastewater treatment through photocatalysis. The first part briefly discusses photocatalysis and the later part discusses in detail, some designs of the photoreactors, with the hope that the readers will get an overview of the requirements of a proper and suitable photoreactor.***

Key Words: *photocatalysis, solar light, photoreactor, TiO2, composites*

1. Introduction

Wastewater produced by industries is required be treated before it is discharged into the water bodies. Governments of all countries have laid down rules and regulations for the same. The Gujarat Pollution Control Board (GPCB) in Gujarat have also prescribed some standards and norms for wastewater discharge. Conventional treatment methodology involves primary, secondary and tertiary treatment. But in most of the cases, the processes and treatment techniques are energy intensive and usually convert one type of pollution to another type, e.g., the process of adsorption only transfers the pollutant from liquid to solid. Thus, a process is needed which degrades the pollutants and also involves less energy. Photocatalysis is an Advanced Oxidation Process (AOP) which utilises solar energy and degrades the organic contents present in the wastewater to water (H2O) and carbon dioxide (CO2). The required energy that is utilised is solar energy and there is no conversion of pollution from one form to another, rather complete mineralisation takes place.

The equipment where this kind of photocatalytic process can be carried out is known as a photoreactor. The design of such a photoreactor is a challenging process because the reaction kinetics of photoreactions is normally difficult to establish as it is dependent on a number of short-span intermediate products. Nevertheless, continual efforts are being made in the direction of photoreactor design which caters to various applications. This article gives some designs of photoreactors that used for the applications of degradation of industrial effluent containing organic pollutants. The basics of solar photocatalysis, especially in the visible light region, its parameters and basic photoreactor have been reported in literature [1] [2].

2. Solar Photocatalysis, an Advanced Oxidation Process

As mentioned before, photocatalysis is an advanced oxidation process which completely mineralises the organic contents to water and carbon dioxide. Principally, it involves a semiconductor material which has a characteristic energy band gap level difference between its valence band and conduction band sufficient to be overcome by the electrons excited by solar irradiation. This mechanism is depicted in Figure 1. A semiconductor material has two energy levels called the valence band and the conduction band, separated by an energy band gap. When energy is imparted to this material, the electrons gain energy and sufficient to overcome the existing band gap, leave the valence band and reach the conduction band, leaving behind a hole (deficiency of an electron) in the valence band, equation (1). These electrons and holes are highly unstable and are looking forward to get recombined, equation (2). Before recombination takes place, it is imperative that these electrons and holes are captured to give unstable, yet very strong radicals, equations (3), (4). These radicals react with the organic pollutant, form a number of short spanned intermediates, and finally degrade them into water and carbon dioxide as shown in equations (5) and (6).

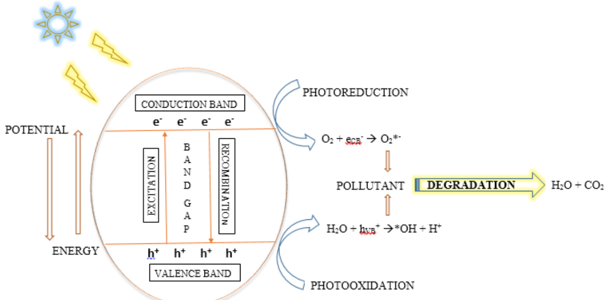

Figure 1: Basic mechanism of semiconductor photocatalysis

The reactions involved in the phenomena may be summarised as follows:

Photocatalyst + hν (energy) → eCB- + hVB+ (1)
eCB- + hVB+ → energy (heat) (2)
O2 + eCB- → O2*– (superoxide radical) (3)
H2O + hVB+ → *OH (hydroxyl radical) + H+ (4)
pollutant + O2*– → Intermediates → H2O + CO2 (5)
pollutant + *OH → Intermediates → H2O + CO2 (6)

A proper photoreactor is the one that helps carry out the above reactions (1), (3), (4), (5) and (6) to the best of its capabilities and brings about demineralisation of the organic pollutants. Some of the functional reactors are discussed in the subsequent section.

3. Photoreactors for wastewater treatment

The function of a photoreactor, as discussed in the previous section is to carry out the reactions (1), (3), (4), (5) and (6). This involves the interaction of all the three phases viz., solid, which is the photocatalyst, liquid, which is the pollutant and gas, which is oxygen. moreover, the intermediates and the radicals are also short spanned. Hence the design of a photoreactor is a very complex phenomena, however, for proper reactions to take place, proper contact of all the three phases is a must, this is ensured by high turbulence. Also, the reactants and the phases must be properly illuminated so as to bring about an activation of the photocatalyst. The design, hence, involves multiple reactions, multiple phases and multiple phenomena occurring simultaneously. Following are the some of the photoreactors designed by researchers.

3.1 Parabolic trough Photoreactors (PTP)

This type of photoreactor has a parabolic reflector that collects the solar radiations and concentrate them on to a photoreactor kept at the focal line. The photoreactor is a transparent tube containing the effluent with a proper amount of, generally suspended, photocatalyst in it. For photocatalytic operations the concentration ratio of a PTP is maintained between 5 and 30. The layout of a typical PTP is depicted in Figure 2.

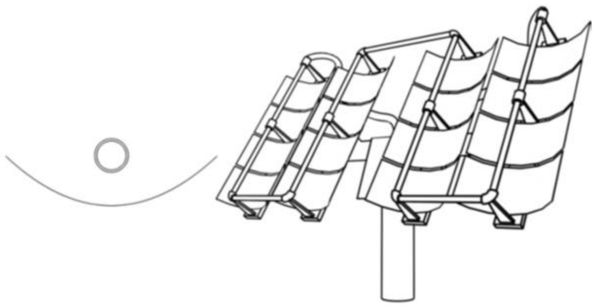

Figure 2: Parabolic trough collector/photoreactor [3]

As all the radiations are concentrated on to the focal line, hence this type of a solar collector/photoreactor needs a tracking system. The tracking is single axis, which follows the sun from morning till afternoon/evening and/or dual axis, where its orientation needs to be changed on diurnal basis plus seasonal basis. Barring this limitation, a PTP concentrates the maximum amount of radiations falling over it.

3.2 Compound Parabolic Photoreactors (CPP)

The geometry and layout of a CPP is as depicted in Figure 3. The concentration ratio (CR) of a CPP is given by

$$CR = \frac{1}{sin\theta_a}$$

where θ_a is its acceptance angle. If the concentration ratio is equal to 1, then the acceptance angle is 1 and the trajectory of the collector is a simple involute. This type of a collector, then, would not need a diurnal tracking system, which is the biggest advantage of a CPP.

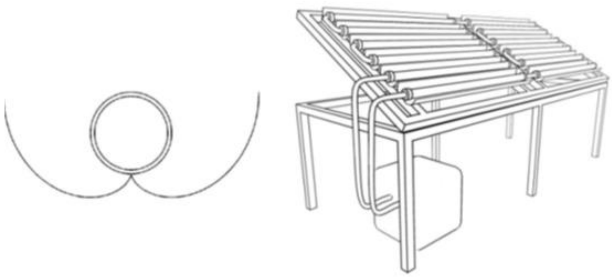

Figure 3: Compound Parabolic Collector/Photoreactor [3]

Another advantage of a CPP is that it can also collect the diffuse radiations alongwith beam radiations. A number of CPP based pilot plant constructions have been fabricated on various types of effluents, notable among them being "Solardetox" project [4] [5] and Solwater project [6].

3.3 Inclined Plane Photoreactors (IPP)

The IPP is essentially an inclined surface over which the effluent, along with the photocatalyst dispersed, is made to flow. It is exposed to the light source as it flows down in a thin film form under the action of gravity. The inclined surface can either be smooth or rough (step-wise) in order to induce more turbulence (Figure 4).

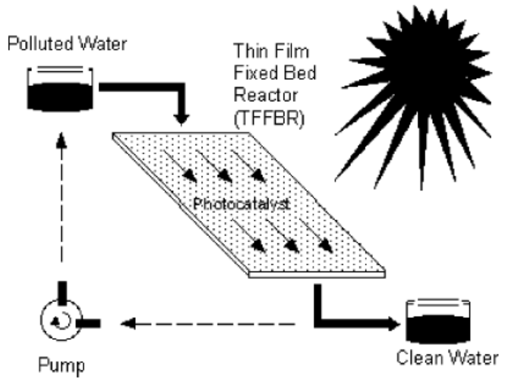

Figure 4: Non-tracking Inclined Plane Photoreactor. [7]

The Inclined Plane Photoreactor has an advantage of not needing a tracking system.

3.3 Double Skin Sheet Photoreactors (DSSP)

A double skin sheet photoreactor is essentially a non-tracking photoreactor. It consists of a transparent and flat channelled box. The pollutant alongwith the photocatalyst is made to flow through these channels and in the process of flowing the catalyst works on the pollutant and degrades it to harmless constituents. It also has an advantage of being able to utilise both the beam and the diffuse radiations and needs no tracking mechanism. Figure 5

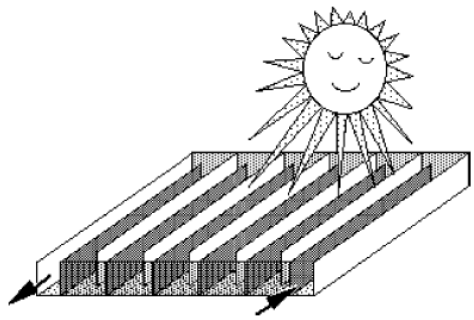

Figure 5: Non-tracking Double Skin Sheet Photoreactors [7]

4. CONCLUSIONS

A review of the photoreactor case studies has been discussed in the preceding sections. PTPs have the advantage of concentrating the radiations so that the intensity increases and hence the amount of photocatalyst required reduces. However, this needs a tracking system and a slight imperfection may result in high loss of optical efficiency. Also, only bean radiations can be concentrated and hence a large part of the solar radiations that is diffuse is wasted. However, a significant number of examples of successful deployment of PTPs for wastewater degradation including contaminants like pesticides, metal complexes, organics and microbes have been observed and reported. In most of the cases, the catalyst is in the suspended form, although a few installations have used it in the supported form as well.

CPPs provide such a geometry that the entire absorber tube surface receives the radiations almost homogeneously. Moreover, no sun tracking is required and hence the design and operational complexity reduces significantly. This has made them about 30-200% more efficient, as reported, than PTPs. It is more suitable for supported catalysts.

IPPs are the ones that maximise the optical requirement of photocatalysis, viz., the contact of wastewater, the catalyst and the photons. The catalyst can be deposited by coating or by using a photocatalyst -coated mesh or -impregnated paper. The “step” design ensures reduction in mass transfer barriers and increased oxygen transfer from the atmosphere. Also adding corrugations increase the efficiency. However, the major concern is about achieving a layer, about 100-200 μm thin which typically calls for a very small flow rate of about 0.15-1 L/min.m2, typically giving a laminar flow. Open IPPs are also susceptible to evaporative losses, which can be controlled by enclosing the unit with a transparent material.

Although simple in design, DSSPs have not been investigated much. In the installations so far, the average photonic efficiency of about 2% compared to about 0.4% of IPP, has been reported. It calls for a very high surface area for actual treatment using the principles of photocatalysts and hence make them relatively infeasible for large volumes.

A combination of natural and artificial light source could be a good configuration though.

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