Chapter 6

Design improvement and performance evaluation of solar photocatalytic detoxification reactor for industrial effluent
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Testing of the catalyst in a prototype reactor system is considered necessary to simulate its employability and predict its performance in the field conditions. This chapter presents the details of the design components and materials used in a linear compound parabolic reactor (CPR) constructed with an aim to use the photocatalyst for solar photocatalytic applications. A CPR has been designed and engineered to exploit both UV and visible part of the solar irradiation. The performance of the CPR has been evaluated in terms of degradation of a probe pollutant using the parameters such as rate constant, residence time and photonic efficiency. An attempt has been made to assess the performance in different ranges of solar spectrum. Finally the developed CPR has been employed for the photocatalytic treatment of a paper mill effluent using Degussa P25 as the photocatalyst. The paper mill effluent collected from Nagaon paper mill, Assam, India has been treated under both batch mode and continuous mode using Degussa P25 photocatalyst under artificial and natural solar radiation, respectively. The photocatalytic degradation kinetics of the paper mill effluent has been determined using the reduction in total organic carbon (TOC) values of the effluent.

6.1 Introduction

The generation of hazardous industrial effluents is one of the most serious problems experienced by both the developed and developing nations. Most of the industries such as petrochemical, pharmaceutical, textile, agricultural, food, and chemical industries, generate waste effluent contaminated with organic compounds such as aromatics, haloaromatics, aliphatic, dyes, dioxins and a wide range of other polluting materials which are noxious in nature. So these pollutants should be treated prior to discharge. Among them water pollution from the pulp and paper industry is one of the important concerns in this part of the country due to the large quantity and
toxicity of the effluents created during pulp and paper production[1]. For production of 1 ton of paper 60 m$^3$ of liquid effluent is generated that is heavily loaded with organic compounds depending on the nature of the raw materials, process, product and extent of water reused [2,3]. The use of different chlorine based compounds as bleaching chemicals generate various toxic chlorinated organics called adsorbable organic halides (phenols, resin, fatty acids, furans and dioxins) in the bleach plant effluents [2,3]. Among them some are toxic, mutagenic, and biodegradation resistant [2]. Adsorbable organic halides (AOX) in the bleaching effluent generate from chlorination of outstanding lignin in the pulp. Thus, O$_2$ delignification and the substitution of molecular chlorine by chlorine dioxide in the ECF (Elemental Chlorine Free) bleaching process reduces the amount of chlorinated organics formed [1]. Conventional waste treatment systems using techniques such as coagulation, chlorination or ozonation which employ potentially hazardous or polluting materials [4-6]. Thus, Solar photocatalysis provides a better alternative of treatment of such industrial waste water effluents [6-11].

Many studies are available on the development of various type of photocatalytic reactors working under solar or artificial illumination [12-17]. The types of photocatalytic reactors reported have been successfully employed for detoxification, disinfection, and hydrogen production, applications. Most of the solar photocatalytic reactors use only UV part of the solar irradiation for waste water treatment. The dependency of reaction rate on solar irradiation has led the researchers to use the concentrator based reactors for photocatalytic applications [18-23]. Among the different concentrating type photocatalytic reactors the solar compound parabolic reactor is the most studied one because of its efficient light harvesting characterization [23]. For the treatment of contaminated water researchers have used the involute reflector in a compound parabolic reactor (CPR) [18-27]. Since the development of visible active photocatalysts, these involute reflector based CPR have not been tested considering the visible part of the spectrum. Also the reactors have not been tested under cloudy weather conditions, with high diffuse component in radiation usual in Indian subcontinent. Due to high acceptance angle of CPR, it is possible to realize good performance through such design. These
observations made us to develop an indigenous CPR which can make use of both the UV and visible part of solar spectrum.

The present chapter reports the work done to develop a linear CPR with high acceptance angle along with the wide spectrum reflector to receive both UV and visible radiation, even if it has only moderately high concentration ratio. The performance of the system was measured in UV-Visible and visible using Degussa P25 as the photocatalyst and MB as the probe pollutant. Phenol degradation study was also performed using Degussa P25 as the probe catalyst. As discussed in foregoing chapters Degussa P25 is a mixed phase catalyst which shows moderate visible light activity, which has been reported widely earlier [22]. Also a study of the photocatalytic degradation of paper mill effluent collected from the Nagaon Paper Mill, Assam, India under both batch type and continuous type reactor using Degussa P25 as a probe catalyst is described. The Nagaon paper mill effluent characteristics has been studied and the details are available[28].

6.2 Experimental section

6.2.1 Degradation in continuous type reactor

Photocatalytic reactors based on compound parabolic collectors (CPCs) were fabricated for carry out the experiments under solar irradiation as shown in the schematic diagram of the reactor (Figure. 6.1). It was a compound parabolic collector(CPC concentration ratio, C 1.14, acceptance angle,$\theta_a=120^\circ$) module with receiver in the form of four tubular channels each of a circular cross section (length of each reactor tube 1.03 m, inner diameter 0.03 m, outer diameter of the tube 0.034 m) connected in series. The fixed concentrating collectors, designed here, had a reflective surface of front coated aluminum reflector with quartz absorber tube at the focus. Such a system is expected to give the most efficient light-harvesting but can acheive low concentration ratio. The performance of the CPR was investigated under total and visible irradiation using Methylene Blue (MB) as the probe pollutant and Degussa P25 as the catalyst. Large part of UV as well as IR of the total solar radiation was eliminated using one glass cover over the reactor for visible light studies. The reactors with glass and without glass cover are shown in Figure.6.2.
Figure 6.1: Schematic diagram of the compound parabolic reactor with different parts

The aqueous pollutant along with the catalyst circulated under completely mixed conditions inside the CPR absorber tubes in a closed recirculating loop. The hydraulic system of the photocatalytic reactor had a continuously stirred tank, a peristaltic pump and a solar collector with four CPC modules arranged in series and placed on fixed supports. The aperture plane was inclined with respect to the horizontal plane to receive maximum radiation on the day. The total volume of the effluent in the experiments was 6 ltr. and the effluent irradiated in the solar reactor channels was 3.8 ltr. The whole experimental set up is shown in Figure. 6.3. For the experimentation the aqueous pollutant solution was initially mixed with of 0.5gm/l photocatalyst loading and was kept in dark for 3-4 hrs to ensure adsorption-desorption equilibrium. After that the solution was fed in to the reactor using a peristaltic pump [Miclins, PP30EX, India] at a rate of 10 ltr./hr for degradation study. The incident radiation intensity was measured with the help of research radiometer (International light, USA with detectors SD 005, SD 033). The experiments was performed under total
radiation intensity of 650-850 W/m² (24-33 W/m² of UV component of radiation). The TOC concentration of the samples was estimated with the help of TOC analyzer (Liqui TOC, Elementer; Germany). Sample were taken at regular intervals.

Figure 6.2. The compound parabolic reactor with glass (B) and without glass (A) cover

6.2.2 Degradation in batch type reactor

Initially the photocatalytic degradation was studied in batch mode reactor under UV (λ<380 nm) with a radiation intensity of 42.5 W/m². The catalytic material loading of the experiment was kept at 0.5 g/l and the average reactor temperature was maintained at 30 °C. The experiments were carried out by simultaneous exposure of the catalysts Degussa P25 having 200 ml of effluent under stirred condition. To ensure adsorption-desorption equilibrium the effluent solutions were kept in dark for 2 hrs before exposing them to irradiation. The samples were taken from the reactor at regular interval.
Among the different linear CPR receivers (flat plate, vertical plate, wedge plate, and tubular), tubular receiver, seems to be more suitable to meet the practical requirements. As fluid circulation is required in the solar reactors and also that the solar reactor should be economical and efficient, the use of tubular photo reactors is an apparent choice. Hence, the compound parabolic reactor with tubular transparent receiver has been selected in the design of our photocatalytic solar reactors. Another advantage of this reactor is that solar irradiation can be received around the perimeter of the receiver. The design of CPR is based on a non-imaging theory. Figure 6.4 shows the schematic representation of CPR with a cylindrical absorber of circular cross-section. Curve GH and IH are involutes of the developed CPR. Curve GA and IC are the two symmetrical parabolas with their focus locating at point I and G, respectively. Line AC is the aperture of the CPR. The maximum acceptance half angle is the angle between the principal axis of the parabola and the vertical line ($\theta_a$).
Figure 6.4: Schematic representation of CPR with a round absorber.

Theoretically all the incoming light with incident angle smaller than the maximum half acceptance angle could be line focused on the absorber. This geometry helps all the solar irradiation with incident angle equal to or less than $\theta_a$ to be focused on the absorber.

Shah et. al. proposed a design methodology for CPC. Same methodology has been adopted in this work [29,31]. The concentration ratio of a two-dimensional linear CPR with tubular absorber is given by:

$$C = \frac{1}{\sin \theta_a} = \frac{w}{2\pi r_e}$$

where $r_e$ is the outer radius of the tubular absorber and $w$ the aperture width of the CPR. In some cases the upper ends of CPR was also truncated as shown in Figure. 6.4 for aperture DE. In this situation, cost of the CPC will be considerably reduced while its concentration factor is not strongly affected.

The height of the aperture is given by [30,31]:

$$H = \frac{w}{2} \left(1 + C\right) \left(1 - \frac{1}{C^2}\right)^{\frac{1}{2}}$$
In Cartesian coordinates the reflector is given by the locus of the point [29]

\[\begin{align*}
x &= r_o [\sin \theta - M(\theta) \cos \theta]; \\
y &= -r_o [\cos \theta + M(\theta) \sin \theta]
\end{align*}\]  
(6.3)

where, \[M(\theta) = \frac{\theta + \theta_a + \pi / 2 + 2\beta - \cos(\theta - \theta_a)}{1 + \sin(\theta - \theta_a)}\] & \[\theta' = \theta + \beta\]

where the range of “\(\theta\)" is: \(\left[\theta_a + \frac{\pi}{2}\right] \leq \theta \leq \left[\frac{3\pi}{2} - \theta_a\right]\)

\(r_o\) is the inner radius of the tubular absorber

\(\theta' = \angle HRK, \theta = \angle KMH\) and \(\beta = \angle ROH\) are the design angle used in the receiver

In Cartesian coordinate the involute is given by the locus of the point [29]

\[\begin{align*}
x &= r_o \left(\sin \theta - \theta' \cos \theta\right) \\
y &= -r_o \left(\cos \theta + \theta' \sin \theta\right)
\end{align*}\]  
(6.4)

where the range of “\(\theta\)" is: \(\cos^{-1}\left[\frac{r_o}{r_e}\right] \leq \theta \leq \left[\theta_a + \frac{\pi}{2}\right]\).

Area of the concentrator is given by\([30,31]\]

\[A = wL \sin \theta_a (1 + \sin \theta_a) \left[\cos \frac{\theta_a}{\sin^2 \theta_a} + \ln\left\{\left(\frac{1 + \sin \theta_a}{1 + \cos \theta_a}\right)\right\} - \frac{\sqrt{2} \cos \theta_a}{\left(1 + \sin \theta_a\right)^{3/2}}\right]\]  
(6.5)

where \(L\) is the length of the absorber

6.3.2. Materials used in designing and testing of the CPR:

The materials used in designing CPR are the materials of collector and receiver. A commercial polished aluminum with an anodized aluminum layer has been used as the material for reflector in this work. The reflectance of this material along with other commonly used reflectors in all the wavelength ranges is shown in Figure. 6.5. For the receiver material cylindrical tubes made from quartz has been taken. The transmittance of the quarts tube along with normal glass tube is shown in

6.8
Figure 6.5: Reflectance spectra of different reflector materials

Figure 6.6: Transmittance spectra of different receiver materials

Figure 6.6. The material used in testing the performance of the CPR was Degussa P25
catalyst, which is a mixed phase catalyst with high activity under UV radiation and moderate to low activity under visible radiation.

6.3.3. Performance testing

Photocatalytic performance of the catalyst is measured in terms of reaction rate constant by measuring change in concentration with time. If the reaction rate constant is determined using Langmuir-Hinshelwood (L-H) kinetics by simply using the concentration time history in the tank, the result would be in error unless the tank volume (V_T) is negligible as compared to the reactor volume (V_R), which is usually not the case. Wulfrum and Turchi [23, 32] suggested that an apparent reaction rate constant k_{app} may be calculated by using the equation (6.6) and the concentration-time history in the tank. Hence the values of actual rate constant “k” and k_{app} is given by equation (6.5) and (6.6), respectively.

\[
k = k_{app} \left( \frac{1 + \gamma}{\gamma} \right)
\]

(6.5)

where, \( \gamma = \frac{V_R}{V_T} \) and \( k_{app} = \frac{\ln \left( \frac{C_i}{C_f} \right)}{\Delta t} \) (6.6)

i. e. the value of k_{app} can be determined from the slope of the concentration-time plot. Here, \( C_i \) and \( C_f \) are the initial and final concentration of the reactant in the whole reaction respectively.

6.3.4. The residence time determination:

In photocatalytic detoxification application residence time refers to the amount of time that water spends in a reactor. Flocculation tanks are part of drinking water treatment facilities where the chemically treated water needs enough time to form flocks before reaching the sedimentation basin. These processes are dependent on an adapted version of residence time. In this situation, the important parameter is how long a fluid of given concentration needs to remain in the system in order to be adequately treated [33, 34]. The residence time “\( \tau \)” is given by the equation (6.7).
\[ \tau = \frac{\ln \left( \frac{C_i}{C_f} \right)}{k} \]  

(6.7)

6.4 Results and discussion

6.4.1. Designing of the CPR

The CPR was designed using the methodology described in the Section 6.3. The final reactor was a combination of four numbers of CPR channels after theoretical performance optimization taking in to account truncation, material and design parameters [35]. The length of the each receiver tube was 1.03 m and the inner and outer diameter of the reactor tube was 0.030 and 0.034 m, respectively. The optimum values of the acceptance angle, concentration ratio and aperture height, aperture width after truncation of the concentrator were 120°, 1.14, 0.072 m and 0.108 m, respectively enabling it to collect both beam and diffuse radiation. The area of the single CPR was 0.0946 m² and the total area of the reactor was 0.3784 m². Hence it could receive almost 88 % UV radiation incident on it [18]. The designed CPR with four channels is shown in Figure 6.3.

The values of various parameters associated with the flow system of reactor such as a single reactor channel volume, total reactor channel volume, tank volume and the total silicon pipe volume are 0.0935 m² (0.94 ltr.), 0.3740 m² (3.74 ltr.), 6 ltr. and 0.64 ltr., respectively. According to the reactor design methodology the value of \( \gamma \) should be always be less than one [34]. In this case the value of \( \gamma \) is found to be 0.63. This value may be used for the calculations of the actual rate constant \( k \).

After fabricating the CPR the reactor test set-up was prepared by connecting a peristaltic pump, and a tank, in series using silicone pipes. The translucent silicon pipes were wrapped with aluminum foil. The schematic diagram and the photograph of the reactor test set-up have been shown in Figures. 6.2 and 6.3, respectively.
6.4.2. *Photocatalytic performance testing of the designed CPR under total and visible part of solar irradiation:*

For carrying out the performance testing of the CPR 0.01 mM of 6 ltr. aqueous methylene blue (MB) solution was prepared.

![Graph showing MB degradation spectra](image)

Figure 6.7: MB degradation spectra of Degussa P25 under total and visible part of solar radiation.

Degussa P 25 catalyst was loaded at 0.5 gm/l in MB solution to treat it in slurry mode. After this it was fed into the reactor for detoxification. The whole experiment was carried out under normal solar irradiation. First, the experiments were conducted to check the performance of the CPR under total radiation. After that the performance of the CPR was also determined for the radiation excluding the large part of UV and IR of the solar radiation by placing a glass cover over it. The same probe pollutant was used here also. Sampling was done at a specific interval of time. The change in concentration was measured in terms of absorbance using spectrophotometer. The $-\ln(C/C_0)$ vs. time graph was plotted in every case for determination of the apparent rate constant. Thereafter the actual rate constant was calculated using the equation 6.5. The normalized concentration vs. time plot was used for the determination of the degradation kinetics. The concentration time plots for total radiation...
Figure 6.8: Rate constant calculation spectra of Degussa P25 under total and visible part of solar radiation.

(Including and excluding large UV part) of the MB dye has been given in the Figure 6.7. Again the plots for the calculation of apparent rate constants in degradation (including and excluding large UV part) have also been given in Figure 6.8, respectively. The values of all other parameters are tabulated in Table 6.1.

Table 6.1: Values of the kinetic parameters of degradation of MB under total and visible solar irradiation

<table>
<thead>
<tr>
<th>Irradiation Type</th>
<th>Apparent rate constant (min⁻¹)</th>
<th>Rate constant (min⁻¹)</th>
<th>Residence time (min)</th>
<th>Photonic efficiency (%) Under total radiation</th>
<th>Photonic efficiency (%) Under UV radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solar Irradiation</td>
<td>0.0350</td>
<td>0.0878</td>
<td>23.15</td>
<td>0.0065</td>
<td>0.106</td>
</tr>
<tr>
<td>Visible Irradiation</td>
<td>0.0156</td>
<td>0.0404</td>
<td>63.91</td>
<td>0.0023</td>
<td>NA</td>
</tr>
</tbody>
</table>

From all these data it is seen that this CPR gives the values of kinetic parameters which are comparable with the earlier reports [36-37]. The system performance with respect to the radiation intensity was studied by calculating photonic efficiency. The system showed high photonic efficiency in the UV and less in total and visible
radiation. The moderately better degradation performance of the MB in visible part may be ascribed to the effective use of visible part of the radiation by the indigenous CPR. This interesting result needs further verification even though it can be assumed that the CPR may be effectively used for other visible active photocatalysts as well.

The performance testing of the indigenous reactor was further carried out using phenol as the probe pollutant and Degussa P25 as the probe catalyst to ensure the performance by excluding self-photolysis commonly observed in dyes. 0.6 mM of 6 l contaminated phenol solution was prepared. Degussa P 25 catalyst was added at 0.5 gm/l for the test in slurry mode. Then it was fed into the reactor for detoxification similar to the above experiment. The whole experiment was carried out under normal solar irradiation. The indigenous CPR could photodegrade the phenol effectively.

![Figure 6.9: Phenol degradation spectra of Degussa P25 under total solar irradiation](image)

The apparent rate constant was calculated by plotting $-\ln(C/C_0)$ vs. time as shown in Figure 6.10 and the values are given in Table 6.2. Thereafter, the actual rate constant was calculated using the equation 6.5. The photonic efficiency values also showed better result as shown in Table 6.2.
The photocatalytic treatment of Nagon paper mill effluent was carried out under both batch and continuous mode. The treatment was carried out over the designed indigenous reactor using Degussa P25 as the probe catalyst. The test was performed by taking 6 l of contaminated effluent. Degussa P 25 catalyst was added with 0.5 gm/l in slurry mode to the above solution. Then it was fed into the reactor for detoxification similar to the above experiment. The paper mill effluent consisted of a number of different constituents such as phenolic derivatives and AOX. It is difficult to measure the degradation of this contaminant through spectrophotometric measurement because of the presence of a number of pollutant and degradation product molecule. Hence TOC measurements were considered to determine the appropriate kinetics. The TOC concentration of the treated effluent was estimated using the TOC analyzer. The normalized carbon (TOC) content vs. time plots were used to show the degradation (Figure. 6.11) along with the “-ln(C/C_0) vs. time” plot (Figure.6.12). From the graph it is clear that the degradation pattern follows pseudo-first order kinetics. The various parameters, considered in this case, were calculated using equation (6.5), (6.6), (6.7) and given in Table 6. 2.
Figure 6.11: Paper mill effluent degradation spectra of Degussa P25 under total solar irradiation

The rate constant value under batch mode and continuous mode are relatively similar. It implies that the CPR is effective for the degradation of paper mill effluent as well. The photocatalytic treatment of paper mill effluent in batch mode showed

Table 6.2: Values of the kinetic parameters of degradation of paper mill effluent and phenol under total solar irradiation

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Continuous mode</th>
<th>Batch mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Apparent rate constant (hr⁻¹)</td>
<td>Rate constant (hr⁻¹)</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.143</td>
<td>0.370</td>
</tr>
<tr>
<td>Paper mill effluent</td>
<td>0.115</td>
<td>0.297</td>
</tr>
</tbody>
</table>

apparent rate constant value of 0.099 hr⁻¹. Under continuous mode, the actual rate constant value was 0.297 hr⁻¹ which was double compared to the batch mode. The results of the values of the parameters were compared with the values reported earlier [38-39], which were slightly higher than the present values. This was because the
Figure 6.12 Rate constant calculation spectra of paper mill effluent using Degussa P25 under total solar irradiation

number of photons available in continuous mode is higher than in the batch reactor mode and also the impact of visible light in mixed phase catalyst

6. 5. Conclusion

In this chapter design and construction of a CPR developed with an aim to increase the utilization of total solar radiation successfully for the photocatalytic degradation applications in the field conditions has been reported. The developed CPR could receive almost 88% of UV radiation along with a major part of visible radiation. The working of the system has been successfully demonstrated through MB degradation experiments in slurry mode with the photocatalyst Degussa P 25. The utilization of small visible light activity of Degussa P25 has been demonstrated in the system. The photocatalytic degradation study of the paper mill effluent emerging out from the Nagaon paper mill was conducted. The photocatalyst Degussa P25 was found to be considerably successful in the treatment of the effluent in both batch mode as well as continuous mode.
References


