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Photoelectrochemistry and the environment

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This article builds upon a companion review on electrochemical techniques [1] and discusses photocatalytic methods for the treatment and analysis of pollutants in water and air. Organic, inorganic and microbiological pollutants are considered. Areas wherein further research and development are needed are identified. Finally, perspectives on commercialization of this technology are presented.

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1. Introduction and scope of review

In a companion article [1], electrochemical methods for the analysis and destruction of hazardous chemicals were reviewed. Additionally, the applicability of these methods in the drinking water industry and in disinfection scenarios was also considered. In this paper the utility of photoelectrochemical strategies for similar applications is discussed. Within the framework of this review, 'photoelectrochemical' (PEC) is taken to mean an electrochemical process which occurs on irradiation of a semiconductor (usually inorganic) electrode or particle. A photocatalytic (PC) system comprises a subset of this wherein the rate of a thermodynamically 'downhill' process is accelerated by light. On the one hand, the principles underpinning photoelectrochemistry and photocatalysis have been reviewed elsewhere [2–13]. There are also conference proceedings, book chapters and review articles specifically devoted to environmental applications of photocatalysis [14–27]. On the other hand, PEC methods for the analysis of toxic chemicals are at an early stage of development.

In a historical context, it is interesting to note that much of the research in the 1970s and the early 1980s was oriented toward the photovoltaic conversion and energy storage possibilities with PEC devices. The late 1980s and the plummeting of oil prices prompted a reorientation of PEC studies toward materials synthesis, processing, and characterization particularly with the electronics industry as a target consumer [28]. Concomitant with this trend was the realization that PEC methods, and specifically PC techniques, can play a useful role in hazardous waste treatment [14–27]. It is this reviewer's opinion that the field of photoelectrochemistry will perhaps carve out a niche in the 1990s in environment-related technologies. This is already borne out by the fact that TiO_2-based photocatalysis is generating commercial interest as discussed in more detail below.

From a technological perspective, the PC methodology will have to be evaluated against current air and water remediation methods: thermal incineration, air stripping and granular activated carbon adsorption. Comparative performance and economic data will be provided below where possible. The PC method may also be considered under the umbrella of a number of new technologies, collectively known as 'advanced oxidation processes' (AOP). These technologies almost all rely on the generation of very reactive free radicals (e.g., $OH^\bullet$) which are subsequently used to degrade the organic pollutants or microorganisms. The approaches to AOP under development include [29]:

(i) *Homogeneous photolysis*: These processes employ direct u.v. photolysis of solutions containing oxidants such as H_2O_2, ozone or combinations thereof.

(ii) *Heterogeneous photolysis*: This involves the use of semiconductor suspensions to harness the light, and generate $OH^\bullet$ radicals at the photocatalyst/solution interface. This photocatalytic (PC) process constitutes the main topic of this review. This process is 'heterogeneous' and must be distinguished from its 'homogeneous' counterpart wherein the catalyst (usually a macrocycle or an organometallic complex) is dissolved in the solution. Only the heterogeneous PC approach is considered in this article and the term 'PC' is used with the implicit recognition that it is the heterogeneous approach that is considered.

(iii) *Radiolysis*: High energy radiation (e.g., γ-rays) is used to irradiate the water to be treated. Again, radicals are created by the radiation process.

(iv) *Indirect electrolysis*: Here, radicals such as $OH^\bullet$ are generated at a *dark* electrode/solution interface containing additives such as H_2O_2 or Fenton's reagent. This approach was considered in the companion review [1].

2. Heterogeneous photocatalysis

2.1. *Principles*

The absorption of bandgap light by the semiconductor (SC) at the particle/electrolyte interface results in

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the formation of an electron-hole pair:

$$SC \xrightarrow{h\nu > E_g} e^-_{CB} + h^+_{VB} \tag{1}$$

E_g represents the SC energy bandgap and the subscripts attached to the (photogenerated) electronic carriers specify their location in the conduction band and valence band, respectively, in the semiconductor. A major distinction can be drawn with regard to the interphasial situation at semiconductor slurries/suspensions and their immobilized counterparts. Specifically, when the latter are attached to a conductive support, the possibility exists for imposing a bias potential across the semiconductor/electrolyte interface, and thus modifying the electrostatics to bring about better electron-hole separation. In the former case involving semiconductor suspensions, the extent to which the (deleterious) electron-hole pair recombination is suppressed is determined solely by the dynamics of carrier transport across each semiconductor particle [30, 31] and by the efficacy with which the carrier-intercepting surface reactions occur.

In terms of applicability to pollutant removal (or remediation) strategies, the reactions involving photogenerated electrons and holes are best discussed separately. Thus, the photogenerated holes oxidize water or adsorbed OH^- (on the photocatalyst surface) to hydroxyl radicals:

$$OH^- + h^+_{VB} \xrightarrow[h\nu]{SC} OH^\bullet \tag{2}$$

These highly-reactive radicals can then be used to mineralize or at least partially degrade most organic pollutants. Indeed, the range of compounds that have been successfully treated is impressive as the compilation in Table 1 illustrates. (A more extensive listing may be found in [26]). The $OH^\bullet$ radicals are also nonselective in their attack of microorganisms and cause biological cell deactivation in many cases [73]. Table 2 provides a summary of the microorganisms that have been treated to date.

Paralleling Reaction 2 is the possibility of *direct* attack of an organic substrate by the photogenerated hole. This pathway appears to be particularly important in gas-phase photocatalysis.

*Table 1. Organic pollutants successfully treated by TiO_2-based photocatalysis**

Pollutant category	*References*
BTEX	[32, 33]
Phenols	[34–38]
TCE and other halogenated hydrocarbon solvents	[39–53]
DDT, dioxins, other pesticides and herbicides	[54–58]
Kraft lignin	[59, 60]
Dye stuffs, organophosphates and surfactants	[61–68]
Gasoline	[70, 71]

* Also see [20, 22, 26, 72].

BTEX = benzene, toluene, ethylbenzene and xylene. TCE = trichloroethylene, DDT = dichlorodiphenyltrichloroethane [or more correctly, 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane], PCB = polychlorinated biphenyls.

Table 2. Microorganisms deactivated via TiO_2-based photocatalysis

Microorganisms	*References*
Escherichia coli	[74–78]
Lactobacillus acidophilus	[74]
Saccharomyces cerevisiae	[74]
Fecal coliforms	[79]

Inorganic pollutants may be either reduced to the elemental form, and thus removed from the process stream:

$$M^{n+}_{(aq)} + ne^-_{CB} \xrightarrow[h\nu]{SC} M^0_{(s)} \tag{3}$$

or converted to an environmentally more benign element in a different oxidation state as exemplified by the Cr(VI) ⟶ Cr(III) PC system [80]. Strategies incorporating simultaneous pH adjustment also serve to immobilize the pollutant as an (insoluble) oxide onto the photocatalyst to be subsequently regenerated in a separate step. This approach has been recently demonstrated in our laboratory using the Cr(VI) ⟶ Cr(III) model system [80]. Table 3 contains examples of inorganic pollutants that have been treated using the PC methology.

Indeed, the capability exists with the PC approach for *simultaneously* treating a water (or air) stream contaminated with all three types of pollutants, viz. organic, biological or inorganic. This is particularly relevant in the drinking water industry, wherein the raw water often contains odour or colour-producing organic chemicals, inorganic species such as Pb(II), As(III) etc., and microorganisms such as bacteria, protozoa or viruses.

Figure 1 summarizes the photodriven events at a single semiconductor particle. Thus, within an environmental context, 'Ox_1' could be a metal ion (e.g., Pb^{2+}) and 'Red_2' could be either an organic substrate or a microorganism.

The *simple* recombination of the e^-–h^+ pairs often involves a mediating 'surface state' (located in the bandgap of the semiconductor) and *results in no net chemical change in the system.* The concept of *conjugate* reactions is useful for analysing the PC process. Thus Reaction 2 may be alternately expressed as

$$2H_2O + 4h^+ \xrightarrow[h\nu]{SC} O_2 + 4H^+ \tag{4}$$

Table 3. Some inorganic pollutants treated by photocatalytic techniques

Pollutant(s)	*References*
Cyanide	[81–90]
Hydrogen sulfide	[91–93]
Mercury and cadmium	[94, 95]
Chromium	[80, 96–102]
Sulfite	[82]
Manganese	[103]

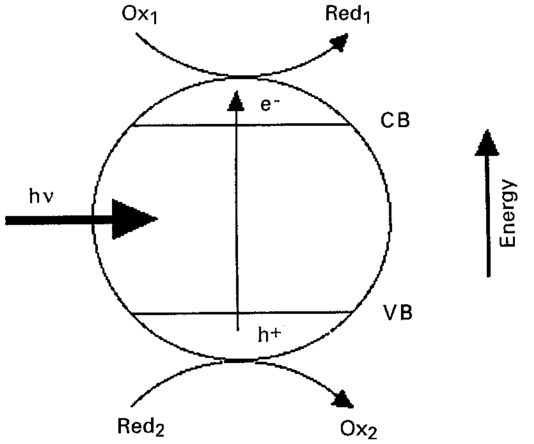

Fig. 1. A schematic of photodriven events at a TiO_2 particle in contact with a medium containing an oxidant, Ox_1 (e.g., O_2) and a reductant, Red_2 (e.g., an organic substrate).

Now O_2 functions as an electron acceptor to *chemically reverse* this process:

$$O_2 + 4H^+ + 4e^- \underset{h\nu}{\xrightarrow{SC}} 2H_2O \quad (5)$$

If the carrier fluxes due to Reactinos 4 and 5 are exactly balanced, the holes and electrons have been effectively recombined as can be demonstrated by simple addition of Reactions 4 and 5. Again there is no net chemistry and O_2 has functioned in the role of a 'chemical surface-state' for mediating the e^-–h^+ recombination process (c.f. Fig. 2). More complicated chemical scenarios can be envisaged which involve the surface hydroxyl groups at the semiconductor surface as the carrier recombination mediators, but the conclusion remains the same.

The foregoing discussion underlines the fact that net chemistry can only occur at the semiconductor surface if either Reaction 4 or 5 is intercepted at an intermediate stage. Alternatively, *the e^- and h^+ at the semiconductor surface have to react with different redox couples in the contacting medium*, as illustrated in Fig. 1.

In pollutant degradation, either Reaction 4 or Reaction 5 constitutes one-half of the conjugate reaction pair, the other half of the pair or partner comprising the pollutant molecule, ion or microorganism.

To illustrate, Reactions 6 and 5′ form a conjugate pair in the photocatalytic degradation of an organic substrate:

$$4OH^- + 4h^+ \longrightarrow 4OH^\bullet \quad (6a)$$

$$4OH^\bullet + \text{organic substrate} \longrightarrow \text{products} \quad (6b)$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad (5')$$

Net reaction:

$$[(5') + (6)] \quad \text{organic substrate} + O_2 + 2H_2O \underset{h\nu}{\xrightarrow{SC}} \text{products} \quad (7)$$

A second example involves the photoreduction of a toxic metal ion (e.g., Pb^{2+}) at the semiconductor surface. In this instance, Reactions 4 and 8 form a conjugate pair:

$$2H_2O + 4h^+ \longrightarrow O_2 + 4H^+ \quad (4)$$

$$2Pb^{2+} + 4e^- \longrightarrow 2Pb \quad (8)$$

Net reaction:

$$[(4) + (8)] \quad 2Pb^{2+} + 2H_2O \underset{h\nu}{\xrightarrow{SC}} 2Pb + O_2 + 4H^+ \quad (9)$$

2.2. *Quantum yield*

The concept of quantum yield is of great value in photochemistry [104]. The quantum yield is generally defined as the number of events occurring per photon absorbed. The difficulty with defining such a parameter for heterogeneous systems is related to uncertainties arising from light scattering by the photocatalyst particles. (Catalyst particle size is comparable in many cases to the incident photon wavelength.) Accordingly, an *apparent* quantum yield is often quoted wherein the inherent assumption is that all the incident light is absorbed by the semiconductor particle. However, a special sample cell has been designed to minimize losses due to scattering [105]. This cell was tested using a model system comprising the PC bleaching of methylene blue using irradiated TiO_2 [105].

2.3. *Thermodynamic aspects*

Let us now consider the energetics of Reactions 7 and 9 as written. Reaction 7 is photocatalytic because it involves a negative Gibbs free energy change ($\Delta G^\circ < 0$). Thus the reaction is driven in the spontaneous direction by the light, and the radiant energy simply serves to overcome the activation barrier for the process. On the other hand Reaction 9 involves a positive ΔG° of $+48$ kJ and is photosynthetic. Here the light drives the reaction in the thermodynamically 'up-hill' direction. Indeed, most reactions of this type are photosynthetic except when the metal ions are reduced at very positive potentials; i.e. when they have standard reduction potentials which are more positive relative to the O_2/H_2O redox couple.

An important ramification of the preceding discussion is that the 'back-reaction' is important only for photosynthetic systems. For example, consider the deposition of copper on TiO_2. The back-reaction between Cu and O_2 (which has a *negative* ΔG°) serves to chemically reverse (the forward) Reaction 4. In other words, a situation arises akin to that in Fig. 2 except that the $Cu^{2+/0}$ redox couple has acted as a 'mediator' or 'electron relay' (c.f. Fig. 3). Alternatively stated, the Cu^{2+} ions have 'short-circuited' the semiconductor microelectrode. Experimental examples of this effect are available [34, 106]. In many instances, however, the thermodynamically down-hill ($\Delta G^\circ < 0$) back-reaction is *kinetically* slow.

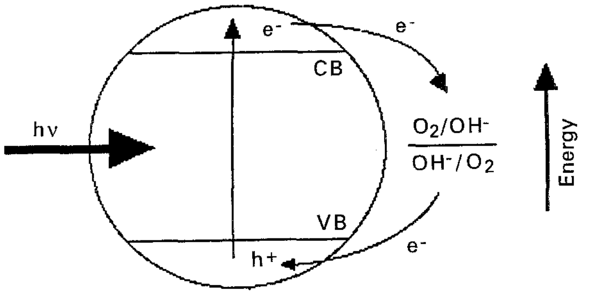

Fig. 2. Short-circuiting of an irradiated TiO_2 'microelectrode' particle by the O_2/OH^- redox couple.

A second important point is that the conjugate reaction partner plays a pivotal role in dictating whether a given reaction is photocatalytic or photosynthetic. For example, the reaction:

$$2Cu^{2+} + 2H_2O \xrightarrow[h\nu]{SC} 2Cu + O_2 + 4H^+ \qquad (10)$$

is photosynthetic ($\Delta G^\circ = 164\,kJ\,mol^{-1}$). On the other hand, addition of a hole scavenger such as acetic acid to the medium causes the resultant reaction:

$$Cu^{2+} + 2CH_3COO^- \xrightarrow[h\nu]{SC} Cu + C_2H_6 + 2CO_2 \qquad (11)$$

to be photocatalytic ($\Delta G^\circ = -136\,kJ\,mol^{-1}$) [108].

2.4. *Photocatalytic process modelling*

A useful model framework for discussing conjugate reactions at a photocatalytic particle can be borrowed from the corrosion field [109, 110]. The underlying idea is that, on a 'microelectrode' particle at steady-state, the net rates of the oxidation and the reduction components must be the same, i.e. the anodic and the cathodic current branches must have the same magnitude [111–114]. This is illustrated in Figs 4 and 5. For an n-type semiconductor such as TiO_2, the anodic current branch reflects the flux of the minority carriers, i.e. holes. On the other hand, the cathodic component originates in the flow of majority carriers, i.e., electrons in this case.

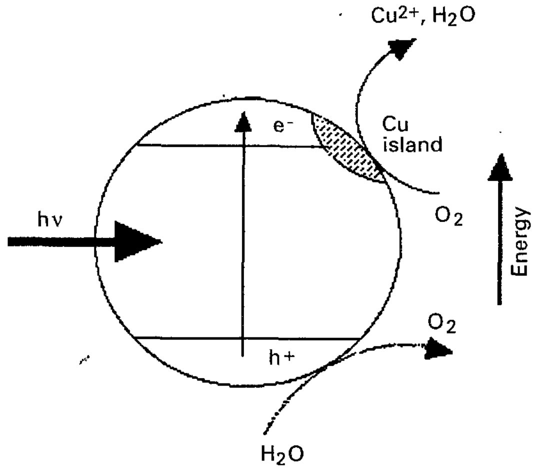

Fig. 3. The short-circuiting of a Cu-modified TiO_2 particle under band-gap irradiation. The oxygen that is evolved via the hole reaction is reconverted back to H_2O at the Cu site which mediates the electron conjugate process.

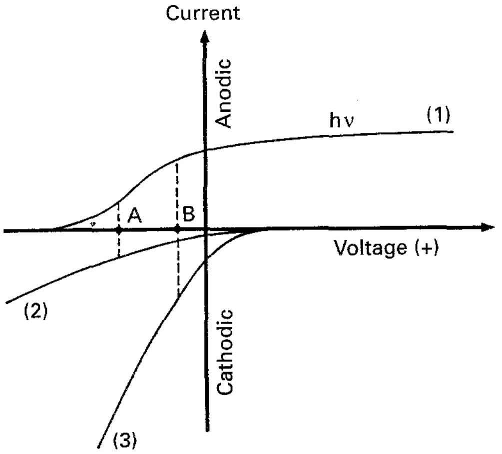

Fig. 4. A Wagner diagram (c.f. [109]) of the conjugate processes at an irradiated TiO_2 particle. The hole process is shown as curve 1; two different cases are shown for the conjugate electron process involving one with sluggish (curve 2) and facile (curve 3) kinetics. The (dashed) 'tie-lines' correspond to particle potentials (A and B) at which the anodic and cathodic branches are balanced.

Suppose that the desired reaction is the photoanodic degradation of a pollutant (c.f. Reaction 7). Two scenarios are shown in Fig. 4 wherein this oxidation reaction (curve 1) is coupled with a sluggish (curve 2) and facile (curve 3) cathodic conjugate reaction. In the former case, the particle at steady state attains a 'mixed-potential' represented by the point, A. In the latter case, this potential shifts in the desirable direction of higher (i.e. more positive) reaction overpotential (point B). Thus, the rate of the conjugate reaction partner (Reaction 5 in the preceding example) must be optimized to afford faster photodegradation of the organic pollutant [115–117].

Figure 5(a) contains symmetrical considerations for a *photoreduction* target system (curve 3). In this case, a faster conjugate photooxidation reaction (curve 2 instead of curve 1) leads to a shift of the reaction overpotential in the desired negative direction. Thus, if the removal of a toxic metal ion is the goal (c.f. Reaction 9) an efficient hole scavenger can be added to accelerate the clean-up process. However, if the toxic metal ion is present only in low concentration (p.p.m. levels) as is usually the case, then the cathodic branch will be mass-transport limited and will exhibit a plateau (curve 3, Fig. 5(b)). In this case, the available hole flux may be more than sufficient to balance the maximum cathodic current that can be sustained at the particle surface. Economically speaking, the cases illustrated in Fig. 5(a) may thus be more appropriate to a metal recovery or 'photoelectrowinning' scheme wherein higher levels (millimolar) of metal ions exist in the waste stream. Silver recovery from a photoprocessing operation is such a case [118].

The modelling strategy of balancing carrier fluxes has been used by previous authors for explaining the beneficial influence of metal catalyst islands on semiconductor particles [111, 112], and for analysing the

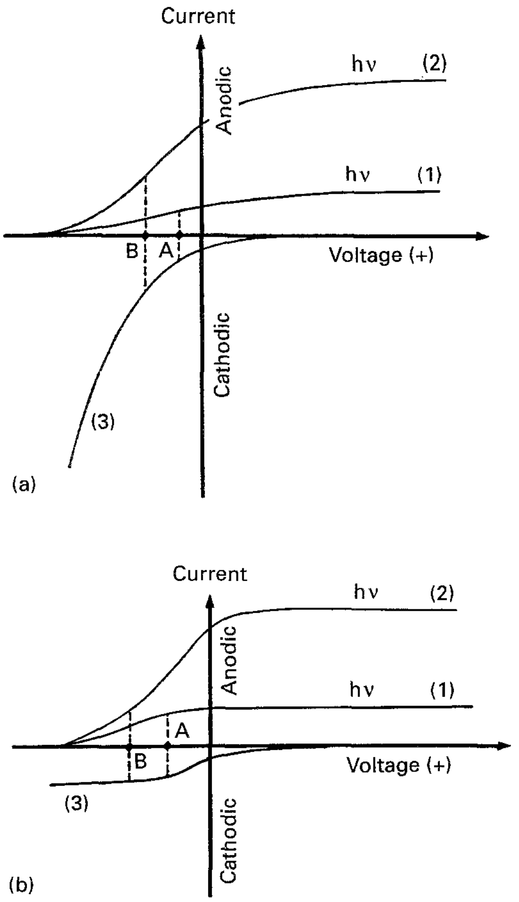

Fig. 5. Wagner diagrams for a targeted photoreduction at TiO_2 for the cases wherein the cathodic process is not (a) and is (b) mass-transport limited. The medium is assumed to be agitated in the latter case. Curves 1 and 2 correspond to a slow and fast anodic process respectively for the *same* photon flux incident on the TiO_2 particle surface. The tie-lines have the same significance as in Fig. 4.

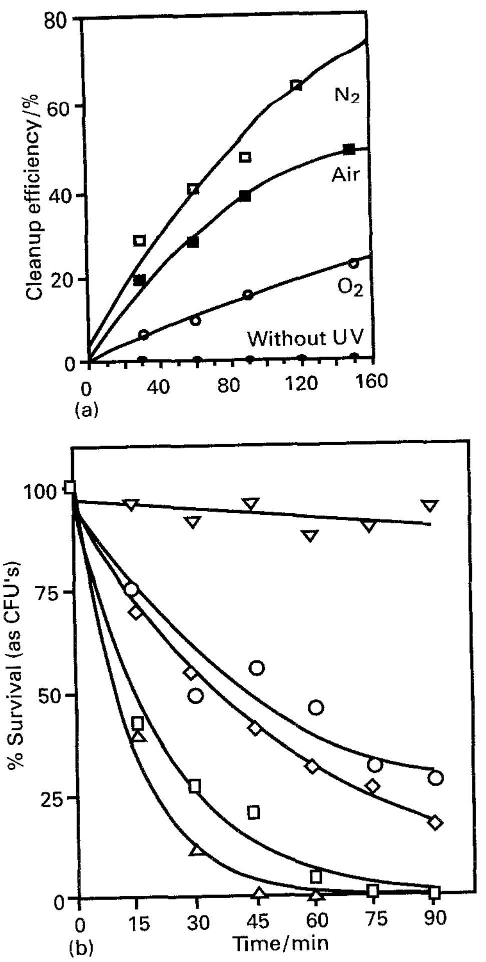

Fig. 6. Influence of oxygen on the efficiency of TiO_2 to reduce Cr(VI) (a) or to kill *E. coli* (b). The data in (a) and (b) are from [80] and [78], respectively. The bactericidal activity of TiO_2 in (b) is expressed as the percentage survival of colony forming units (CFUs).

influence of oxygen reduction kinetics on the organic degradation pathway [117]. This approach was used for analysing photon flux effects and competitive reaction pathways [119]. For example, Fig. 6 contains two examples for the contrasting influence of oxygen on photoreduction of Cr(VI) (Fig. 6(a)) and the rate of killing of *E. coli* (Fig. 6(b)) at TiO_2. These data are taken from recent research in our laboratory [78, 80]. In the former case (Fig. 6(a)), oxygen is deleterious because it competes with Cr(VI) for the photogenerated electrons. On the other hand, the photoanodic (hole) reaction rate is enhanced in Fig. 6(b) by improving the kinetics of the (cathodic) reaction conjugate as in the model case in Fig. 4. This is done by increasing the concentration of the electron acceptor (O_2 in this case) in the electrolyte. Interestingly enough, too high a concentration would possibly have reversed this trend (by short circuiting this cell), although this limit was fortuitously not attained in Fig. 6(b) because of the finite solubility of oxygen in water!

2.5. *Choice of semiconductor photocatalyst*

In terms of criteria for choosing an appropriate semiconductor photocatalyst, the most important appears to be factors related to the location of the band-edges at the surface. That is, the conduction and valence band-edges have to be located at energies (potentials) such that processes such as Reactions 4 and 5 may be photodriven. Thus the valence band has to be placed at potentials which are at least +2.85 V (with respect to the standard hydrogen electrode) [120]. Only then will the photogenerated holes (c.f. Reaction 1) have sufficient energy to oxidize water to $OH^•$. Similarly, if O_2 is used as the electron acceptor (c.f. Reaction 5), the conduction band would have to lie at a value negative of the standard potential for the reduction of oxygen.

In addition to surface energetics, the stability of the semiconductor particle to photocorrosion is a crucial factor. Finally, in terms of practical considerations, cost is also an issue.

Titanium dioxide has been by far the most popular photocatalyst. Both the anatase and rutile modifications have been used although commercial samples (e.g., Degussa P-25) often contain a mixture of the two. The energy bandgaps of anatase (3.23 eV, 384 nm) and rutile (3.02 eV, 411 nm) combine with the valence-band positions to create a favourable situation for the photogeneration of highly energetic holes at the interface. However, anatase is superior

Table 4. Semiconductors that have been employed in photocatalysis studies

Material	*Band-gap energy*/eV
Si	1.1
TiO_2	3.0 (rutile) 3.2 (anatase)
ZnO	3.2
WO_3	2.7
CdS	2.4
ZnS	3.7
$SrTiO_3$	3.4
SnO_2	3.5
WSe_2	1.2
Fe_2O_3	2.2

to rutile for PC applications. First, the conduction band location for anatase is more favourable for driving conjugate reactions involving electrons. Other variant reasons have been given. For example, the poorer PC activity of rutile was attributed to its high e^-–h^+ recombination rate and its lower oxygen photoadsorption capacity [121]. A more recent study concludes that very stable surface peroxo groups can be formed at the anatase during photo-oxidation reactions but not at the rutile surface [122]. The implication is that the degradation of organic compounds such as 4-chlorophenol proceeds through an *indirect* pathway involving these surface species. The decrease noted in the PC activity when titania (prepared by a precipitation method) is annealed at temperatures higher than 600 °C [123] appears to have a similar mechanistic origin in the extent of hydroxylation of the oxide surface. Other semiconductors have also been employed, and a representative listing appears in Table 4. However, none of these appear to match (at least to date) the attributes of TiO_2.

The bandgaps as listed in Table 4 are for the semiconductors in 'massive' form or for colloidal particles of several hundred nm size. Size quantization, however, can cause sizable shifts in these bandgap energies [124–126]. For example, TiO_2 microcrystallites as small as 2 nm have been prepared in Nafion® and clay interlayers with a corresponding bandgap energy as high as 3.95 eV [127]. Similar trends have been observed for Fe_2O_3 [128] and ZnS [129]. Very high activities have been observed for Fe_2O_3 nanosized particles (relative to bulk α-Fe_2O_3 powder) for model photoreactions such as the decomposition of saturated carboxylic acids [130].

The vast majority of the semiconductor photocatalysts listed in Table 4 have rather high bandgaps. Large bandgap semiconductors in general tend to be more stable against photo-corrosion [131, 132]. Oxidation of many pollutants, especially organic species, requires high potentials with the result that the valence band location at the semiconductor/electrolyte interface has to be rather positive as exemplified by TiO_2 and CdS. In these instances, the photogenerated holes will have sufficient energy to oxidize the organics either directly or via the generation of hydroxyl radical intermediates (see below). Nonetheless, some of the candidates listed in Table 4 do not have long-term stability in aqueous media, notably Si, CdS and ZnO. The photooxidation kinetics are also poor in some instances, as for example, for n-Si [133]. Thus the positive attributes of this material in terms of its good match with the solar spectrum and the advanced technology which exists on it, are offset unfortunately by these other handicaps.

2.6. *Photocatalyst configuration*

Single crystal materials can safely be discarded as serious candidates for remediation purposes both in terms of economic considerations, and, perhaps more importantly, from a technical perspective, because of finite reaction cross-section with the (pollutant) substrate. Semiconductor thin films are attractive for use in solar (photovoltaic) devices but are inadequate for PEC or PC waste treatment applications unless special efforts are made to tailor their surface morphology (see below). This then leaves the option of PC reactors containing semiconductor slurries or suspensions. These offer the advantage of high surface dispersion, and consequently optimization of the encounter frequency of the active surface with the pollutant substrate. However, photocatalyst recovery after use becomes an issue of major practical concern. Immobilized photocatalysts in the form of highly microporous particles which are attached to a solid support represent an effective compromise incorporating, to a degree, the positive features with the use of a semiconductor suspension. Thus TiO_2 has been immobilized on beads [70, 71, 116, 134], hollow tubes [135–137], Vycor® glass [138], woven fabric [139], silica gel [36], and even sand [37]. Porous thin films of TiO_2 have been immobilized on conductive SnO_2 glass [140]. Such 'particulate' films have been synthesized by thermally fusing ZnO or TiO_2 particles onto conducting glass (e.g., indium tin oxide) [141, 142]. Other than the ease of handling the photocatalyst after use in the reactor, another crucial advantage with this type of immobilization approach is that a bias potential may be applied to the photocatalyst film to separate the photogenerated carriers thereby improving the quantum yield [140–142].

In general, however, immobilized photocatalyst reactor configurations result in lower PC activity relative to their slurry counterparts (see below). A major factor relates to substrate mass transport, an aspect discussed in more detail below. Photocatalyst regeneration (e.g., with an acid wash) is perhaps easier with the use of suspensions, and there are indications that the thin-film photocatalyst configuration may be more susceptible to poisoning and permanent deactivation [143]. Incomplete mineralization has also been observed with the use of porous supports such as silica gel [79]. This has been attributed to the competitive adsorption of organics at TiO_2 and the (unreactive) SiO_2 sites. The partially hydroxylated degradation products apparently escape further encounters with the TiO_2 sites by partitioning at the silica/solution interface. Interestingly enough, this effect was not observed at *compact* supports such as glass [79].

2.6.1. Other variables related to photocatalysts. For a given semiconductor, factors such as the dopant ion, crystal modification, surface area, and surface morphology play an important role in the PC efficiency, although detailed studies on semiconductors other than TiO_2 are rare. The influence of surface chemistry was mentioned earlier within the context of the superior performance of anatase relative to rutile.

Using a flame reactor to produce nonporous anatase samples of varying surface area, the degradation rate of 3-chlorophenol has been observed [144] to increase with surface area up to $\sim 150\,m^2\,g^{-1}$. A decrease in the rate was observed for finer particles thereafter, and this trend was attributed to defect-induced e^-–h^+ recombination. Some dopant ions such as Cr(III) were found to have a deleterious influence on the PC activity of the parent oxide for similar reasons [145]. The influence of dopant ions on the e^-–h^+ recombination rate in TiO_2 has also been recognized [146].

It was recognized early in the history of photoelectrochemistry that noble metal islands on a photocathode surface accelerated reactions such as the reduction of water [9]. Parallel efforts have gone into modifying semiconductor particles and to show that metal or metal oxide centres on these particles promote their PC activity [111, 116, 147–162]. Apart from Pt, other metals such as Pd [116, 160], Au [152] and Ag [156–158] on TiO_2 have been shown to accelerate the photodegradation of organic compounds such as 2,2-dichloropropionate [115], 1,4-dichlorobenzene [159], 2-propanol [157] and salicylic acid [161]. These catalyst centres possibly serve to channel the photogenerated e^-–h^+ pairs (Equation 1) into physically separated reaction sites. It is possible that oxides such as RuO_2 and NiO also serve a similar role. For example, in the case of NiO–$SrTiO_3$, the NiO has been proposed [162] as an e^--scavenging site:

$$2H^+(ads) + 2e^- \longrightarrow 2H^\bullet(ads) \longrightarrow H_2(ads) \longrightarrow H_2(g) \qquad (12)$$

Electron transfer kinetics to oxidants such as to O_2 are also improved in the presence of the catalyst, and recent authors [116] have emphasized the important role that the kinetics of the conjugate Reaction 5 plays in the PC degradation of organic compounds. Research also has focused on improving the visible light response of wide band-gap semiconductors such as TiO_2 [9]. These studies have been mainly carried out from a photovoltaic application perspective although there is at least one instance wherein TiO_2 modified with a sensitizer such as zinc tetraphenylporphyrin has been used for the photodegradation of PCBs [50].

2.7. *Photocatalytic oxidation of organic pollutants*

2.7.1. Influence of electrolyte composition, pH, and additives. An early report described the inhibition of PC activity by the products of the photoprocess such as HCl and HBr [20]. Since then, there have been attempts to systematically study the influence of anions such as Cl^-, SO_4^{2-}, NO_3^-, ClO_4^-, HCO_3^-, and PO_4^{3-} on the PC activity of TiO_2 towards selected organic substrates [51, 144, 163, 164]. These studies are in agreement that anions such as NO_3^- and ClO_4^- have no effect. On the other hand, the inhibitory effect of the other ionic species was either attributed to specific adsorption [144] or to an alternative mechanism [163, 164] involving competitive adsorption at the TiO_2 surface of the anions followed by radical anion generation by reaction with the photogenerated holes. The deleterious influence of hydroxyl scavenging species such as HCO_3^- (c.f. Reaction 13) has also been noted [120]:

$$HCO_3^- + OH^\bullet \longrightarrow CO_3^{\bar{\bullet}} + H_2O \qquad (13)$$

Electrolyte pH shifts the standard potentials of Reactions 4 and 5 at the rate of $-59\,mV\,(pH)^{-1}$ at 25 °C. The surface energetics at the TiO_2/solution (and at other oxide semiconductor/solution) interfaces are also affected in a similar manner. This is a consequence of the varying surface charge at the semiconductor surface as a function of electrolyte pH. This affects the adsorption of the organic substrate at the semiconductor (e.g., TiO_2) surface and, consequently, its reactivity. Variant trends have been observed for the influence of electrolyte pH on the PC reaction rate and yield. For example, the pH reaction dependence of the PC rate was found to be weak in the range from ~ 1.3 to ~ 6.3 for nitrobenzene, benzamide, 3-chlorophenol and 1,2-dimethoxybenzene [144]. A similar trend was observed in a field test for BTEX [33]. On the other hand, the photon flux dependence of the PC reaction rate (see below) was observed to switch from linear at pH 2.6, 7 and 11 to a power (1/2) law at pH 5 [51, 72]. This was attributed to a 'zero proton condition' at the TiO_2 surface at the latter pH which was estimated to correspond to the point of zero charge (pzc) of TiO_2. A strong effect of pH was also noted in the PC treatment of biologically pretreated landfill effluent [165].

These contrasting results are not surprising given that *heterogeneous* processes such as specific adsorption can be expected to be crucially dependent on the surface characteristics of the photocatalyst used and the chemical structure of the adsorbing substrate molecule.

Cations such as Cu(II), Fe(III) and Ag(I) have been shown to enhance the oxidation rates of organic substrates [34, 94, 106, 107, 158, 166–168]. A likely mechanism is the reduction in the extent of e^-–h^+ recombination via the trapping of the photogenerated species by these electron acceptors. The beneficial influence of enhancing the rate of the conjugate process was discussed earlier.

Finally, the influence of additives such as H_2O_2 on the PC reaction rates at TiO_2 deserves mention. The PC degradation rates were enhanced several-fold for substrates such as chloroethylenes, phenol and chloral hydrate [55, 123, 168]. The H_2O_2 presumably increases the oxidation rate in these cases via its role as an electron scavenger. Comparisons between TiO_2–u.v. and H_2O_2–u.v. processes have also been made [144]. The synergistic effect observed in the TiO_2-H_2O_2-u.v. case shows that the photoaction spectrum of H_2O_2 is effectively shifted to longer wavelengths by TiO_2 and its oxidizing power released by solar illumination [123]. On the other hand, in the presence of a large excess of H_2O_2, the PC activity may be adversely affected via short-circuiting of the semiconductor microelectrode. That is, the excess H_2O_2 begins to consume $OH^•$ via Reactions 14 and 15 [169, 170]:

$$H_2O_2 + OH^• \longrightarrow H_2O + HO_2 \qquad (14)$$

$$HO_2 + OH^• \longrightarrow H_2O + O_2 \qquad (15)$$

This is similar to the deleterious influence of O_2 and Cu^{2+} ions discussed earlier (c.f. Figs 2 and 3).

A recent study attempts to map the relative effectiveness of several electron acceptors on the degradation rates of model chlorinated organics [171]. Oxone or potassium peroxymonosulfate was found to be an effective agent for accelerating the PC process in both single and multipass reactor scenarios.

2.7.2. Influence of irradiation wavelength. Photochemical reactors employing conventional chemical oxidants (e.g., H_2O_2, ozone) employ short-wavelength u.v.-B or u.v.-C light. On the other hand, PC experiments with TiO_2 are usually conducted with u.v.-A (i.e., long-wavelength) light. A variety of insolation conditions have been employed ranging from high to medium-high pressure mercury arc lamps (major emission at ~ 365 nm), broad-band solar simulators, 'black light' fluorescent tubes, germicidal lamps and outdoor sunlight. In an attempt towards systematic examination of the influence of irradiation wavelength, a comparison of 254 nm and 350 nm excitation of TiO_2 using phenol and salicylic acid as model water contaminants [172] has revealed the shorter wavelength to be considerably more effective. As the authors comment, however, it is debatable whether the rate enhancement is sufficient to offset the negative aspects with the practical use of short-wavelength u.v. light.

2.7.3. Influence of temperature. Intense illumination with solar radiation (even without concentration) causes a heating of the reactant solution unless i.r. filters are used. Therefore, the temperature dependence of the PC degradation rate is of both fundamental and practical significance. However, the trends reported to date have been contradictory. Thus an increase in the PC rate with increasing temperature was reported for salicyclic acid and phenol as the model substrates [35, 136]. These results obeyed the Arrhenius law. On the other hand, for chloroform, a decrease of the PC reaction rate was noted with increasing temperature [72]. Further work is required to resolve this variance. In particular, temperature affects both reaction rates and adsorption equilibria, and the overall effect on PC performance will depend on the relative importance of these phenomena.

2.7.4. Kinetics and mechanistic aspects. There appears to be little doubt that $OH^•$ radicals are the causal agents for the PC destruction of the numerous organics that have been studied to date. Indeed, the striking similarity of the PC reaction rates measured for a very wide range of substrates is an argument in favour of either a lack of selectivity of $OH^•$ radicals or a rate-determining step involving $OH^•$ radical formation. There is ample evidence from ESR, photo-conductivity, work function and other probes for the generation of $OH^•$ radicals at the semiconductor/electrolyte interface [173–175]. The anticipated generation of H_2O_2 via follow-up reactions involving these species has also been experimentally verified [176–178]. There are experimental difficulties to the detection of H_2O_2, however (c.f. [179]), mainly arising from its proclivity to u.v. degradation [180].

The reaction between the organic substrate and the photogenerated $OH^•$ has four possible routes [181]: (a) The reaction occurs between the two species in the adsorbed state; (b) a non-bound $OH^•$ radical reacts with an adsorbed organic molecule; (c) an adsorbed $OH^•$ radical reacts with a freely mobile organic molecule arriving at the catalyst surface; and (d) reaction occurs between the two species in the fluid phase. Unfortunately, all four mechanisms yield rate expressions akin to the Langmuir–Hinshelwood model [30]:

$$r_i = -\frac{dC_i}{dt} = \frac{kKC_i}{1 + KC_i} \qquad (16)$$

In Equation 16, r_i is the initial rate, C_i is the initial concentration of the substrate, k is the observed value of the rate constant and K is a binding constant. A variety of organic degradation data are found to adhere to the rate law embodied by Equation 16. While the two parameters k and K have distinctly different significance for the four reaction possibilities listed above, simple analysis of the rate data (usually performed via $1/r_i$ against $1/C_i$ plots) do not afford insights into the component terms in k and K [181].

Analysis of PEC slurry cell data indicates that the $OH^•$ radicals can escape into the fluid phase [170]. On the other hand, a value for k of $\sim 7 \times 10^3\ \text{M}^{-1}\,\text{s}^{-1}$ computed for chloroform [72] is severalfold smaller than the known rate constant for $OH^•$ radicals with chloroform in *homogeneous* media. Thus these bound $OH^•$ radicals appear to have lower reactivity but similar chemical properties to their homogeneous counterparts. Slurry cell data also indicate that the back-reaction of $OH^{\bullet}$ with the semiconductor surface, that is:

$$(TiO_2)OH^- \xrightarrow{h\nu>E_g} TiO_2^- + OH^{\bullet} \tag{17a}$$

$$TiO_2^- + OH^{\bullet} \longrightarrow TiO_2 + OH^- \longrightarrow (TiO_2)OH^- \tag{17b}$$

is significant [170]. A half-life of 1.6 ms has been estimated for the oxidizing intermediate $[(TiO_2^-)OH\bullet]$ in Reaction 17(a) [72]. Whether this bound-radical will be consumed in a bimolecular reaction with an adsorbed (or freely diffusing) organic substrate or whether it undergoes diffusion away from its surface formation site will obviously depend on the magnitude of the bimolecular reaction rate constant.

The form of the dependence of the PC reaction rate on the incident photon flux offers mechanistic insights. A linear dependence has been observed especially at low photon fluxes [51]. This gives way to a square-root dependence at higher light intensities, and even ultimately to a photon flux-independent regime at very high rates of photon incidence. This has ramifications in the use of solar concentrator technology for PC reactor designs as discussed later. The quantum yield (c.f. Section 2.2) is constant in the linear regime, varies as $I_0^{-0.5}$ (I_0 is the absorbed photon flux) in the intermediate regime and degrades to I_0^{-1} in the plateau region. The transition between these boundaries depends on the catalyst material [137], although it appears that the linear regime may be extended to much higher I_0 by adding better electron acceptors (than O_2) [22]. Two explanations have been forwarded for the square-root dependence. In the first, carrier recombination (i.e., $e^- + h^+ \longrightarrow$ heat) is thought to dominate at the higher light intensities [34, 182]. On the other hand, a kinetic model [51] shows that the bimolecular recombination of $OH^{\bullet}$:

$$2OH^{\bullet} \longrightarrow H_2O_2 \tag{18}$$

can also account for the square-root dependence.

Further progress in the mechanistic aspects of photocatalysis should be possible with the advent of new measurement probes such as photoacoustic spectroscopy [183, 184] and time-resolved microwave conductivity [184, 185]. Another important aspect concerns a systematic study of adsorption patterns of organics at the TiO_2 surface. Valuable information is emerging on this aspect [186, 187].

2.8. *Photocatalytic treatment of inorganic pollutants*

A comparison of Tables 1 and 3 reveals that, in contrast to their organic counterparts, documented instances for the PC treatment of inorganic pollutants appear to be fewer in variety. In the case of the treatment of metal ions, it is also noteworthy that the conceptual basis is the same as in metal recovery or catalytic modification of the semiconductor: two processes with very different objectives. In some instances, however, there is an environmental relevance in metal recovery applications as in the treatment of metal plating bath formulations, many of which also contain pollutants such as cyanide [81]. In two of the studies cited in Table 3, organic pollutants were also present in addition to the inorganic species, (e.g., [87] and [94]). As pointed out earlier, photocatalysis offers an elegant approach to waste treatment in these cases by using both the conjugate electron and hole-driven photoprocesses at the semiconductor particle/electrolyte interphase.

As in the organic systems discussed earlier, substrate (photo) adsorption (at the semiconductor surface) appears to be a fairly common trend as exemplified by chromium [80], manganese [103], and silver [118]. The kinetics of the disappearance of these species have also been analyzed by the Langmuir–Hinshelwood model [80, 103, 118]. An important point to note with the inorganic pollutants is that their toxicity may be dependent on the oxidation state, e.g., chromium and arsenic. Thus, reduction of the metal ion to the elemental state is often not required, and solubility differences can be exploited to 'immobilize' the pollutant. This is exemplified by the chromium system wherein remediation is accomplished by Cr(VI) $\longrightarrow$ Cr(III) reduction at TiO_2 followed by precipitation of Cr(III) as the hydroxide [80].

Again, as with the organic counterparts, the vast majority of the species contained in Table 3 have been treated with TiO_2 photocatalyst, although, in a few instances, the other candidates listed in Table 4 have also been utilized.

2.9. *Photocatalysis in the gas phase and the treatment of air-borne pollutants*

Air-borne pollutants (e.g., VOCs or volatile organic compounds) can be treated in a PC reactor either directly in the gas phase or after partitioning them in a fluid phase. Initial results [39, 40] indicate that the PC reaction rates for some compounds (e.g., TCE) are orders of magnitude faster in the gas phase than in aqueous media. In general, substrate mass-transport will be much more efficient in the gas phase than in condensed media. Second, oxidant starvation (see below) may be less of a problem with gas phase PC reactors. On the other hand, the available data for TCE indicate the lack of complete mineralization and the formation of byproducts such as phosgene and dichloroacetyl chloride [40]. However, this in itself should not be a limitation since a caustic scrubber can be incorporated at the 'end of the pipe' (Fig. 7). Thus, a two-step treatment scheme has been considered [188] wherein the (contaminated) groundwater is first air-stripped in a packed tower, and the contaminant-laden air from the stripper is routed to the PC reactor where the pollutant subsequently is degraded.

Air-borne pollutants such as ozone and CO_2 have been treated after partitioning into the liquid phase.

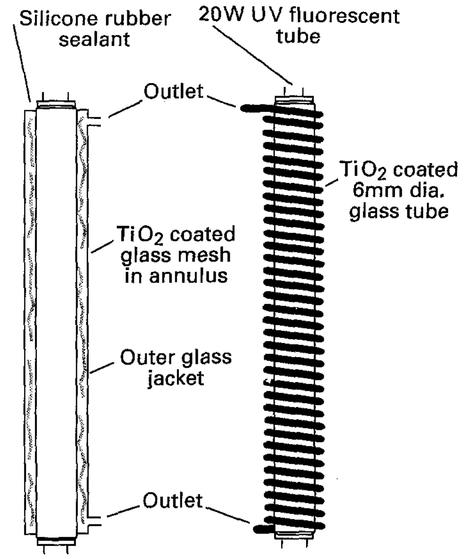

Fig. 7. Annular and spiral reactors for PC treatment of pollutants. (Reprinted with permission from [18] and [79]).

The conversion and fixation of CO_2 has both environmental and energy implications. The global accumulation of CO_2 has been associated with the 'greenhouse' effect. On the other hand, the reduction of CO_2 yields energy-rich fuels. Recent advances in this area have been reviewed [189].

There are two basic approaches for converting CO_2 to useful chemicals: direct reduction of CO_2 to CO, formic acid, formaldehyde, methanol, methane, etc. and the fixation of CO_2 in organic and biological molecules. It was first demonstrated that CO_2 could be photoreduced at p-GaP photocathodes [190]. Subsequent work from the same group as well as others has shown that other materials such as $SrTiO_3$ single crystals [191] as well as semiconductor powders including $SrTiO_3$, WO_3 and TiO_2 [192, 193] can be used. [It must be noted that the photoreduction of CO_2, like the splitting of water is an energetically 'up-hill' process (i.e., positive ΔG) contrasting with many of the organic photooxidation reactions discussed in a preceding section, which are photocatalytic.] Size-quantized semiconductor particles (e.g., ZnS) have also been used, and the quantum efficiencies for the formation of formic acid (a reduction product) have been found to increase with particle dimension in the range from 3.4 to 5.3 nm [194]. Catalysts such as crown ethers have been found to assist in the photoelectrochemical reduction of CO_2 at p-GaP in lithium carbonate electrolytes [195].

A main difficulty in achieving high coulombic efficiency in this process as well as the reduction of CO [196] is the prevalence of competing side-reactions such as hydrogen evolution. Another problem is the low solubility of substrates such as CO in aqueous media. Macrocycles such as metallated tetraphenylporphyrins have been effectively used to counter this by reversibly binding CO and thus enhancing the effective surface concentration of the substrate [196].

A second approach has been to use organic acids such as pyruvic acid to fix CO_2 in a scheme involving an electron relay such as methyl viologen and malic enzyme (ME) along with ferredoxin-$NADP^+$-reductase, FNR (NADP = nicotinamide adenine dinucleotide phosphate) [197]. The net reaction has an associated Gibbs free energy change of $+57.7\,kJ\,mol^{-1}$. This approach appears to be promising in the search for the conversion of CO_2 under mild conditions. However, some problems remain to be solved in terms of the unfavourable effect of substrates such as lactic acid on the activities of ME and FNR [197].

Although there have been efforts to fix molecules such as N_2 via PEC means (e.g., [198]), we are not aware of documented attempts to photoreduce other air-borne pollutant species such as NO_x and SO_x. However, an early study describes the fixation of NO at illuminated TiO_2 catalyst in $HClO_4$ [199]; the main product was found to be N_2.

2.10. *Photocatalytic disinfection of air and water*

An intriguing practical application of gas phase photocatalysis is the possibility of coating interior walls and floor tiles with a photoactive material such as TiO_2 and using either natural sunlight or room lighting (e.g., fluorescent) for disinfection and deodorizing purposes [200, 201]. This application is particularly attractive in a hospital setting for example. The bactericidal activity of TiO_2 photocatalyst was first demonstrated in 1985 [74]. These authors showed that several microorganisms (c.f. Table 2) were sterilized when they were incubated with platinized TiO_2 particles under metal halide lamp irradiation for 60–120 min. Subsequent efforts from this group have sought to improve the practicality of this concept by using a flow system in conjunction with membrane-immobilized semiconductor powders [75]. More recently, an optical fibre bundle has been utilized to more efficiently 'pipe' light into the semiconductor particle/water interphase [76]. An independent verification of this photocatalytic disinfection concept has been conducted [77, 78]. Kinetic aspects as well as the influence of variables including photocatalyst loading and incident light intensity were elaborated in this latter study. Outdoor tests under an August noonday sun in Texas have further verified the efficacy of this concept [78].

The PC water disinfection approach is particularly amenable to rural and remote (e.g., camping, military) applications for treatment of potable water. Unlike the ozonation and the direct u.v.-radiation approaches [202], the PC approach does not require high-voltage supplies and can use natural sunlight along with an abundantly available photocatalyst material (see above). It is also an attractive approach for the removal of taste and odour-causing organics, and for lowering the total organic content (TOC) of the water prior to a chlorination step. On the other hand, no residual disinfection capacity is inherently built into this method.

Further work is needed to better understand the mechanistic aspects of the bactericidal activity of the TiO_2 photocatalyst. Some authors [74, 75], based on their previous research [203, 204], believe that the direct oxidation of the intracellular coenzyme A (CoA) is responsible for the bactericidal activity. On the other hand, the harmful influence of the $OH^•$ radicals – formed via the irradiation of TiO_2 – on microorganisms is well-documented [73].

3. Practical photocatalysis systems

3.1. *Reactor designs*

The major issues are whether to use: (a) suspended or supported photocatalyst, (b) solar or u.v. light, and (c) if solar energy is used, whether to use concentrated or nonconcentrated sunlight.

The relative merits of slurry versus immobilized photocatalyzed reactor configurations were discussed earlier. From a reactor design standpoint, the low pressure drop attendant with the use of slurry reactors is an added advantage. Strategies to remove the catalyst particles after use have been devised using commercially available membrane filtration units [205]. These units can be operated either in direct-flow (also called 'dead-end') or cross-flow modes. The former was found to be preferable since in the cross-flow mode, a large volume of treated water is constantly recycled with the catalyst particles thereby reducing the effective capacity of the reactor by an equivalent amount [205]. Slurry and supported TiO_2 photocatalysts have been compared [139] using TCE as a model pollutant; the slurry system was found to outperform the suspended photocatalyst almost by a factor of two. This has been the trend without exception in the tests conducted by a number of laboratories to date, viz. the slurry systems are more efficient than their immobilized photocatalyst reactor counterparts.

The obvious tradeoff in solar against u.v. PC technology is treatment cost. On the one hand, unless the locale is favourable in terms of electricity cost (e.g., proximity to a hydroelectric generation site), the high cost of electrically generated u.v. light will always be a handicap relative to its solar counterpart. On the other hand, the direct u.v. (especially in conjunction with oxidants) technology is relatively well advanced (see above), and many elements of it could be borrowed for use with the photocatalysis approach. This may indeed prove to be the preferred route in certain specialized (especially indoor) applications. Annular and spiral reactors are used for photocatalysis with u.v. radiation, and representative designs are contained in Fig. 7 [79].

Solar photoreactors for water detoxification were originally configured with parabolic trough concentrators [139]. This is partly due to the extant technology base for solar thermal conversion. The concentrator approach has the advantage of compactness. By contrast, nonconcentrating or 'one-sun' photoreactors can capture diffuse sunlight as well as the direct radiation. The diffuse component can amount to $\sim 50\%$ of the total available u.v. light even on a clear day [139]. Under cloudy conditions only the diffuse light is available, and a nonconcentrator design could be operated even under these conditions (albeit at low conversion rates) while the trough unit will have to be shut down. Another major disadvantage with concentrator units is the loss in quantum efficiency at high photon fluxes (see above).

Other hybrid types of solar collectors (e.g., the compound parabolic concentrator), which are a cross between the trough concentrators and the one-sun units, have been considered for PC treatment applications [206].

The system design for a solar PC reactor has to incorporate provisions for intermittent operation. In particular, the system design is simplified (and attendant costs lower) if only daylight operation is needed. Otherwise, the solar unit will have to be coupled with nonsolar back-up such as u.v. lamps or carbon adsorption. Other factors to be taken into account in the solar system design include those related to the diurnal and seasonal variations in the u.v. flux to the surface of the earth. The effect of these on the degradation rate of phenol has been considered using a borosilicate glass dish reactor [37].

Using the slurry approach, recent authors [207] have modelled a variety of PC reactor designs, and have concluded that falling film or slit fluid flow geometries can yield superior performance. Two types of reactors comprising thin liquid films can be envisioned: spinning disc or falling film reactors [208]. The former afford high liquid throughput and ozonolysis reactors of this type have demonstrated good mass transfer characteristics. The characteristic of a falling film reactor have been established using a 2.5 kW medium pressure u.v. lamp and several model pollutants [208]. It must be noted that this type of design can accommodate both slurries and immobilized photocatalyst reactor configurations. It is also compatible with both solar and the electric (u.v. lamp) approaches.

Another reactor design consideration relates to continuous flow against batch operation. In the latter, shallow panels or tanks hold the water for several days to allow for complete destruction of the pollutant (and/or microorganisms). Geometries simulating shallow lagoons have been tested [37]. Indeed operating concepts incorporating both of the above designs have been envisioned. For example, in the Lazy River concept [206], the fluid continuously enters and exits a long serpentine channel. This channel, which serves the dual functions of photoreactor and holding tank, is dimensioned such that the fluid residence time is adequate for complete detoxification.

Progress is being made in the modelling of the fluid hydrodynamics and flow inside PC reactors [188]. In most cases, reactant mass transport from the bulk fluid phase to the 'wall' must be considered since the photoreaction mainly occurs at the latter. The tube geometry is obviously important here, and results have been presented [209] for mass transfer to a coiled tube geometry of the type used in conjunction with u.v. lamps [210]. Other aspects to be yet considered in the development of a process model include oxidant (e.g., O_2) mass transport, homogeneous reaction chemistry (i.e., reaction of $OH^\bullet$ radicals with the substrate in the bulk fluid phase away from the wall) and the effect of interparticle distance on the convective-diffusive substrate mass transport in reactors using immobilized photocatalyst [22].

Reaction design issues for gas-phase photocatalysis are also receiving attention. A bench-scale flat-plate fluidized-bed photoreactor has been tested for the treatment of TCE in contaminated airstreams [39]. The fluidized catalyst bed was reported to respond quickly to step changes in feed flow rate, composition, and photon flux. The problems typically encountered are not uncommon to other forms of gas-phase catalysis, viz. poisoning or fouling, mass transfer and pressure drop. The need for catalyst illumination does compound the reactor complexity.

3.2. *Field tests and commercialization efforts*

Several field tests have been conducted [33, 206, 211]. The target pollutants in these tests were TCE and BTEX. Although these were successfully destroyed during the tests, pronounced interference from non-target constituents in the water were also noted [33]. In two cases, the site characteristics necessitated supplemented water treatment in addition to the PC reaction while at one site, pH adjustment was necessary to offset bicarbonate ion inhibition (see above).

A reactor consisting of six parabolic trough modules connected in series was used for the treatment of effluent from a phenolic resin factory [211]. The considerable decrease with time in the total organic carbon (TOC) in the (dark) control run was attributed by the authors [211] to the vaporization of volatiles from the effluent water. This is a general problem that must be dealt with in open reactor systems with gas injection.

Commercialization of the PC treatment concept is certainly gaining momentum as evidenced by the increasing number of patents issued in this area. This reviewer is aware of at least five companies in the United States and Canada that are marketing PC water treatment units.

3.3. *Comparison with other technologies and economic considerations*

Table 5. Competing technologies for the treatment of organic-, metal- and microorganism-laden air and water

Organics	*Metals*	*Microorganisms*
Thermal incineration	Precipitation/ coagulation	High-energy (γ)-irradiation
Air stripping	Membrane separation	Filtration
Carbon adsorption	Distillation	Carbon adsorption
Microbial treatment	Chemical treatment	Direct u.v. irradiation
		Ozonation
		Chorination

Table 5 contains a listing of the technologies that the PC approach will have to compete against for the treatment of organics, metals and microorganisms. Electrochemical treatment methods were considered in the companion review [1], and are not further considered in this comparative discussion. In many instances, there are clearcut advantages to the adoption of the PC approach. For example, unlike in this approach wherein complete mineralization of toxic organic compounds is possible, air stripping generates secondary pollutants and, in many cases, unacceptable air emission. Similarly, the carbon adsorption technology simply transfers the pollutant from one phase to the other, and the spent carbon will have to be disposed of. In the case of metal treatment, the solid waste from current technologies may be a sludge or a contaminated (resin) adsorbant. On the other hand, metal recycling may be readily built into a PC reactor as we have demonstrated for the Cr(VI) ⟶ Cr(III) system [80].

Economic comparisons have been made between the PC approach, and some of the current technologies listed in Table 5 [79, 188, 212]. A cost comparison with the GAC technology reveals that the PC treatment of phenolic wastewaters could be competitive in favourable circumstances [79]. Two separate scenarios were considered by this author comprising an (electric) u.v.-lamp based PC approach and a solar-based (one-sun) PC reactor system respectively. First, the cost of electricity becomes a key component (see above), and therefore improvements in photocatalyst efficiency would have a major economic impact. Second, in the (nonconcentrated) solar aproach, the photocatalyst lifetime and land area costs assume critical proportions.

Within the PC treatment framework itself, cost comparisons of electric-u.v. lamp and solar units have yielded interesting insights [188]. The gas phase and aqueous phase PC treatment approaches were

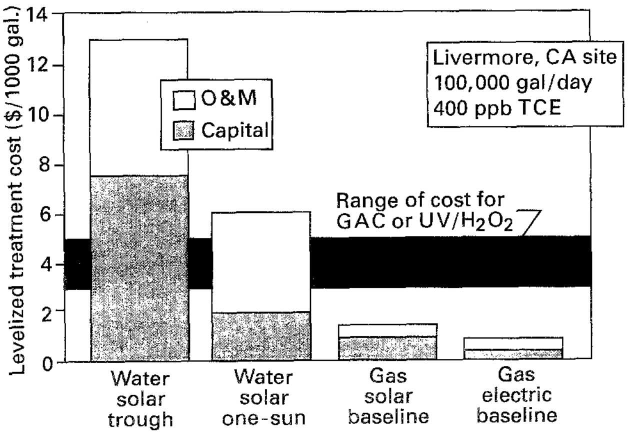

Fig. 8. Estimated treatment costs for a field test site for a variety of technologies. (Reprinted with permission from [188]).

also compared in this study [188]. Figure 8 illustrates the results for one test case. Interestingly enough, the gas phase PC approach appears to outperform both GAC and AOP in this estimation.

3.4. *Problems and prospects for the photocatalysis technology*

Although particular advances have been made in this field since the early 1980s, many problems remain. First, the quantum yields have remained rather low for TiO_2-based PC reactors. On the other hand, gas-phase PC systems have shown very high quantum yields (close to 1). Improvements in the conjugate reaction kinetics and/or oxidant supply and strategies for suppression of carrier recombination in the photocatalyst remain as challenges. Second, the solar PC approach suffers from the poor overlap of the absorption profile of TiO_2 with the solar spectrum. (Only about 5% of the available energy is utilized.) Attempts to extend the photoresponse of TiO_2 have yielded rather disappointing results. This is an area which warrants further careful research. Third, the poor performance of immobilized TiO_2 *vis-à-vis* its slurry reactor counterpart remains a problem. There are also indications that photocatalyst film-based reactors may be more prone to poisoning and deactivation. The surface chemistry in these deleterious situations must be properly understood so that steps may be taken to avoid catalyst fouling. Much can be learned from the heterogeneous catalysis community in this area. Finally, ingenuity is required to devise reactor designs for overcoming the mass transfer limitations with the immobilized photocatalyst. Approaches incorporating turbulent fluid flow remain to be tested.

Notwithstanding the above shortcomings, the PC treatment approach has the potential to fare well against competing technologies in the 1990s and into the next decade. In particular, this approach is compatible with many of the water treatment technologies currently used. Other advantages with the PC approach include potentially low operating costs and the intrinsic ability to handle difficult compounds.

4. Photoelectrochemical sensors

As pointed out in an introductory paragraph, PEC sensors are at an early stage of development relative to their EC counterparts. Detection strategies based on photoexcitation of analytes have been termed 'photoelectrochemical' [213, 214], although distinction must be drawn between this methodology and our present definition of PEC techniques (see above) as those involving photoexcitation of an *electrode* (usually a semiconductor).

Two studies employing this latter strategy describe the use of TiO_2 for LC detection applications. In the first study, an anodized titanium substrate was used with quoted detection limits ranging from 1.6 to 210 μg for aniline and benzyl alcohol, respectively [215]. The second study was prompted by the possibility of light-addressable spatially-resolved detection for use with whole column detection chromatography [216]. Some 25 analytes were examined encompassing a wide variety of organic functionalities; detection limits of 40 pmol and 140 pmol were reported for *p*-amino-acetanilide and diethylamine respectively [216].

It must be pointed out that TiO_2-based O_2 sensors are in commercial use in vehicles for controlling the air-to-fuel ratio of the engines at the stoichiometric value. However, these sensors operate in the 'dark' (i.e., nonilluminated) mode.

Another interesting class of photoelectrochemical systems comprises biological sensing units which are immobilized on a support electrode surface. Thus photomicrobial sensors consisting of *Chlorella vulgaris* and *Chromatium sp.* have been constructed for the determination of phosphate and sulfide, respectively [217, 218]. The electrode irradiation appears to bring out different mechanistic effects in the two cases. In the first, oxygen is evolved by the green algae under irradiation, and this is enhanced in the presence of the phosphate ion [217]. In the second case, sulfide is oxidized by an enzyme in *Chromatium sp.* with concomitant reduction of c-type cytochrome. This triggers a sequence of steps culminating in the evolution of hydrogen gas which is detected at a coupled hydrogen electrode [218]. Contrasting with these limited number of PEC examples, bioelectrochemical sensors operating in the dark mode are under intense development for clinical (e.g., glucose sensing) applications as reviewed earlier [1].

5. Concluding remarks

This review has described the advances that have been made in the use of PEC (and specifically PC) methods for the treatment of contaminated water and air. The corresponding progress in pollutant sensor applications has been somewhat less spectacular. Nonetheless, both types of applications hold exciting future opportunities for scientists and engineers from a very wide range of disciplines such as electrochemistry, electrochemical engineering, materials science, photochemistry, air/water pollution science and engineering, microbiology and toxicology.

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