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# Development of a new photocatalytic reactor for water purification

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## Abstract

The purification of water by heterogeneous photocatalysis is one of the most rapidly growing areas of interest to both research workers and water purification plants. Recent literature has demonstrated on a laboratory scale the potential of this promising technology to completely destroy organic pollutants dissolved or dispersed in water into harmless substances. However, to date no viable pilot plant exists using this technology. New reactor design ideas are necessary that must be able to address the two most important parameters, namely, light distribution inside the reactor through the absorbing and scattering liquid to the catalyst, and providing high surface areas for catalyst per unit volume of reactor. In this paper, a new reactor design addressing the solution to both the above problems is proposed for water treatment. The reactor consists of several hollow tubes coated on its outside surface with the catalysts. The hollow tubes have been employed as a means of light delivery to the catalyst. Experiments performed in a reactor containing 54 densely packed hollow tubes of 0.006 m diameter showed promising results. The new reactor aims at developing a technical solution to the design of a commercial photocatalytic reactor. © 1998 Elsevier Science B.V.

*Keywords:* Semiconductor photocatalysis; Advanced oxidation; Photoreactor; Titanium dioxide

## 1. Introduction

The treatment of water contaminated with traces of toxic organic compounds is a common problem throughout the world. In recent years, application of advanced oxidation technologies involving strongly oxidising hydroxyl radical has gained increasing interest for treatment of industrial waste waters, and contaminated ground and drinking water [1,2]. In particular, heterogeneous photocatalytic degradation in the presence of a semiconductor catalyst has been shown to be a promising method for the destruction of toxic chemi-

cals [3]. The appeal of this process technology is the prospect of complete mineralisation of the pollutants into environmentally harmless compounds.

In recent years, interest has focused on the use of  $\text{TiO}_2$  as a photocatalyst for the destruction of polluting materials [1,2]. Activation of the semiconductor catalyst is achieved through the absorption of a photon of ultraviolet band gap energy resulting in the formation of electron donor (reducing) sites and electron acceptor (oxidising) sites. The carbon containing pollutants are oxidised to carbon dioxide and water, while the other elements bonded to the organic compounds are converted to anions such as nitrate, sulphate or chloride.

The semiconductor catalyst can be employed either in a colloidal form or as an immobilised film. In photoreactors operated with catalyst particles as a slurry [4], the reaction rate is predominantly deter-

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mined by the light intensity on the surface, the quantum efficiency of the catalyst and the adsorption properties of the reacting and non-reacting components in solution. However, the use of suspensions requires the separation and recycling of the ultrafine catalyst from the treated liquid and can be an inconvenient, time consuming expensive process. In addition, the depth of penetration of UV light is limited because of strong absorptions by both catalyst particles and dissolved organic species. The above problems could be avoided in photoreactors where catalyst particles are immobilised [5]. However, immobilisation of a semiconductor on a support generates a unique problem. The reaction occurs at the liquid–solid interface and mass transfer from the bulk of the liquid to the catalyst surface may now play an important role in the overall rate.

Research on photocatalytic processes to achieve complete mineralisation of both organic and inorganic pollutants has been widely tested, but only on a laboratory scale [3,6,7]. However, to date no viable pilot plant has yet been developed successfully using this technology. Several engineering and scale-up issues must be addressed before commercial process units can be realised. In this paper, design concepts of a new photocatalytic reactor for water purification are presented.

## 2. Major challenges in the development of photocatalytic reactor

The problem of scale-up of multiphase photocatalytic reactors is considerably more complex than that of conventional chemical reactors. The demand for catalyst illumination is an added engineering factor in the reactor design, besides conventional reactor scale-up complications such as mixing and mass transfer, reactant–catalyst contacting, flow patterns, reaction kinetics, catalyst installation, temperature control, etc. The illumination factor is of utmost importance since the amount of catalyst that can be activated determines the water treatment capacity of the reactor. The volume of the photocatalytic reactor can be expressed as

$$V_R = \frac{QC_{in}X}{\kappa\mathfrak{R}}, \quad (1)$$

where  $Q$  is the volumetric flow rate ( $\text{m}^3/\text{s}$ ),  $C_{in}$  the inlet pollutant concentration ( $\text{mol}/\text{m}^3$ ),  $X$  the fractional

conversion desired,  $\kappa$  the illuminated catalyst surface area in contact with reaction liquid inside the reactor volume ( $\text{m}^2/\text{m}^3$ ) and  $\mathfrak{R}$  is the average mass destruction rate ( $\text{mol}/\text{m}^2 \text{ s}$ ). Hence, the smallest reactor volume will result when  $\kappa$  and  $\mathfrak{R}$  are as large as possible for specified values of  $Q$ ,  $C_{in}$ , and  $X$ .  $\mathfrak{R}$  is a *reaction specific* parameter as it expresses the performance of a catalyst for the breakdown of a specific model component, while  $\kappa$  is a *reactor specific* parameter representing the amount of catalyst inside the reactor that is sufficiently illuminated so that it is active and is in contact with the reaction liquid.

One major barrier in the development of a photocatalytic reactor is that the reaction rate is usually slow compared to conventional chemical reaction rates, due to low concentration levels of the pollutants. An increase in  $\mathfrak{R}$  can be accomplished by modifying the physical nature of the catalyst in terms of its structure and morphology or by the addition of additional oxidising agents. Improving the breakdown rates would lead to the need of a less demanding amount of catalyst to be illuminated and therefore, a smaller reactor volume.

Other crucial hurdle in the development of photocatalytic reactor design is the need to provide large amounts of active catalyst inside the reactor. Even though the effective surface area of the porous anatase catalyst coating is high, there can only be a thin coating (about  $1 \mu\text{m}$  thick) applied to a surface. Thus, the amount of active catalyst in the reactor is limited and, even if individual degradation processes can be made relatively efficient, the overall conversion efficiency will still be low. This problem severely restricts the processing capacity of the reactor and the time required to achieve high conversions are measured in hours, if not days.

New reactor configurations, therefore, must address the two most important parameters, namely, light distribution inside the reactor through the absorbing and scattering liquid to the catalyst, and providing high surface areas for catalyst coating per unit volume of reactor. New reactor design concepts must provide a high ratio of activated immobilised catalyst to illuminated surface and also must have a high density of active catalyst in contact with the liquid to be treated inside the reactor. For comparison of the design efficiency of different photocatalytic reactors in terms of their efficacy to install as much as activated catalyst

per unit volume of reaction liquid inside the reactor, we propose a parameter  $\kappa$ , namely the illuminated specific surface area, representing the total illuminated surface area of catalyst within the reactor in contact with the reaction liquid.

A number of photocatalytic reactors have been patented in recent years but none has so far been developed to pilot scale level. Based on the arrangement of the light source and reactor vessel, all these reactor configurations fall under the categories of immersion type with lamp(s) immersed within the reactor, *external* type with lamps outside the reactor or *distributive* type with the light distributed from the source to the reactor by optical means such as reflectors or optical fibres.  $\kappa$  is defined as total illuminated specific surface area and derivation of its formula for different reactor configurations is shown in Appendix A. In calculating  $\kappa$ , total surface area illuminated was determined and was divided by the volume reaction liquid present inside the reactor. Of course, at times it may be difficult to determine the actual surface area that is illuminated. In such cases, it was assumed that entire catalyst present on the surface is illuminated. Hence, for those situations  $\kappa$  value calculated is larger and consequently, the value is safer to be used for comparison purposes. Majority of reactors patented are in fact variation of the classical annular reactor of immersion or external type in which catalyst is immobilised on reactor wall [8,9], on pipes internally [10], on ceramic membranes [11], on glass wool matrix between plates [12], on semipermeable membranes [13,14] embedded in water permeable capsules [15], on a mesh of fibreglass [16], on beads [17], on fused silica glass fibres [18], on porous filter pipes [19], on glass fibre cloth [20], etc. The reactors are either helical [21], spiral [22], shallow cross flow basins [23] or optical fibre [24]. However, all these reactor designs are limited solely to small scales by the low values of the key parameter  $\kappa$ . The only way to apply these systems for large-scale applications is by using multiple units of more than 10 000 for treatment capacity of 10 m<sup>3</sup>/h.

In order to overcome some of these deficiencies inherent in conventional photocatalytic reactor designs, we believe that distributive type of photocatalytic reactor design in which catalyst is fixed to a structure in the form of glass slabs (plates), rods or tubes inside the reactor, has the greatest potential for

scale-up. This will allow for high values of  $\kappa$  and will also eliminate light passage through the reaction liquid. This is advantageous because when light approaches the catalyst through the bulk liquid phase, some radiation is lost due to absorption in the liquid. In particular this effect is more pronounced for highly coloured dye pollutants as they are strong UV absorber and will therefore, significantly screen the TiO<sub>2</sub> from receiving UV light. In this paper a new reactor design based on hollow glass tubes is presented that allows for a much higher illuminated surface area per unit reactor volume and is flexible enough to be scaled-up for commercial scale applications.

### 3. Basic concept of the reactor

In photocatalytic reactor scale-up, consideration must be addressed for high surface areas to volume and efficient light distribution to the catalyst phase. The limitation in the size of the reactor with light conductors is the UV transparency of the material and the light distribution to the catalyst particles. The critical and probably the most intricate factor is the distribution of the available light in the conductors to the catalyst particles, and to ensure that each particle receives at least the minimum amount of light necessary for activation. Top view of one such configuration conceptually applicable to photocatalysts satisfying most of the above mentioned requirements is shown in Fig. 1. The reactor is a rectangular vessel in which light conductors as glass slabs (or rods) coated on its outside surface with catalysts are embedded vertically. The lamps together with reflectors are placed on two

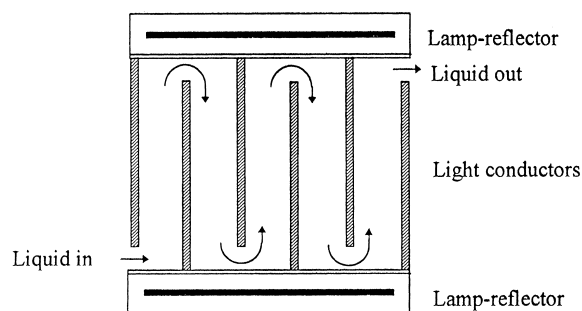


Fig. 1. Top view of a distributive type photocatalytic reactor where glass slabs or rods are applied as a light conducting material.

sides of the reactor while liquid enters and exits from the other two sides. Light rays entering the conductors through one end are repeatedly internally reflected down the length and at each reflection come in contact with the catalyst present around the outer surface of the conductors. Thus, conducting materials might be considered as a means of light carrier to the catalyst. Since the ratio of the surface area on which catalyst is present to the light entering area could be as high as 500, a large catalyst area can be illuminated. Moreover, a large number of such light conducting material may be packed inside the reactor, the configuration provides a high total light transfer area and allows for a higher illuminated catalyst area per unit reactor volume. By densely packing the reactor with light conducting objects it not only increases the surface to volume ratio, but also reduces the effective mass transfer diffusion length for the pollutant to catalyst surface.

The vital issue in the distributive type reactor concept is how to introduce light from the external source efficiently into the light conductors, and likewise, how to get it out again at the proper location and in the

apropos amount. The predominant obstacle in the use of glass slabs (or rods) as the light conducting object is the occurrence of total internal reflection. It transpires when light travels from denser to rarer medium and is determined by the critical angle given by

$$\theta_c = \sin^{-1}[n_2/n_1], \quad (2)$$

where  $n_1$  and  $n_2$  are the refractive indices of the denser and rarer medium, respectively. In the case of light travelling from air, to glass to air (or water) as depicted in Fig. 2 where medium 1, 2 and 3 are glass, air (or water) and air, respectively, the angle  $\theta$  will always exceed the critical angle,  $\theta_c$ , for the interface between glass and air (or water), irrespective of angle of incidence,  $\alpha$  ( $0-90^\circ$ ). In other words, all the light rays that are entering through the top surface will experience the phenomena of total internal reflection and will come out axially rather than emerging from the lateral surface. However, refractive index of  $\text{TiO}_2$  (2.4–2.8) is higher than that of glass (about 1.5) in the wavelength range 200–400 nm and it is likely that total internal reflection would not take place when the glass surface is coated with titania. Nevertheless, if coating consists

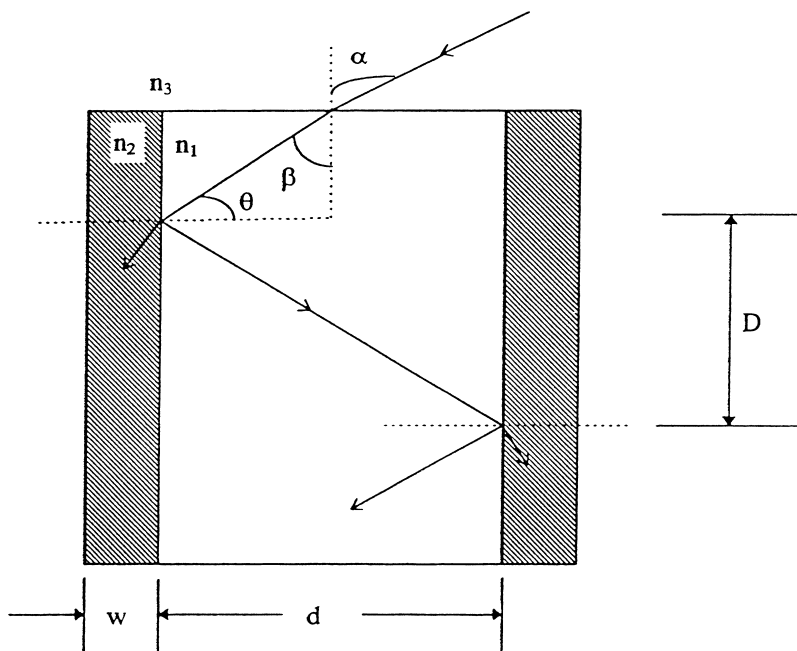


Fig. 2. Distribution of light rays in a glass slab or rod (1: glass; 2: air/water/catalyst; 3: air;  $n_1=1.5$ ;  $n_2=1$  (air), 1.33 (water), 2.8 (catalyst);  $n_3=1$ ;  $\theta_c=41.8^\circ$  (glass–air);  $\theta_c=62.5^\circ$  (glass–water)).

of small spheres of catalyst particles dispersed along the surface, the actual glass–titania interface will be small as most of the glass surface will still be in contact with water.

One way of avoiding total internal reflection is by surface roughening. Moreover, surface roughening assists in achieving better catalyst adhesion to the substrate. Both are indeed found out to be the case experimentally. In fact, when lateral surface was roughened by sand blasting most of the light emerged within few centimetres, and hardly any light remained thereafter in the axial direction. This is not only because roughenings desist total internal reflection phenomena but also UV-transparency of most light conducting material is very poor. Use of Quartz as light conductors will naturally help to overcome light transmission problem, but it will certainly make the overall reactor set-up more expensive.

The total internal reflection problem can also be effectively avoided when the surfaces light has to pass through are parallel instead of perpendicular. One such configuration is a hollow glass tube coated on its surface with semiconductor catalysts as shown in

Fig. 3. Although total internal reflection could be avoided completely in this configuration, the angle of incidence of light will be a critical factor. When light falls on the glass surface, a part of it is reflected and the rest is transmitted. The ratio between the reflection and transmission of light is a strong function of angle of incidence. When the light beam is nearly parallel with the surface ( $\alpha$  close to  $0^\circ$ ), most of the light is reflected and exits axially rather than laterally, while for light rays with  $\alpha$  close to  $90^\circ$  most of the light will emerge laterally within few centimetres and barely any light will remain thereafter as reflection is only 4% for a glass–air interface. Table 1 shows calculated values of percentage of light that remain from top for different values of  $\alpha$ . The angle of incidence has an immense influence on the amount of light coming out from the lateral and axial directions. Therefore, in the design of reactor based on hollow tubes light must be guided into the conductors at a very precise angle through a combination of optical lenses and reflectors.

A new concept using hollow tubes as light conductors satisfying most of the design criteria for the

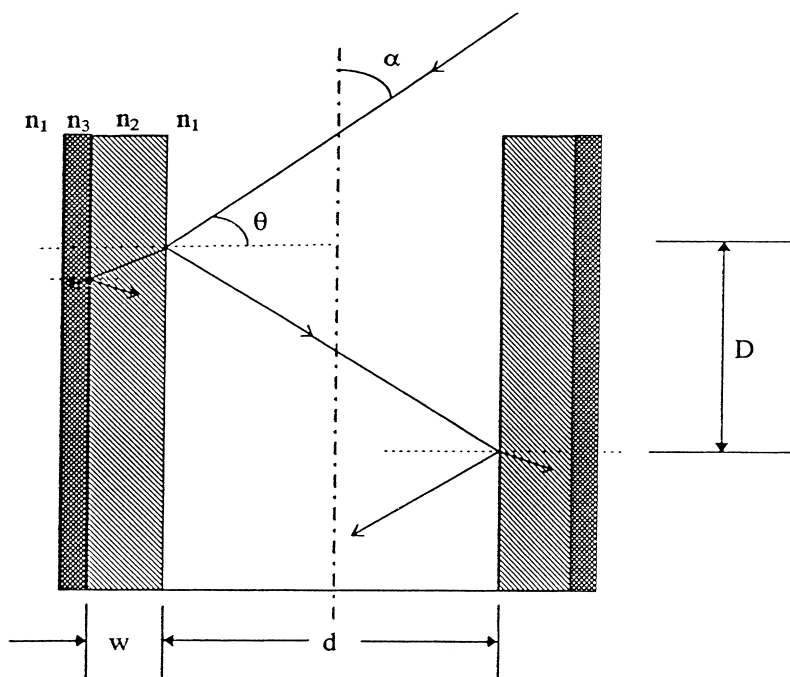


Fig. 3. Distribution of light rays in a hollow glass tube (1: air; 2: glass; 3: catalyst;  $n_1=1$ ;  $n_2=1.5$ ;  $n_3=2.8$ ).

Table 1  
Percentage of light still remaining at  $x$  m from light source for a single ray in a hollow space between walls

$\alpha$ (°)	$\theta$ [ $\equiv 90 - \alpha$ ]	Percentage of light intensity remaining at $x$ m				$D$ [ $\equiv d \tan \theta$ ] $d=0.006$ m
		0.05	0.2	0.5	1.0	
30	60	0.005	—	—	—	0.0104
10	80	48.0	5.0	0.06	—	0.0340
5	85	82.0	45.0	13.0	1.8	0.0686
3	87	93.0	76.0	50.0	25.0	0.1145
1	89	99.0	96.0	91.0	83.0	0.3437

scale-up of photocatalytic reactor is considered. The new design allows for a large surface area of catalyst within a relatively small reactor volume compared to classical reactor consisting of several lamps externally surrounding a cylindrical vessel. A 70–100 fold increase in surface area per  $\text{m}^3$  reactor volume can be obtained over classical annular reactor design. The hollow tube might be considered as a pore carrying light to the catalyst. In this novel configuration, light rays entering through one end of the hollow tube are repeatedly internally reflected down the length of the tube and at each reflection come across the annular catalyst coating present around the outer surface of the tube. Since the ratio of the cylindrical surface area to the circular end surface (light entrance area) of the tube is of the order of 500, evidently a very large catalyst area can be illuminated. This new configuration provides a high light transfer area and allows for a higher illuminated catalyst area per reactor volume. Another potential advantage of distributing light within hollow tubes is that light does not have to pass through the reactant and product phases in the reactor. The reactor is abbreviated in this paper as “MTR” for multiple tube reactor.

## 4. Experimental details

### 4.1. The reactor

Fig. 4 shows schematic drawing of the novel bench-scale reactor system based on hollow tubes. The reactor consists of a cylindrical vessel of diameter 0.056 m within which 54 hollow Quartz glass tubes of diameter 0.006 m coated on its peripheral surface with catalyst were placed. The tubes were held securely within the reactor by two teflon end plates on which 54 holes were drilled. The reactor resembles that of a shell- and tube-heat exchanger with reaction liquid flowing through the shell-side over the outside surfaces of the coated tubes while light travels through the inside of hollow tubes. The tubes were arranged in triangular pitch of 0.007 m thereby achieving a very high surface area per unit volume. The feed was introduced through four equally distributed ports at one end of the vessel thereby minimising formation of any dead zones. Similarly, the exit flow from the reactor was collected through four ports distributed at the other end of the reactor. One end of each tube was closed to prevent any reaction liquid entering the

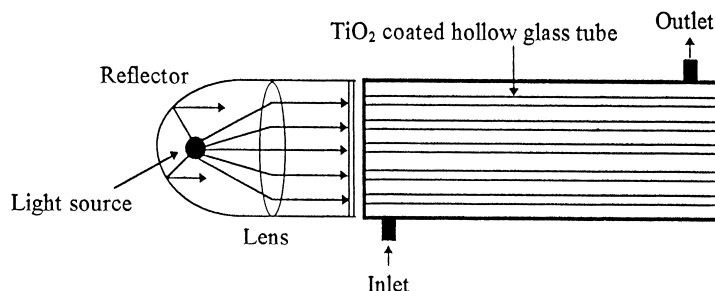


Fig. 4. Schematic diagram of multiple tube reactor (MTR).

inside of the tubes. The closed ends were also coated with aluminium for better utilisation of axially exiting light. The glass material used was quartz instead of Pyrex. Although quartz is expensive than Pyrex glass when glass slabs or rods are considered, but the price difference is not that appreciable when glass test tubes are considered. The quartz was used in the set-up particularly for two reasons: (a) transmission of light in Pyrex is very poor compared to quartz and therefore, the length of hollow glass tubes that can be used in the reactor will be restricted, and (b) when using large number of 5–6 mm test tubes, use of quartz tubes will increase the strength of the reactor and it will be much easier to handle bundle of long but narrow diameter hollow test tubes without worrying about breakage of the tubes. Of course, if one uses Pyrex tubes, reactor will be cheaper but then the length of the reactor has to be reduced.

#### 4.2. Experimental set-up

A gear pump (Verder model 2036) was used for pumping the reactant between the reactor and the reservoir via a flow-through cuvette placed inside a universal photometer for continuous on-line measurement of the model component (see Fig. 5). Two three-way glass valves were used between the water and specially designed reactant reservoir for initial zero setting of the analytical instrument before the start of an experiment, introduction of the reactant into the system, elimination of bubbles formed during experiment, and final flushing of the entire system.

The light source (Philips GBF 6436, 12 V, 40 W) used was a low voltage halogen lamp optically positioned in a light weight highly glossy anodised aluminium reflector spanning 0.056 m for a clearly defined beam spread. In addition, a condenser lens

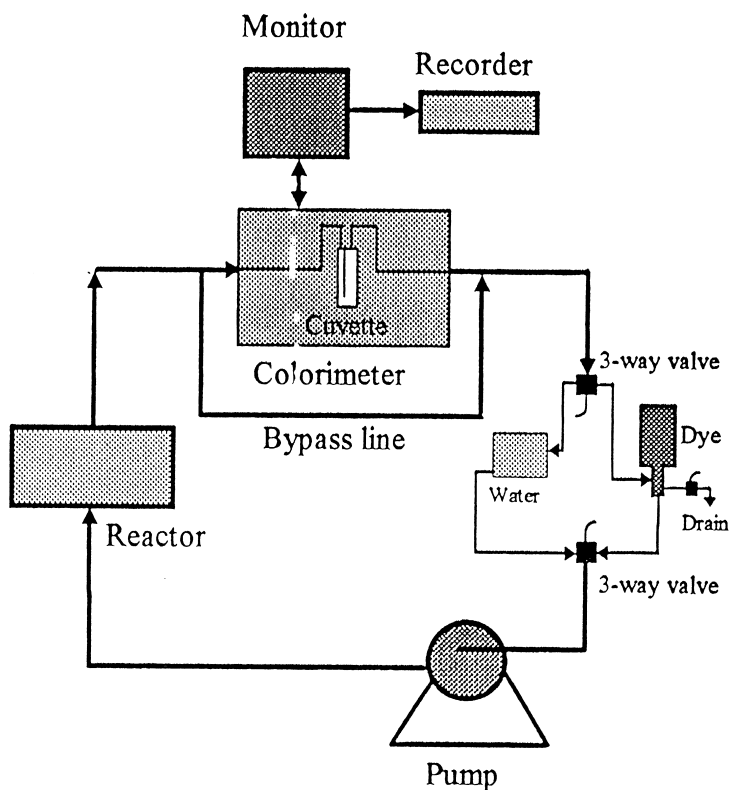


Fig. 5. Flow diagram of the experimental set-up.

of focal length 0.04 m was placed between the lamp and the reactor to obtain light beam at a half intensity beam angle between  $2^\circ$  and  $4^\circ$ .

#### 4.3. Catalyst

Degussa P25 grade  $\text{TiO}_2$  was used as catalyst for all the experiments. The crystalline product is non-porous primarily in the anatase form (70:30 anatase to rutile) and is used without further treatment. It has a BET surface area of  $(5.5 \pm 1.5) \times 10^4 \text{ m}^2/\text{kg}$  and crystallite sizes of 30 nm.

#### 4.4. Catalyst immobilisation

For better catalyst fixation and its durability, the glass surface of the tubes on which titania was deposited was roughened by sand blasting. This makes the catalyst surface uneven but increases the strength and amount of catalyst per unit area that could be deposited. The tube surfaces were coated with catalyst in a dip-coating apparatus [25].

#### 4.5. Model component

The model component used was a brightly coloured water soluble acid dye, Special Brilliant Blue (SBB, MW 812), laboratory reagent grade (in 20% solution) of which was obtained from Bayer (catalogue number 42735).

#### 4.6. Analysis

Changes in SBB dye concentration were measured on-line by flowing a bypass stream of the dye from reactor outlet continuously through a bottom loader flow-through cuvette (Hellma, path length 0.001 m) placed inside a Colorimeter (Vitatron Universal Photometer 6000).

#### 4.7. Experimental procedure

At the start of every experiment the reactor was rinsed with Milli-Q water for several times before zero-setting the analytical instrument. The reactor and connecting lines were then filled with the dye solution with the help of the three-way valves and it was ensured that no air bubbles remained in the system.

The change in the dye concentration was continuously analysed and recorded. New silicon connecting tubes and fresh catalyst were found to adsorb the dye for about an hour, but no noticeable adsorption by the entire system was observed afterwards. Light was turned on only when the colorimeter reading was stabilised.

#### 4.8. Results and discussions

The catalyst coating on the tube's surface was found out to be durable and the activity of catalyst did not deteriorate during the course of the experiments. Fig. 6 shows experimental results in the multiple tube reactor for the photocatalytic destruction of the SBB dye for various starting concentration. Experimental results show that photocatalytic destruction of the dye pollutant is possible in the present configuration and it also reveals that 90% of the pollutant was degraded in about 100 min. This is in spite of the fact that the reactor was far from optimum. In fact, performance of the reactor can be instantly improved by decreasing the length of the hollow tubes used. At present, 0.5 m long tubes have been used and it is very much likely that catalyst is almost inactive near the end of the tube away from the light source.

In Table 2 reactor specifications and experimental conditions used for multiple tube reactor are compared with a classical annular reactor (CAR) [26] and a tube light reactor (TLR) [27]. A classical annular reactor is one in which a lamp is placed inside the inner tube while the reaction liquid is flowing through the annulus, and the inside of the outer annulus is coated with catalyst. The classical annular reactor (CAR) was of 0.099 m outside diameter and 0.065 m inside diameter and 0.77 m long, surrounded externally with 10 Philips TLK 40W/10R lamps. The tube light reactor (TLR) considered was of immersion type reactor in which 21 lamps of extremely narrow diameter ( $d_0=0.0045 \text{ m}$ ) coated with catalyst on its surface were immersed inside the reaction liquid.

The efficiency of the reactor was expressed in terms of moles converted per unit time per unit reactor volume per unit electrical power consumed. From engineering point of view defining efficiency in terms of per unit reactor volume is more appropriate than per unit surface area of immobilised catalyst since it will allow one to compare the design efficiency of different



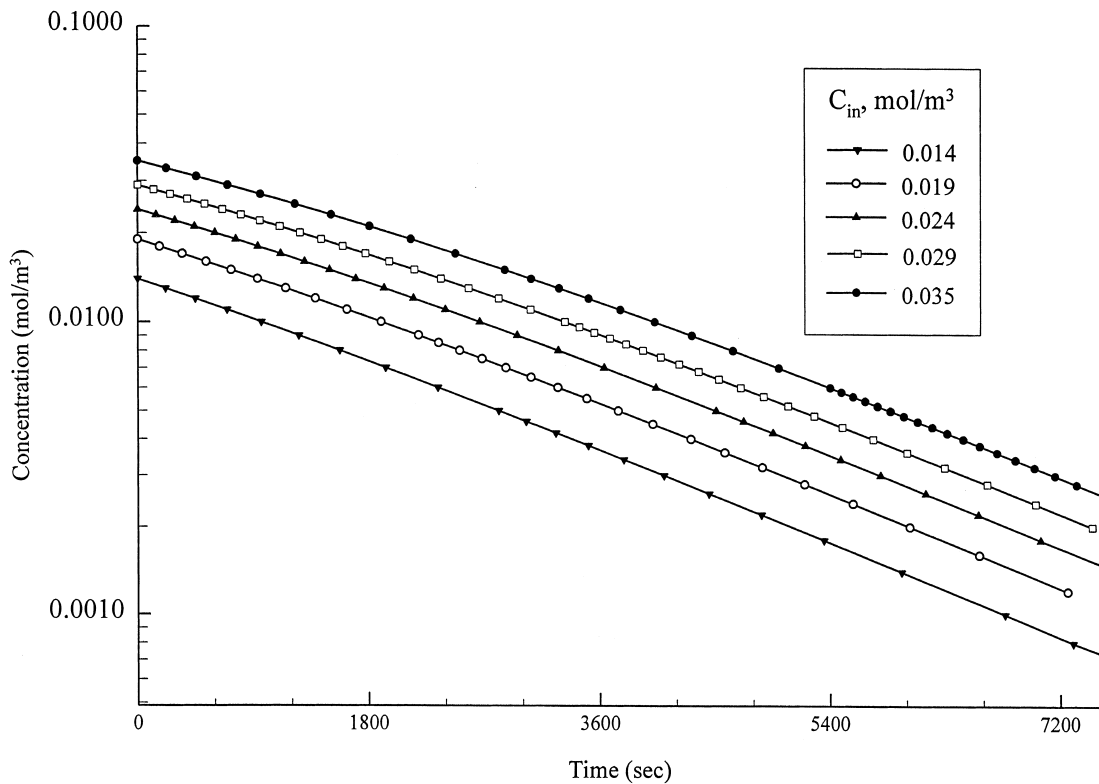


Fig. 6. Photocatalytic degradation of SBB dye for various initial concentration (reactor specification: reactor volume= $1.23 \times 10^{-3} \text{ m}^3$ ; illuminated catalyst surface area= $0.51 \text{ m}^2$ ; number of hollow tubes=54; catalyst amount= $3.8 \times 10^{-3} \text{ kg/m}^2$ ; experimental condition: flow rate= $3.00 \times 10^{-5} \text{ m}^3/\text{s}$ ; volume of liquid treated= $7.50 \times 10^{-4} \text{ m}^3$ ).

Table 2

Comparison of reactor specifications and experimental conditions applied in a classical annular reactor (CAR), tube light reactor (TLR) and multiple tube reactor (MTR)

Specifications	CAR [26]	TLR [25]	MTR
Volume of reactor, $\text{m}^3$	$3.48 \times 10^{-3}$	$5.36 \times 10^{-4}$	$1.23 \times 10^{-3}$
Catalyst surface area, $\text{m}^2$	0.18	0.15	0.51
Parameter $\kappa$ , $\text{m}^2/\text{m}^3$	69	618	1087
Volumetric flow rate, $\text{m}^3/\text{s}$	$8.42 \times 10^{-5}$	$1.67 \times 10^{-5}$	$3.00 \times 10^{-5}$
Electrical energy input, W	400	126	40
Scale-up possibilities	No	Yes	Yes

photocatalytic reactors in terms of their efficacy to install as much as activated catalyst per unit volume of reaction liquid inside the reactor.

When the efficiency of this test reactor is compared for the same model component with that of a classical annular reactor an increase of about 450% was observed (Table 3). This increase in efficiency is

inspite of the fact that the design of this test reactor was far from optimum with respect to mass transfer of pollutant to catalyst surface, flow distribution of reaction liquid inside the reactor, length and other dimensions of the reactor and the angle of incidence of light. In addition, the design of CAR is restricted only to a small reactor capacity. It is expected that the perfor-

Table 3  
Comparison of reactor performance efficiency

$C_{\text{initial}}$ (mol/m <sup>3</sup> )	Reactor performance efficiency <sup>a</sup> , $\eta$ ( $\mu\text{mol/s m}^3 \text{ W}$ )			Percentage increase in efficiency	
	CAR [26]	TLR [25]	MTR	$\eta_{\text{TLR}}/\eta_{\text{CAR}}$	$\eta_{\text{MTR}}/\eta_{\text{CAR}}$
0.035	$1.25 \times 10^{-2}$	0.1032	$7.09 \times 10^{-2}$	725	467
0.029	$1.09 \times 10^{-2}$	0.0885	$6.08 \times 10^{-2}$	712	458
0.024	$9.50 \times 10^{-3}$	0.0755	$5.09 \times 10^{-2}$	695	436
0.019	$7.98 \times 10^{-3}$	0.0617	$4.12 \times 10^{-2}$	673	417
0.014	$6.38 \times 10^{-3}$	0.0469	$3.11 \times 10^{-2}$	635	388

<sup>a</sup>Efficiency of reactor performance is expressed as 90% pollutant (SBB dye) converted ( $\mu\text{mol/s}$ ) per unit reactor volume ( $\text{m}^3$ ) per unit electrical energy (W) used.

mance of TLR will surpass that of MTR because of superior catalyst activation, but the overall reactor efficiency may be greatly suppressed due to the application of a large excess of light energy than is required for catalyst activation. It is apparent that MTR design idea creates great opportunities for building much more efficient photocatalytic reactor for water purification as the reactor most likely will be economical. We believe that MTR reactor will be cost effective when it is compared to other photocatalytic reactors since it consists of inexpensive hollow glass tubes, the catalyst is cheap and it requires only a low wattage (40 W lamp was used in the present study) lamp. It needs a reflector which usually comes with the lamp and of course, a lens to direct the light entry at proper angle. The hollow test tubes could easily be replaced. It is well known that water purification by photocatalysis will not be cheaper than for example, by bio-treatment. However, if one is interested in purifying water containing toxic chemicals the best method may be to break open the benzene ring first by photocatalysis to eliminate the toxic chemicals and then send the water for bio-treatment. Therefore, it will not be necessary to completely mineralise the pollutants present in water by a photocatalytic reactor. A combination of two methods could be best suited for water purification and may be more economical.

The main obstacle in the development of MTR design concept is that it is impossible to obtain uniform light distribution along the length of the tubes and thereby severely restricting the maximum length of tubes that can be used. One way of avoiding this is to place one extremely narrow diameter novel tube-light lamp [27] inside each of the hollow tubes. In this way all the advantages of the MTR concept can be

utilised while eliminating the basic drawback of uniform light distribution dilemma. Moreover, this will also eliminate the main problem experienced in the TLR with the prolonged use of the novel lamps immersed in polluted water.

## 5. Conclusions

Heterogeneous photocatalysis on semiconductor particles has been shown to be an effective means of removing organic and inorganic pollutants from water. A fixed bed reactor in which catalyst is immobilised onto a support permits continuous processing of waste streams while eliminating the need of any post processing filtration required when catalyst is used as a slurry. In conventional fixed bed photocatalytic reactors the catalyst is coated either on the walls of the reactor or around a casing containing the light source. However, these reactor configurations suffer from drawbacks such as low surface-to-volume ratios and absorption and scattering of the light by the reaction medium.

To overcome these deficiencies inherent in conventional photocatalytic reactor designs, we proposed in this paper a distributive type fixed bed reactor system that employs hollow glass tubes as a means of light conductors and distribution to catalyst particles. The reactor configuration increases the surface-to-volume ratio while eliminating the possibility of light loss by absorption and scattering of the reaction medium.

The aim of this paper was to see whether we can achieve photocatalytic degradation by using hollow tubes as a means of delivering light to the catalyst.

Experiments performed to study the degradation of a textile dye showed very promising results.

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## Appendix A

### Calculation of $\hat{\epsilon}$ for different reactors

*Slurry reactor:* A mass balance for the catalyst particle results

$$\left[ \frac{\pi d_p^3}{6} \right] N_p \rho_c = C_c V_L$$

where  $d_p$  and  $N_p$  are the particle diameter (m) and number of particles respectively,  $\rho_c$  (kg/m<sup>3</sup>) are the density and concentration of catalyst respectively, and  $V_L$  (m<sup>3</sup>) is the volume of liquid inside the reactor. The  $\hat{\epsilon}$  can be calculated as

$$\kappa = \frac{\pi d_p^2 N_p}{V_L} = \pi d_p^2 \left[ \frac{6C_c}{\pi d_p^3 \rho_c} \right] = \left[ \frac{6C_c}{\rho_c} \right] \frac{1}{d_p}$$

*External type reactor:* A classical annular reactor is considered in which a lamp is placed inside the inner tube while the reaction liquid is flowing through the annulus and inside of the outer annulus is coated with catalyst. The  $\hat{\epsilon}$  can be calculated as

$$\kappa = \frac{\pi d_0 L}{\frac{\pi}{4} (d_0^2 - d_i^2) L} = \frac{4d_0}{(d_0^2 - d_i^2)}$$

where  $d_0$  (m) and  $d_i$  (m) are the outside and inside diameter of the annulus respectively, and  $L$  (m) is the length of the reactor.

*Immersion type reactor:* An immersion type reactor is considered in which several lamps of diameter  $d_0$  (m) coated with catalyst on its surface are immersed inside

the reaction liquid. If  $\hat{a}$  is defined as the fractional volume of the reactor occupied by the lamps, then  $V_{\text{lamps}} = \hat{a} V_R$  and  $V_L = (1 - \hat{a}) V_R$ . Also, the surface area to volume ratio is equal to  $A_{\text{lamps}}/V_{\text{lamps}} = 4/d_0$ . The  $\hat{\epsilon}$  can be calculated as

$$\kappa = \frac{A_{\text{lamps}}}{V_L} = \frac{A_{\text{lamps}}}{(1 - \hat{a}) V_R} = \frac{\epsilon A_{\text{lamps}}}{(1 - \epsilon) V_{\text{lamps}}} = \left[ \frac{4\epsilon}{(1 - \epsilon)} \right] \frac{1}{d_0}$$

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