Novel Solar-Based Photocatalytic Reactor for Degradation of Refractory Pollutants

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Considerable information on the chemical aspects of photocatalytic degradation (PCD) is available in the literature, which was recently reviewed by Bhatkhande et al. (2001). Notwithstanding the substantial advantages of PCD, this technique is yet to be implemented on large scale for treatment of industrial wastes. The main hurdle in the commercialization is the lack of suitable hardware—that is, a reactor—which gives high space–time yields. The PCD process is discussed in detail by Bhatkhande et al. (2001). The electrons generated in the process are removed by oxygen supplied through air. Thus, the supply of oxygen to the catalyst is of significant importance. Further, it is now established (Mills et al., 1993a; Turchi and Ollis 1990) that PCD occurs by attack of photogenerated $OH^{\bullet}$ on the adsorbed substrate. The latter needs to diffuse from the bulk liquid to the catalyst surface before it is adsorbed. The adsorption process can be considered as relatively rapid and hence at equilibrium. The mechanism outlined above indicates that a commercial reactor should have the following attributes:

(1) High catalyst surface area per unit volume

(2) Maximum penetration of the incident radiation to all parts of the reaction volume

(3) High rates of oxygen and substrate mass transfer from the respective phases to the catalyst surface

Degussa P-25, a mixture of anatase (70%) and rutile (30%), is the most widely used photocatalyst. This catalyst has a very small particle size (30 nm), and thus its use in free form creates serious problems of filtration. In view of this, most investigators have used the catalyst in immobilized forms. Two types of immobilized photocatalysts have been used:

(1) Catalyst immobilized on fixed surfaces (such as Pyrex glass tubes and optical fibers; Anderson et al., 1993; Hofstadler et al., 1994; Yatmaz et al., 1993; Yue and Puma, 1999).

(2) Catalyst immobilized on silica particles (Haarstrick et al., 1996; Ray, 1999).

In the first type the drawbacks of poor diffusive transport and low catalyst surface far outweigh the advantage derived by immobilizing the catalyst (that is, no filtration). In the second case the catalyst carrying particles are fluidized, thus allowing turbulent mass transfer. This type has three drawbacks: (1) limited surface area, (2) loss of catalyst resulting from attrition, and (3) low catalyst loading needed to allow good transmission of photons to the interior.

One alternative that can overcome this problem lies in the use of candle filters that rely on surface filtration under conditions such that there is a zone of high shear near the filter surface, which prevents solid deposition. With this alternative it is possible to use fine photocatalysts without any filtration problem. The high surface area per unit mass of this catalyst allows low catalyst loading (<1 wt %). For instance, 0.5 wt % loading of the catalyst in a predominantly aqueous solution affords a surface area of about 200 m^2/m^3 of the reactor volume, which is far greater than what can be achieved with an immobilized catalyst. Further, the low photocatalyst loading can allow better penetration of the incident photons. Figure 1 shows the configuration of the slurry bubble column used. The air passed into the reactor was presaturated with water. The candle filter is located in the vicinity of the air sparger. In this region there is a relatively high (several m/s) liquid circulation velocity, which prevents deposition of the solid on the filter surface. The liquid hydrostatic head in the column serves as the driving force for filtration, allowing retention of the catalyst in the reactor. The small particle size and catalyst loading allow ease of solid suspension at relatively low (0.03–0.05 m/s) air sparging rates. Thus, the energy requirement for air sparging can be kept low. In the case of artificial UV radiation, the efficiency of conversion of electricity is another factor that affects the economics of PCD. The efficiency of conversion of electricity to the UV radiation and its subsequent use in PCD is very low (Mills et al., 1993a). Solar radiation, which is abundantly available in the equatorial and tropical countries (such as South America, African countries, Middle East countries, In-

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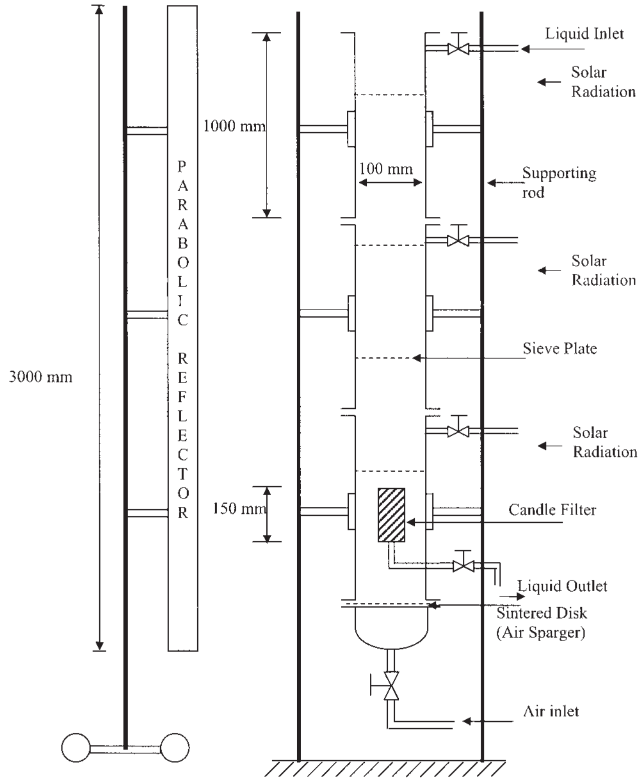

Figure 1. Slurry bubble column reactor.

dian Subcontinent, and Australia), can be a highly economical alternative to artificial UV radiation in the daytime. The solar spectrum reaching the earth's surface mostly consists of radiation of wavelength ≥ 290 nm and can be useful for a semiconductor photocatalyst like TiO_2, which has a $\lambda_{min} \approx 390$ nm (Malitson and Heath, 1980; Mills et al., 1993a). Several studies on PCD using concentrated solar radiation are available in the literature (Bhatkhande et al., 2003a,b; Kamble et al., 2003; Yawalkar et al., 2001), indicating its viability as an alternative to UV radiation for the PCD of refractory compounds.

The work reported in this study deals with the demonstration of the viability of the novel reactor (Figure 1) proposed. The PCD of typical aromatic compounds using concentrated solar radiation was studied for the same. The compounds chosen were nitrobenzene (NB), chlorobenzene (CB), and phenol (PhOH). All these compounds are listed as priority pollutants and their permissible limits are 1, 3, and 0.1–1.0 ppm, respectively. The PCD mechanism of these compounds in the batch mode was reported in our previous work (Bhatkhande et al., 2003a,b; Yawalkar et al., 2001). Extensive information on the PCD of organic compounds is available in the literature (Bhatkhande et al., 2001).

Experimental

Materials

Degussa P-25 TiO_2 (70:30 anatase to rutile % w/w), with an average particle size of 30 nm and approximate BET surface area 55 $m^2\ g^{-1}$, was used as photocatalyst. Nitrobenzene, chlorobenzene, and phenol used were of analytical reagent grade. Solutions for use were prepared in tap water, whereas HPLC mobile phase solutions were prepared in deionized water. Plain solar radiation intensity was measured in W/m^2 by a "daystar meter" (Daystar, Las Cruces, NM) working on the photocell principle. Here, plain solar intensity is the intensity of solar radiation measured at the ground level. Krebsoge Excel (Mumbai, India) sintered stainless steel filter (candle filter) of 1 micron rating [dimensions: OD, 64 mm; ID, 60 mm; length, 150 mm] was used as the surface filter and a sintered stainless steel sintered disk of 20 micron rating (OD, 100 mm; thickness, 2 mm), supplied by Krebsoge Excel, was used for sparging the air at the bottom of the column.

Setup

All the experiments were carried out in a borosilicate glass slurry bubble column reactor (ID, 100 mm; length, 3.0 m; capacity, 19.5 L). The slurry bubble column reactor is shown in Figure 1. The experimental setup was located on the terrace of a three-story building to avoid interference from trees and other buildings. A metering pump was used for delivering solutions to the top of the borosilicate glass column, whereas a diaphragm-type air compressor (Model HS-2, C. P. Enterprises, Mumbai, India) was used to sparge air at the bottom of the column. The catalyst loadings used were 0.30, 0.015, and 0.20% (w/v of solution) for nitrobenzene, chlorobenzene, and phenol, respectively, and were approximately the same as the optimum values reported in our earlier work (Bhatkhande et al., 2003a,b; Yawalkar et al., 2001). A parabolic reflector (height, 3.0 m; total surface area, 6.0 m^2) was used to concentrate the solar radiation, forming a continuous glowing band of concentric light surrounding the wall of the bubble column reactor. After every 15 min the position of the reflector was tracked with respect to the sun so as to maintain the band of light surrounding the column reactor wall. Air was bubbled at sufficiently high velocity (>2 cm/s) to maintain all the TiO_2 in suspension. Each experiment was started at 0930 h local time (IST). After steady state was reached, a sample was taken for analysis and stored in an amber-colored bottle. In all the experiments pH was not controlled.

Analysis

The photocatalytic degradation (PCD) was monitored by HPLC (Knauer GmbH, Berlin, Germany). Details of the columns and mobile phases used are given by Bhatkhande et al. (2003a) for NB, Bhatkhande et al. (2003b) for CB, and Yawalkar et al. (2001) for phenol, respectively. Total organic carbon (TOC) was calculated from HPLC analysis and verified using a Total Organic Carbon Analyzer (ANATOC™-II, Australia). These values matched within ±2%, indicating that the HPLC analysis could detect all the intermediates.

Results and Discussion

The experiments were carried out in the month of January 2003 in Mumbai (India), 18.58°N and 72.50°E. During this period the sky was brilliant blue (no clouds) and the average solar intensity was approximately (±5%) constant at 368 W/m^2, as measured at the ground level.

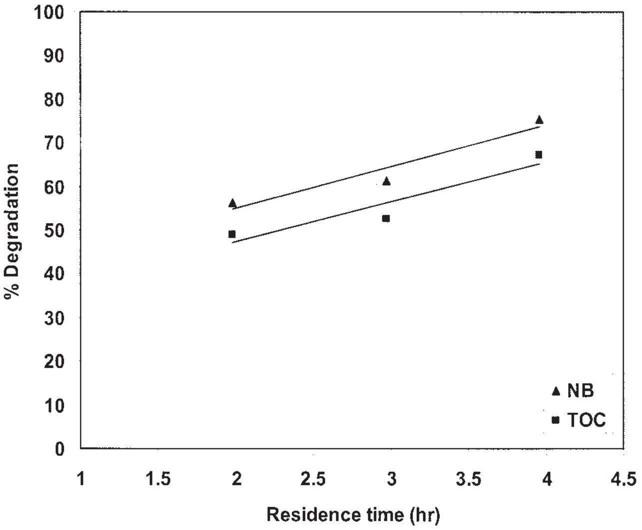

Figure 2. Variation of extent of photocatalytic degradation of nitrobenzene with residence time in the slurry bubble column (initial concentration 100 mg/L, catalyst loading 0.30 w/v of the solution).

▲, Nitrobenzene; ■, total organic carbon (TOC).

Variation of extent of PCD with residence time in the column

Figures 2, 3, and 4 show the variation of extent of PCD with residence time for nitrobenzene (NB), chlorobenzene (CB), and phenol (PhOH), respectively. As expected, an increase in the residence time yields higher photocatalytic degradation (PCD). These figures also show the reduction in TOC with residence time. The latter also show a similar behavior. The degradation rates of the parent organics and intermediates are nearly same and, further, the data indicate an apparent zero-order kinetics. Similar observations in the literature support this behavior (Yawalkar et al., 2001; Yue and Puma, 1999).

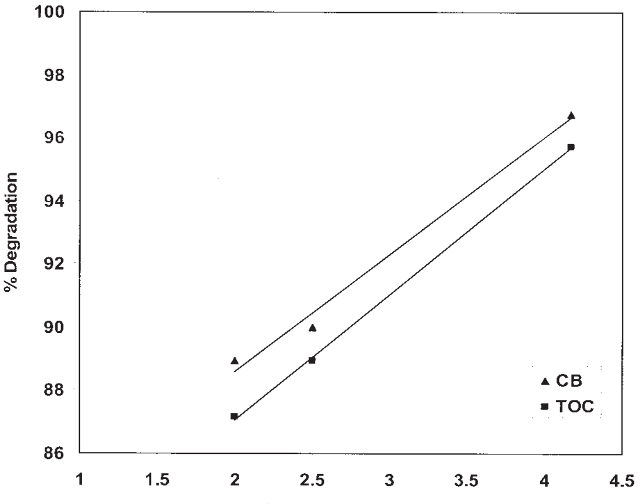

Figure 3. Variation of extent of photocatalytic degradation of chlorobenzene with residence time in the slurry bubble column (initial concentration 100 mg/L, catalyst loading 0.015 w/v of the solution).

▲, Chlorobenzene; ■, TOC.

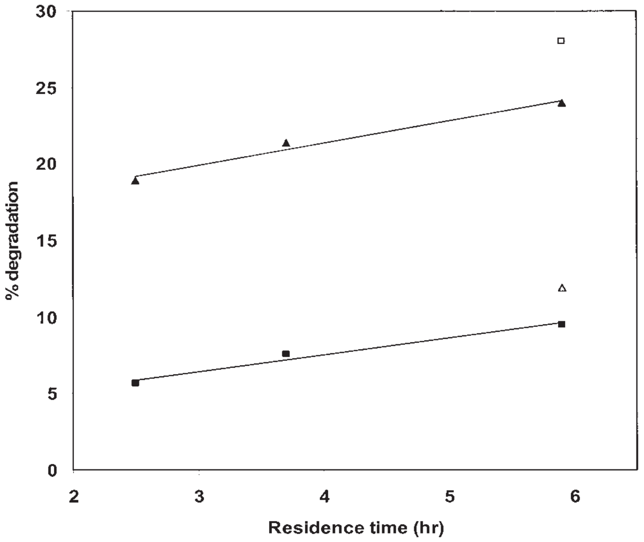

Figure 4. Variation of extent of photocatalytic degradation of phenol with sieve plate and without sieve plate with respect to residence time in the slurry bubble column (initial concentration 100 mg/L, catalyst loading 0.20 w/v of the solution).

□, Phenol with sieve plate; ▲, phenol without sieve plate; ■, TOC without sieve plate; △, TOC with sieve plate.

It is known that the PCD of a substrate is strongly affected by its adsorbability on the photocatalyst. CB and NB, which exhibit greater adsorption, are degraded more rapidly than phenol, which is poorly adsorbed on Degussa P-25 (Bhatkhande et al., 2003a,b).

Effect of reduced backmixing in the slurry bubble column on PCD

Bubble columns exhibit significant axial mixing in the liquid phase. This mixing is detrimental to its performance as a reactor. Sectionalization of the bubble column can reduce the backmixing. To study this effect, acrylic sieve plates were introduced into the column.

Mixing between the two sections can be completely prevented if the sieve plates operate above the weep point, found to be given by Prince et al. (1960) as

$$F_h = V_h \sqrt{\rho_G} = 10 \qquad \text{(SI units)} \qquad (1)$$

In the present case no downcomer for the liquid was provided and therefore some weeping had to be allowed. Further, this study was exploratory in nature. The sieve plates were thus designed for $F_h = 5$ to allow passage of liquid (weeping) between the sections. Phenol, which degrades slowest and hence is likely to benefit most from reduction in axial mixing, was chosen as the substrate. Figure 4 shows that the presence of the sieve plates increases the percentage degradation by about 25% over that in their absence. Thus, it is obvious that the sectionalization has a beneficial effect on the extent of PCD. A more detailed study with carefully designed sieve plates with downcomers for the liquid is in progress and will be reported in a future communication.

Effect of reused catalyst

An experiment was performed with a used catalyst to determine its reusability. The catalyst retained in the reactor after the first experiments was used for the next similar experiment. It was found that the reused catalyst showed reasonable stability under the conditions of this study. The proposed reactor system was also used for a pharmaceutical waste for close to 50 h and the results were found to be promising from a commercial vantage point.

Conclusions

A novel slurry bubble column reactor with on-line catalyst filtration is shown to be a viable proposal for photocatalytic degradation (PCD) using concentrated solar radiation. The efficiency of PCD can be increased by curtailing the axial mixing in the column.

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Notation

E_{bg} = band gap energy of the photocatalyst
F_h = F factor through holes defined by Eq. 2
V_h = velocity of gas through the hole in the sieve plate (m/s)

Greek letters

ρ_G = density of gas (kg/m^3)
λ_{min} = minimum wavelength required to promote an electron, given by $E_{bg} = 1240/\lambda_{min}$

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