Research News

Major Challenges in the Design of a Large-Scale Photocatalytic Reactor for Water Treatment

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Semiconductor photocatalysis is a newly emerging technology for the elimination of harmful chemical compounds from air and water. It couples low-energy ultraviolet light with semiconductors acting as photocatalysts overcoming many of the drawbacks that exist for the traditional water treatment methods. Recent literature has established the potential of this powerful technology to destroy toxic pollutants dissolved or dispersed in water. However, to date no viable pilot plant exists using this technology. In this paper, the challenges that need to be addressed for the scale-up of multiphase photocatalytic reactors are discussed. A new reactor design concept is necessary that must be able to address the two most important parameters, namely, uniform light distribution inside the reactor through the absorbing and scattering liquid to the catalyst, and providing high surface areas for catalyst coating per unit of reactor volume. Two new design configurations for efficient photocatalytic reactors have been discussed that not only address the solution to both of the above problems but also have scale-up potential.

1 Introduction

The treatment of water contaminated with traces of toxic compounds is a common problem throughout the world. To meet the specific standards set, there is need for new treatment methods, which address questions at both local and global level in terms of related research and development of treatment technologies. The most common method of removing pollutants present in wastewater is the primary and secondary treatment involving the use of various physical, chemical and biological processes to destroy commonly found organics and inorganics. However, many of the pollutants found in water and wastewater are not or little affected by the conventional treatment processes. An ever-increasing number of these are the highly complex organic compounds, mainly halogenated organics. Some of them are formed in the course of chlorination of the water supplies and the wastewater generated from textile, chemical, power industries and agricultural use. These are mainly dyes, surfactants, herbicides, pesticides, etc. For the treatment of organic compounds, regulatory reform is forcing industry to develop new technologies and in some cases to rethink the way in which certain traditional water treatment chemicals are used.

The demand for water of very high purity has presented new challenges to scientists and engineers in the area of water purification. For years, engineers have relied on a variety of traditional water treatment processes that include phase transfer, biological treatment, thermal and catalytic oxidation, and chemical treatment using chlorine, potassium permanganate, ozone, hydrogen peroxide and high energy ultraviolet light [1]. However, all the phase transfer technologies currently in use are nondestructive in type, since they rely on the physical separation of organics by merely transferring the pollutant from one phase to another, leaving a problem for the final and ultimate disposal of the transferred material. Proven methods include air or steam stripping [2] and adsorption by activated carbon [3]. The removal of volatile contaminants by air or steam stripping converts a liquid contamination problem into an air pollution problem, and carbon adsorption produces a hazardous solid, which in turn must be disposed of. In recent years, a combination of phase transfer and photooxidation processes has been proposed for destruction of volatile organic compound [4]. The biological treatment process [5] finds some persistent organic chemicals to be lethal for microbes, which are intended to destroy them. Although processes based on aqueous-phase hydroxyl radical chemistry [6] are powerful oxidation methods to destroy toxic organic compounds present in water, all the present chemical treatment processes either use high-energy ultraviolet light or strong oxidants of hazardous and therefore undesirable nature. Some of the chemical treatment processes may be directly destructive in nature, such as direct photolysis, using strong oxidants like H_2O_2/UV, O_3/UV and $H_2O_2/O_3/UV$. However, the selection of operating process parameters is very much dependent on the type of pollutants present [7]. In addition, several intermediates, sometimes of more hazardous nature than the parent compounds, are formed in these processes and because of very low efficiencies, overall treatment cost become high if destruction of intermediates and complete mineralization need to be achieved [8].

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2 Photocatalysis

Heterogeneous photocatalysis [9] is one of the advanced oxidation processes that couples low-energy ultraviolet light with semiconductors acting as photocatalysts. In this process in situ, degradation of traces of organic substances is achieved. The appeal of this process technology is the prospect of complete mineralization of pollutants to environmentally harmless compounds. The carbon-containing pollutants are oxidized to carbon dioxide while the other elements bonded to the organic compounds are converted to anions, such as nitrate, sulphate, or chloride. Literature has established that practically any pollutant that includes aliphatics, aromatics, dyes, surfactants, pesticides, and herbicides can be completely mineralized by this process into harmless substances [10].

Activation of the catalyst is achieved by electron-hole pair formation initiated through the absorption of a photon of ultraviolet bandgap energy. Excited-state conduction band electrons and valence band holes may recombine and dissipate the input energy as heat or they may become separated and involved in electron transfer reactions with species in the solution the material is immersed in [11]. In the presence of suitable scavengers or surface defects they become trapped and subsequently enter into redox reaction with species adsorbed on the surface or present within the electrical double layer of the charged particles. The holes react with electron donors, for example hydroxyl ions or water, to form hydroxyl radicals. The electrons on the other hand react with an electron acceptor, for example, molecular oxygen. For a reaction to take place, it is necessary that the valence band is more oxidizing than the oxidation potential of the species in question or that the conduction band is more reducing than the reduction potential of the species. The redox potential of the valence band holes and conduction band electrons for different semiconductors varies from +4.0 to –1.5 volts vs NHE, respectively [12]. Therefore, by this technology a wide range of species can be converted using the oxidizing power of the activated catalyst. Of all the different semiconductor photocatalysts tested, TiO_2 appears to be the most active [13]. The anatase form of TiO_2 requires photons having energies greater than 3.2 ev ($\lambda < 380$ nm) to initiate bandgap excitation. It satisfies the foremost criteria for degradation of organics as the bandgap domain of the catalyst lies within the redox potential of the $H_2O/OH^\bullet$ ($OH^- \rightarrow OH^\bullet + e^-$, $E^o = -2.8$ V) couple [12]. Besides the advantage of the complete destruction of toxic compounds and the use of atmospheric oxygen as oxidant, TiO_2-based photocatalysis has many advantages over the other conventional chemical oxidation methods. The catalyst is cheap, biologically and chemically inert, insoluble under most conditions, photostable, nontoxic, the reaction rate is relatively high if a large surface area of catalyst is provided, it can be used for an extended period without substantial loss of its activity [14]. Moreover, it uses very low energy ultraviolet light resulting in an energy requirement as low as 1–5 W/m^2 [15] and, more importantly, can even be activated by sunlight.

An estimated process cost of water treatment by activated carbon, UV/O$_3$ and a semiconductor photocatalysis system has been compared in Tab. 1 showing the economic viability of the process for intermediate to large-size water purification systems [13].

Table 1. Estimated process costs for different water purification systems [13].

Capacity	Cost, US$		
m^3/h	Activated carbon	UV/O$_3$	Photocatalysis
5.0	7.79	13.00	9.85
18.0	4.25	6.32	4.36
36.0	3.19	4.92	3.21
145.0	2.21	3.83	2.32
385.0	1.95	3.10	2.00

Inspite of the potential of this promising technology, the development of a practical water treatment system has not yet been successfully achieved. In the last few years, a large number of publications [1,10–13] have appeared based on laboratory-scale studies with generally positive results for very diverse categories of toxic compounds in water. However, the technical development to pilot-scale level has not yet been successfully achieved although there are numerous patents approved worldwide. None of these has been successfully brought out of the laboratory yet.

3 Major Issues in the Design of Large-Scale Reactors

An estimate of the required amount of catalyst and reactor volume can be made if one considers a simple continuous-flow mixed reactor for treating water containing a pollutant at 10 ppm. Tab. 2 lists values for three different application scales (laboratory-scale, intermediate-scale and large-scale), for two different pollutant types (a typical compound, such as monochlorobenzene, and a complex molecule, such as a dye), and for two different reactor types (a slurry reactor and a fixed-bed reactor) for 90% conversion of the pollutants. Considering the fact that light penetration depth in a 0.5 wt.-% catalyst suspension is only about 0.02 m, it appears from the table that the required volume for intermediate- to large-scale applications will not be easy to achieve.

Several factors impede the efficient design of a photocatalytic reactor [16]. The problem of scaling up multiphase photocatalytic reactors is considerably more complex than that of scaling up conventional chemical reactors or homogeneous photoreactors. The need to utilize a solid catalyst makes the entire problem quite complicated as another phase is added to the system. In this type of reactor, besides the requirement for good contact between reactants and catalysts, it is also necessary to achieve efficient exposure of the catalyst to light irradiation. In fact, in a photocatalytic reactor, besides the conventional reactor complications, such as reactant-catalyst contacting, flow patterns, mixing, mass transfer,

Table 2. Typical required dimension of a photocatalytic reactor.

Reactor capacity m^3/s	Reaction rate $mol/s/kg\text{-cat}$	Catalyst load, W kg	Reactor volume, V_R, m^3	
			R_A	R_B
3.0×10^{-6}	k_1	0.0018	3.6×10^{-3}	3.6×10^{-5}
	k_2	0.0054	1.08×10^{-2}	1.08×10^{-4}
2.0×10^{-3}	k_1	1.2	2.4	0.024
	k_2	3.6	7.2	0.072
1.25	k_1	750	1500	15
	k_2	2250	4500	45

k_1: Rate constant for a typical pollutant (e.g., chlorobenzene [19]), 1.5×10^{-4} mol/s/kg-cat.
k_2: Rate constant for a complex pollutant (e.g., dye [15]), 5.0×10^{-5} mol/s/kg-cat.
R_A: Reactor A with 0.5 kg-cat/m^3 (e.g., slurry reactor [19]).
R_B: Reactor B with 50 kg-cat/m^3 (e.g., distributive-type reactor [22]).

reaction kinetics, catalyst installation, temperature control, etc., an additional engineering factor related to the illumination of the catalyst becomes relevant. Without photons of appropriate energy content, the catalyst shows no activity. The problem of photon energy absorption has to be considered regardless of reaction kinetics mechanisms. 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 high degree of interaction between the transport processes, reaction kinetics and light absorption leads to a strong coupling of physicochemical phenomena and no doubt, it is the major obstacle in the development of a photocatalytic reactor [17].

The central problem in a photocatalytic reactor is focused on a uniform distribution of light to a large surface area of the catalyst. For the particular photoreactor geometry, scale-up in the axial and/or radial directions is constrained by the phenomenon of opacity, light scattering, depth of radiation penetration and local volumetric light absorption. The arrangement of the light source/reactor system influences the reactor design in such a strong way that independent consideration is not possible. Moreover, the need for at least one of the reactor walls to transmit the chosen radiation imposes the utilization of transparent materials, such as glass for the reactor construction, and thus imposes size limitations, sealing problems, and breakage risks.

Compared to conventional chemical reaction rates, the reaction rate of photocatalytic processes is usually slow due to the low concentration level of the pollutants and therefore, there is a need to provide large amounts of active catalyst inside the reactor. Although the effective surface area of the porous anatase catalyst coating is high, there can only be a thin coating (about 1 mm thick) applied to a surface [15]. 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 is measured in hours, if not days [18].

Photocatalytic reactions are promoted by solid photocatalyst particles that usually constitute the discrete phase distributed within a continuous fluid phase in the reactor. Therefore, at least two phases, i.e. liquid and solid, are present in the reactor. The solid phase could be dispersed (SPD) [19] or stationary (SPS) within the reactor [18]. SPD photoreactors may be operated with the catalyst particles and the fluid phase(s) agitated by mechanical or other means. Depending on the means of agitation, the photoreactor resembles slurry or fluidized bed reactors. In numerous investigations, an aqueous suspension of the catalyst particles in immersion- or annular-type photoreactors has been used. 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 [19]. In addition, the depth of penetration of UV light is limited because of the strong absorption by both catalyst particles and dissolved organic species [15]. The above problems could be avoided in SPS photoreactors in which the photocatalyst particles are immobilized onto a fixed transparent surface, such as the reactor wall or a fibre mesh, or are supported on particles, such as glass or ceramic beads, that are held in fixed positions in the photoreactor. However, the immobilization of the catalyst on a support generates a unique problem [16]. The reaction occurs at the liquid-solid interface and usually only a part of the catalyst is in contact with the reactant. Hence, the overall rate may be limited to mass transport of the pollutant to the catalyst surface [17]. In addition, the rate of reaction is usually slow because of the low concentration level of the pollutant and therefore, there is a need for a reactor whose design provides a high ratio of illuminated immobilized catalyst to illuminated surface and the possibility of total reactor illumination [16]. The development of a reliable knowledge base is still in its initial stage related to the catalyst preparation and its activation, chemistry and kinetic networks of the pollutant degradation, intrinsic reaction kinetics that at times is mass-transfer-controlled, the process of photon energy absorption, and reactor design.

The volume of a photocatalytic reactor can be expressed as

$$V_R = \frac{QC_{in}X}{\kappa \Re} \tag{1}$$

where Q is the volumetric flow rate (m^3/s), C_{in} is the inlet pollutant concentration (mol/m^3), X is the fractional conversion desired, κ is the illuminated catalyst surface area in contact with the reaction liquid inside the reactor volume (m^2/m^3), and $\Re$ is the average mass destruction rate (mol/m^2/s). Hence, the smallest reactor volume will result when κ and $\Re$ are as large as possible for the specified values of Q, C_{in}, and X. $\Re$ is a *reaction-specific* parameter as it expresses the performance of the catalyst for the breakdown of a specific

model component, while κ is a *reactor-specific* parameter representing the amount of catalyst inside a reactor that is sufficiently illuminated so that it is active, and that is in contact with the reaction liquid. An increase in $\Re$ can be accomplished by modifying the physical nature of the catalyst in terms of its structure and morphology, or by the addition of oxidizing agents. Improving the breakdown rates would lead to the need of a less demanding amount of catalyst to be illuminated and therefore, to a smaller reactor volume. The parameter κ, namely, the illuminated specific surface area, helps to compare the design efficiency of different photocatalytic reactors as it defines the efficacy to install as much active catalyst per unit of reaction liquid volume in the reactor.

The scale-up has been severely limited by the fact that the reactor configurations have not been 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 coating per unit of reactor volume [16]. The new reactor design concepts must provide a high ratio of activated immobilized catalyst to illuminated surface and must have a high density of active catalyst in contact with the liquid to be treated inside the reactor [18,22].

4 Classifications of Photocatalytic Reactors

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 manner in which the catalyst is used, and on the arrangement of the light source and the reactor vessel, all photocatalytic reactor configurations fall under four categories. They are *slurry-type* in which the catalyst particles are in suspension form [19], *immersion*-type with lamp(s) immersed within the reactor [20], *external-type* with lamps outside the reactor [21], and *distributive-type* with the light distributed from the source to the reactor by optical means, such as reflectors and light conductors [22] or optical fibers [23]. The majority of the reactors patented are a variation of the slurry reactor and the classical annular reactor of immersion or the external-type in which the catalyst is immobilized on the reactor wall, on pipes internally, on ceramic membranes, on glass wool matrix between plates, on semipermeable membranes embedded in water-permeable capsules, on a mesh of fiberglass, on beads, on fused silica glass fibers, on porous filter pipes, on glass fiber cloth, etc. [24]. The reactors are either helical, spiral, shallow cross-flow basins or optical fiber. However, all these reactor designs are limited to small scales by the low values of the key parameter, κ. The only way to apply these systems to large-scale applications is by using large numbers of multiple units.

Tab. 3 lists the κ values for the four different classes of photocatalytic reactors. In a slurry reactor, small catalyst particles could provide a large surface area for reaction but essentially most of the catalyst surface area will be inactive, particularly for large reactor dimensions, as the catalyst

particles will not receive enough light from the external light source. This happens since the organics and the liquid medium itself are absorbing light. This is especially true for large reactor dimensions, resulting in low efficiencies and in the drawback of the impossibility of a scale-up to commercial use applications. In addition, the use of suspension requires the separation and recycling of the ultrafine catalyst from the treated effluent by filtration, centrifugation or coagulation and flocculation. These add various levels of complexity to an overall treatment process and clearly decrease the economical viability of the slurry reactors. An external-type reactor will always be limited by low values of κ. An immersion-type reactor could be scaled-up to any dimension but when classical lamps of a diameter between 0.07 to 0.1 m are used, the κ value is very low even if it is assumed that the lamps occupy 75% of the reactor volume.

Many other *innovative-type* reactor designs exist in literature addressing specific problems and applications or being designed especially for treating specific types of pollutants. These are in the form of treatment agents containing novalak resins, photoelectrochemistry or electrophotographic methods, use of magnetic or sound waves, photocatalysis and acoustics, catalyst particles coated with polymers as well as ion-exchange processes [24]. Others include the use of optical fibers as the source of illumination catalyst contained in removable filter units, and water-permeable capsules containing the catalyst. Although innovative in approach, the main problem associated with all these reactor configurations is again the issue of scale-up for commercial use purposes.

5 Two New Designs of a Large-Scale Photocatalytic Reactor

In order to overcome some of these deficiencies inherent in conventional photocatalytic reactor designs, a distributive-type photocatalytic reactor design in which the 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 κ and will 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 colored dye pollutants as they are strong UV absorbers and will therefore significantly screen the TiO_2 from receiving UV light [15].

At the National University of Singapore, we are considering scale-up configurations that contain both high surface areas to volume and efficient light distribution to the catalyst phase. Two ways above deficiencies inherent in conventional photocatalytic reactor designs can be overcome. First, by using a distributive type of photocatalytic reactor design in which the catalyst is fixed to a structure in the form of hollow glass tubes [22], and secondly, by using an immersion-type reactor with very narrow diameter tube lamps [18]. The design

Table 3. Comparison of κ, m^2/m^3 for different reactors.

Photocatalytic reactor	κ, m^2/m^3	Parameters	κ, m^{-1}	Remarks
Slurry Reactor [19]	$\left[\dfrac{6C_C}{\rho_C}\right]\dfrac{1}{d_p}$	$d_P = 0.3$ μm $C_C = 0.5$ kg/m^3	2631[#]	scale-up not possible
External type - annular reactor [21]	$\dfrac{4d_0}{d_0^2 - d_i^2}$	$d_o = 0.2$ m $d_i = 0.1$m	27	scale-up not possible
Immersion type - with classical lamps [16]	$\left[\dfrac{4\varepsilon}{1-\varepsilon}\right]\dfrac{1}{d_o}$	$d_o = 0.09$ m $\varepsilon = 0.75$	133	scale-up possible but large V_R
Immersion type - with novel lamps [18]	$\left[\dfrac{4\varepsilon}{1-\varepsilon}\right]\dfrac{1}{d_o}$	$d_o = 0.0045$ m $\varepsilon = 0.75$	2667	scale-up possible with small V_R
Distributive type - with hollow tubes [22]	$\left[\dfrac{4\varepsilon}{1-\varepsilon}\right]\dfrac{1}{d_o}$	$d_o = 0.006$ $\varepsilon = 0.75$	2000	scale-up possible with small V_R

[#] The value will be much lower than 2631 m^{-1} as all the suspended catalyst particles will not be effectively illuminated. Catalyst concentration $C_C = 0.5$ kg/m^3 is normally used. $\rho_C = 3800$ kg/m^3.

based on hollow glass tubes allows for a much higher illuminated surface area per unit of reactor volume [24], while the other design provides not only much higher values for the active catalyst surface area but the catalyst can also be activated uniformly at its highest possible level [20]. Furthermore, the designs of the reactors are flexible enough to be scaled-up for commercial scale applications.

The limitation to the size of the reactor with light conductors is the UV transparency of the material and the light distribution to the catalyst particle [24]. The critical and probably the most intricate factor is to distribute 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. The reactor configuration conceptually applicable for photocatalysis, satisfying most of the above-mentioned requirements, is a rectangular vessel in which light conductors as glass slabs (or rods) coated on their outside surface with catalysts are embedded vertically [22]. The lamps together with reflectors are placed on two sides of the reactor while liquid enters and exits from the other two sides. Light rays entering the conductor through one end are repeatedly reflected internally down the length and at each reflection they 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 the catalyst is present to the light-entering area could be as high as 500, evidently a very large catalyst area can be illuminated [14]. Moreover, with a large number of such light-conducting material packed inside the reactor, the configuration provides a high total light transfer area and allows for a higher illuminated catalyst area per unit of reactor volume. Densely packing the reactor with the light-conducting object not only increases the surface-to-volume ratio but also reduces the effective mass transfer diffusion length for the pollutant to the catalyst surface [25].

The vital issue in the distributive type of 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 [24]. The

predominant obstacle we came across 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 the denser to the rarer medium and is determined by the critical angle given by

$$\theta_c = \sin^{-1}\left[\frac{n_2}{n_1}\right] \qquad (2)$$

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), the angle θ will always exceed the critical angle, θ_c, for the interface between glass and air (or water) irrespective of the angle of incidence, α (0 to 90°) [24]. 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 emerge from the lateral surface. However, the refractive index of TiO_2 (between 2.4 and 2.8) is higher than that of glass (about 1.5) in the wavelength range from 200 to 400 nm and it is likely that total internal reflection would not take place when the glass surface is coated with titania. Nevertheless, if the coating consists 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. Therefore, it is best, if possible, to avoid the occurrence of total internal reflection entirely.

One way of avoiding total internal reflection is by surface roughening. Moreover, surface roughening assists in achieving a better catalyst adhesion to the substrate. Both are indeed found out to be the case experimentally [14]. In fact, when the lateral surface was roughened by sand blasting, most of the light emerged within few centimeters and hardly any light remained thereafter in the axial direction [22]. This is not only because roughening desists total internal reflection phenomena but also because UV transparency of most light-conducting material is very poor [24]. Although the use of quartz as light conductor will naturally help to overcome the light transmission problem, it will certainly make the overall reactor set-up more expensive [24].

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 [22] is a hollow glass tube coated on its surface with semiconductor catalysts. 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 in contact with the annular catalyst coating present around the outer surface of the tube. 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 the transmission of light is a strong function of the angle of incidence. When the light beam is nearly parallel with the surface (α close to 0°), most of the light is reflected and exits axially rather than laterally, while for light rays with α close to 90° most of the light will emerge laterally within few centimeters and barely any light will remain thereafter as reflection is only 4% for a glass-air interface [24]. Hence, it is important that in the design of a 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.

During the development of this new concept of a photocatalytic reactor based on multiple hollow tubes (MTR), we developed a unique new lamp design. These are extremely narrow-diameter fluorescent tube lamps of low wattage emitting lights in the wavelength of our interest ($\lambda < 365$ nm). These new lamps [18] address many of the solutions to the problems that have restricted the development of technical-scale photocatalytic reactors for water purification. These lamps are available in various shapes and lengths and can be placed inside a reactor to form a variety of different configurations. The development of a reactor using these new lamps will provide all the advantages of the multiple tube reactor, plus the additional advantage that the catalyst could be activated at its highest level. In the reactor, the catalyst was deposited on the outer surface of the low wattage lamps using a dip-coating apparatus [18]. Thus, the main problem encountered in the development of a reactor based on multiple hollow tubes (MTR) was avoided. In the MTR concept, it is impossible to obtain a uniform light distribution along the length of the tubes and therefore, it will severely restrict the maximum length of tubes that can be used inside a reactor and thereby the overall performance of the reactor. The new lamps eliminated this drawback in the development of the MTR reactor concept, as the new design is capable of distributing light uniformly over long tube lengths. Of course, this was possible with classical lamps, too. However, the new lamps allow for a 50 to 100 times larger surface area for the catalyst per unit of reactor volume compared to a classical reactor design [20].

A schematic drawing of the two reactors is shown in Figs. 1 and 2. The MTR reactor consists of a cylindrical vessel (diameter 0.056 m) containing 54 hollow quartz glass tubes (diameter 0.006 m) coated on their peripheral surface with catalyst [22]. The reactor resembles that of a shell and tube heat exchanger with the reaction liquid flowing through the shell side over the outside surfaces of the coated tubes, while light travels through the inside of the hollow tubes. One end of each tube was closed to prevent any reaction liquid entering the inside of the tubes, and they were coated with aluminium for better utilization of axially exiting light. The light source (Philips GBF 6436, 12 V, 40 W) used in the MTR was a low-voltage halogen lamp optically positioned within an aluminium reflector spanning 0.056 m for a clearly defined beam spread. In addition, a condenser lens of focal length 0.04 m was
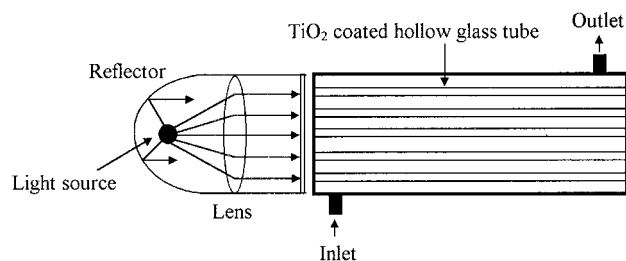

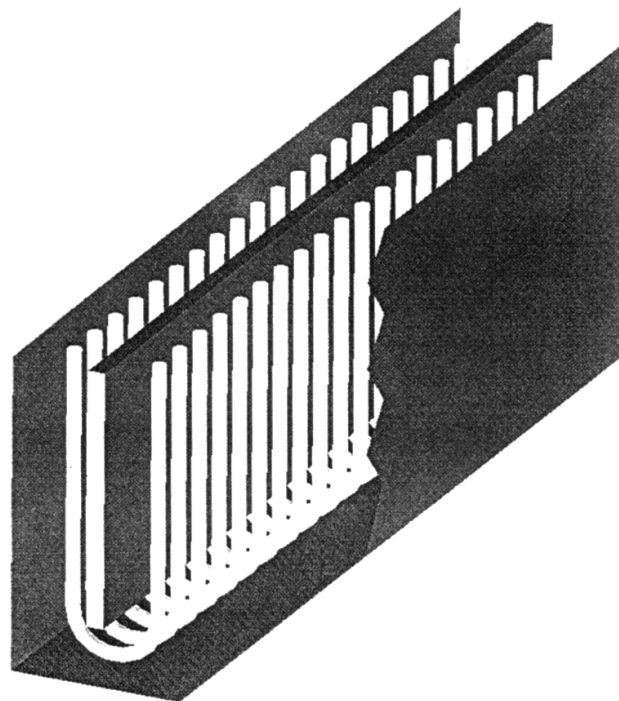**Figure 1.** Schematic diagram of a multiple tube reactor (MTR).

Figure 2. Schematic diagram of the tube light reactor (TLR).

placed between the lamp and the reactor to obtain a light beam at a half intensity beam angle between 2 and 4 degrees. The TLR reactor [18] consists of a stainless steel flattop plate (with 21 holes) onto which another plate was welded. 21 U-shaped lamps were placed around the latter plate and its end extended through the holes for electrical connections. The assembly was put in a rectangular stainless steel reactor vessel. Feed was introduced at the top of the vessel and was equally distributed over the width of the reactor through 5 inlet ports. The novel lamps (Philips NDF-U2 49-6W) used in the TLR were U-shaped, 0.498 m long, and had a diameter of only 0.0045 m. They operate at 1020 V and produce 6 W, of which 15% is in the UV-A region. The light intensity ($\lambda < 380$ nm) on the catalyst particles is 127.8 W/m^2.

Experiments performed in the two reactors showed very promising results [18,22]. The catalyst coatings on the glass tube and lamp surfaces were found durable, and the activity of the catalyst did not deteriorate even after 50 hours of

experimentation. Fig. 3 shows the experimental results for the photocatalytic destruction of the SBB dye [15] in the MTR [22] and TLR [18]. The experimental results show that photocatalytic destruction of the dye pollutant is possible in both configurations. The figure reveals that 90% of the pollutant was degraded in about 100 minutes for the MTR and in about 30 minutes for the TLR, although neither reactor was operated at optimum conditions. The performance of the MTR can be instantly improved by decreasing the length of the hollow tubes used, as it is likely that the catalyst is inactive near the end of the tube away from the light source. In addition, the designs of the reactors are far from optimum with respect to mass transfer of pollutant to catalyst surface, flow distribution of reaction liquid, and efficiency of packing of tubes/lamps inside the reactor. The reaction occurs at the liquid-solid interface and mass transfer from the bulk of the liquid to the catalyst surface plays an important role in the overall rate of destruction of pollutants. Nevertheless, the designs of the reactors have the capability to be scaled-up to any dimensions, whereas the other two reactors are restricted only to a small reactor capacity.
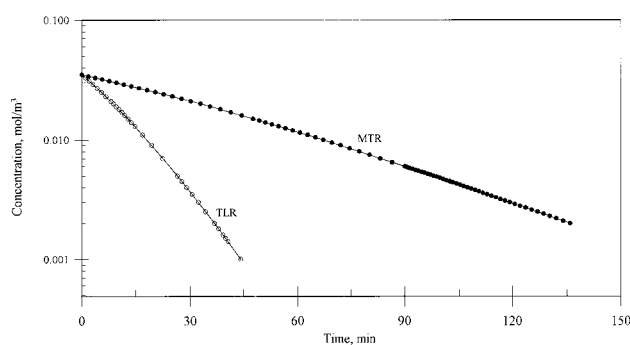
Figure 3. Experimental results for photocatalytic degradation of SBB dye in MTR and TLR.

The efficiency of the reactors (expressed in terms of moles converted per unit of time per unit of reactor volume per unit of electrical power consumed) is compared with two different reactors [21] for the same model component (SBB dye) and the same initial concentration ($C_o = 0.024$ mol/m^3). The slurry reactor (SR) consists of 20 tubes each of the volume 7×10^{-5} m^3

containing 3×10^{-5} m^3 liquid (with a TiO$_2$ concentration of 0.5 kg/m^3), placed on a holder that rotates around a magnetic stirrer and is surrounded by 24 Philips TLK 40 W/10 R lamps. The classical annular reactor (CAR) was of 0.099 m in outside diameter, 0.065 m in inside diameter and 0.77 m in length, surrounded externally by 10 Philips TLK 40 W/10 R lamps. When the efficiencies of these test reactors are compared (see Tab. 4) with the experimental results of CAR and SR [21], an increase of about 695% and 259% was observed for TLR while 436% and 142% were observed for MTR, respectively.

Both the MTR and TLR design concept creates great opportunities for building much more efficient photocatalytic reactors for water purification as the reactors will be more economical. From Tabs. 3 and 4 it can be seen that higher values for the parameter κ can be achieved for both MTR and TLR than for other reactor configurations. It is expected that the performance of TLR will surpass that of MTR because of the superior catalyst activation, but the overall reactor efficiency may be much lower due to the application of a large excess of light energy than is required for the catalyst activation. It is apparent that the MTR design idea creates great opportunities for building a much more efficient photocatalytic reactor for water purification, as the reactor most likely will be economical. We believe that the MTR reactor will be cost-effective compared to other photocatalytic reactors since it consists of inexpensive hollow glass tubes, a cheap catalyst and requires low wattage lamps. It needs a reflector, which usually comes with the lamp and of course, a lens to direct the light entry at a proper angle. Moreover, 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 biotreatment. 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 to send the water for biotreatment. It would then not be necessary to completely mineralize the pollutants present in the water by a photocatalytic reactor. A combination of the two methods could be best suited for water purification and may be more economical.

A problem for the TLR is still the burning stability and lifetime of the lamps, particularly when the lamps are used immersed in water containing toxic chemicals. The main obstacle in the development of the MTR design concept is that it is impossible to obtain uniform light distribution along the length of the tubes, thereby severely restricting the maximum length of tubes that can be used. One way of avoiding both problems is to place one extremely narrow-diameter novel tubelight lamp inside each of the hollow tubes. In this way, all the advantages of the MTR concept can be utilized

Table 4. Reactor specifications, experimental conditions, and reactor performance efficiency for CAR, SR, TLR and MTR.

Photocatalytic reactor	CAR [21]	SR [21]	TLR [18]	MTR [22]
Volume of reactor, m^3	3.48×10^{-3}	1.4×10^{-3}	5.36×10^{-4}	1.23×10^{-3}
Catalyst surface area, m^2	0.18	3.7	0.15	0.51
Parameter κ, m^2/m^3	69	6139 [#]	618	1087
Flow rate, m^3/s	8.42×10^{-5}	Batch	1.67×10^{-5}	3.00×10^{-5}
Electrical energy input, W	400	960	126	40
Efficiency[*], µmol/s/m^3/ W	9.50×10^{-3}	2.10×10^{-2}	7.55×10^{-2}	5.09×10^{-2}
% increase in efficiency	1	121	695	436
Scale-up possibilities	no	no	yes	yes

[*] Efficiency is expressed as 90% pollutant (SBB dye) converted (µmol/s) from a starting concentration of 0.024 mol/ m^3 per unit reactor volume (m^3) per unit electrical energy (W) used.

[#] The value will be much lower than 6139 m^{-1} as all the suspended catalyst particles are not effectively illuminated and the assumption of average particle diameter of 0.3 µm may be too low.

while eliminating the basic drawback of the uniform light distribution dilemma. Moreover, this will also eliminate the main problem experienced in the TLR with the prolonged use of novel lamps immersed in polluted water. A comprehensive experimental program investigating the influence of the operating parameters on the conversion rates is presently being carried out for both reactors.

6 Conclusions

The central problems in the development of a photocatalytic reactor, namely, light distribution inside the reactor and providing high surface areas for the catalyst per unit of reactor volume, are addressed in this paper. Two reactor concepts, one of which is a distributive-type fixed-bed reactor system that employs hollow glass tubes as a means of light delivery to the catalyst particles, while the other is an immersion-type reactor with new extremely narrow diameter artificial fluorescent lamps, are discussed. Both reactors result in a 100- to 150-fold increase in surface area per unit of reaction liquid volume inside the reactor relative to a classical annular reactor design and a 10- to 20-fold increase relative to an immersion-type reactor using classical lamps. The design of both reactors increases the surface-to-volume ratio while eliminating the prospect of light loss by absorption and scattering in the reaction medium. Experiments performed to study the degradation of a textile dye showed promising results for the two test reactors. Both reactor configurations are flexible to be scaled-up for commercial applications.

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