Photochemical Processes for Water Treatment

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1. Introduction

The last 20 years have witnessed a growing awareness of the fragile state of most of the planets' drinking water resources. In order to cope with the growing pollution of our hydrosphere, educational and legislative programs are being implemented and two main strategies of water treatment begin to be applied: (1) chemical treatment of polluted drinking water and surface water and groundwater and (2) chemical treatment of wastewaters containing biocidal or nonbiodegradable components.

Pollutant removal in drinking water may only involve techniques adopted in governmental regulations, such as flocculation, filtration, sterilization, and conservation procedures to which have been added chemical treatment techniques involving a limited number of chemicals, mostly stable precursors for hydroxyl radical production.

Chemical treatment of contaminated surface water and groundwater as well as of wastewaters containing biocidal or nonbiodegradable components is part of a long-term strategy to improve the quality of our drinking water resources by eliminating toxic materials of anthropogenic origin before releasing the used waters into the natural cycles. Contaminated soils may be recovered by percolation with biologically and/or chemically treated waters.

Used waters of normal anthropogenic origin can be efficiently treated in conventional biological treatment stations. Such stations are elementary for the safe guard of the sanitary quality of a more and more urbanized environment. In fact, the rates of natural degradation reactions are in most regions of this world surpassed by the quantity (volume and organic charge) of the waste released. Chemical treatment of wastewater may also be applied where the capacity of biological treatment stations cannot be adapted in accord with the growth of both, regional population density and consumption of water per capita.

Recent developments in the domain of chemical water treatment have led to an improvement in oxidative degradation procedures for organic compounds dissolved or dispersed in aquatic media, in applying catalytic and photochemical methods. They are generally referred to as advanced oxidation processes (AOP). This domain is particularly oriented toward application and has already had a strong impact on design and construction of new light sources, photochemical reactors, and the preparation of new photocatalysts and their support.

This paper reviews AOP's as far as the photochemical technology is concerned and does not include applied work in the areas of disinfection, sewage treatment,

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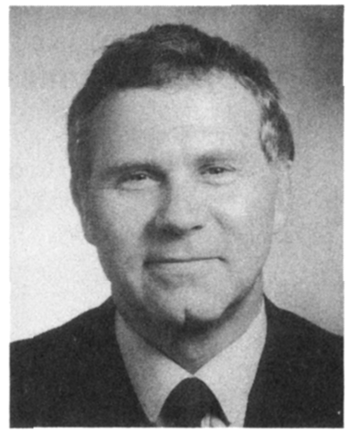

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and chemical after biological treatment. Research work using radiolysis and laser excitation is also outside of this review.

Due to the vast number of publications dealing with AOP's for water treatment, many papers have certainly been omitted, others surfaced from internal reports and less-known journals. Given the fact that authors of a large spectrum of research and development areas are interested in working toward technical solutions of chemical water treatment, emphasis is mostly directed toward the analysis of the aqueous system. Unfortunately, quite a large number of results cannot be reproduced, because important details are missing from the experimental part, and their importance for the development of a technically feasible degradation procedure is rather limited.

With the exception of electron injection (see section 4 "Photochemical Electron-Transfer Processes"), AOP's rely entirely on oxidative degradation reactions, where organic radicals are generated upon photolysis of the organic substrate or by reaction with hydroxyl radical. These radical intermediates are subsequently trapped by dissolved molecular oxygen and lead via peroxyl radicals and peroxides to an enhancement of the overall degradation process and finally to complete mineralization.

The review is divided into sections presenting particular means of photochemical generation of organic and hydroxyl radicals.

2. Pollutant Degradation by Ultraviolet Photolysis

2.1. Introduction

Photooxidation reactions upon electronic excitation of the organic substrate imply in most cases an electron transfer from the excited-state (C^*, eq 1) to ground-state molecular oxygen (eq 2), with subsequent recombination of the radical ions or hydrolysis of the radical cation, or homolysis (eq 3) to form radicals which then react with oxygen (eq 4).

$$C \xrightarrow{h\nu} C^* \quad (1)$$

$$C^* + O_2 \rightarrow C^{\bullet +} + O_2^{\bullet -} \quad (2)$$

$$R\text{-}X \xrightarrow{h\nu} R^{\bullet} + X^{\bullet} \quad (3)$$

$$R^{\bullet} + O_2 \rightarrow RO_2 \quad (4)$$

Rates of such a photooxidation upon electronic excitation of the organic substrate depend on the absorption cross section of the medium, the quantum yield of the process, the photon rate at the wavelength of excitation, and the concentration of dissolved molecular oxygen.

Radical generation upon homolysis of a C–X bond is complementary to processes where the mediated degradation by hydroxyl radicals is found to be rather inefficient. Highly fluorinated or chlorinated saturated aliphatic compounds may be efficiently eliminated upon primary homolysis of a carbon–halogen bond. Corresponding domains of excitation are <190 nm (VUV) for C–F and 210–230 nm for C–Cl bonds.[1]

UV photolysis has been used to eliminate chlorinated and nitrated aromatics,[2-4] phenols,[5] halogenated aliphatics,[6-11] end products of metal finishing, oil, and steel processing,[12] and other hazardous wastes present in water.[3]

This section summarizes the results of recent work focused on the degradation of electronically excited pollutants, in particular of chlorinated aliphatics present in the aqueous environment. For practical reasons, the spectral domain of excitation is used as a means of classification.

2.2. Review of Recent Literature

2.2.1. Irradiation at 253.7 nm

A number of papers have reported the degradation of chemicals in water using the Hg emission at 253.7 nm produced in particular by low-pressure mercury arcs.[13,14] Most of these investigations have been made in order to quantify the contribution of the electronic excitation of the organic pollutant in mediated oxidation processes, such as H_2O_2/UV, O_3/UV, and H_2O_2/O_3/UV (see sections 3.2, 3.3, and 3.4 for references).

The results demonstrate that 253.7-nm irradiation alone cannot be used as an effective procedure for the removal of organics from water. It should, however, be noted that low-pressure Hg arcs are quite efficient for water disinfection purposes.

Frischherz et al.[9] as well as Scholler et al.[10] studied the decomposition of chlorinated hydrocarbons by UV radiation at 253.7 nm. Experiments were carried out with a low-pressure Hg arc (15 W) irradiating ca. 5 L of aqueous solution. The results show that 85% tetrachloroethene, 55% trichloroethene, and 40% 1,1,1-trichloroethane were removed within 60 min of irradiation time.

Nicole et al.[11] investigated the degradation of trihalomethanes (THM) by UV irradiation at 253.7 nm and used model substrates such as $CHCl_3$, $CHCl_2Br$, $CHBr_2Cl$, and $CHBr_3$ in dilute aqueous solutions ($<10^{-6}$ M) at 20 °C. The authors studied, in particular, the effect of the (annular) reactor volume and of mechanical stirring on the rate of substrate degradation. Results showed that only brominated THM's were photolyzed and that organic halogen present in $CHCl_2Br$, $CHBr_2Cl$, and $CHBr_3$ was completely converted into chloride and bromide ions during the time of irradiation (≤30 min). For the three brominated THM's, a quantum yield of photolysis of 0.43 was found. C–Br bonds exhibit much larger absorption cross sections at this wavelength of excitation than C–Cl bonds, and oxidative degradation of chlorobrominated hydrocarbons is therefore started by C–Br homolysis. Loss of chlorine or chloride might originate from the photolysis of e.g. acid chlorides produced intermediately, but no data of consecutive halogen loss have been published so far.

Zeff et al.[15,16] published results on the photolysis of 100 ppm methylene chloride in distilled water (1.8 L) using a low-pressure Hg lamp (15 W of electrical power). Removal of ca. 60% of the initial substrate was found to occur in 25 min of irradiation time.

Weir et al.[17] reported data on the reduction of benzene concentration (initial conditions were 2×10^{-4} M of benzene, total volume 3.3 L, 25 °C, pH 6.8) by about 50% within 90 min of irradiation time using a low-pressure Hg lamp without detailed description.

Sundstrom et al.[7,8] studied the photolysis of a number of halogenated aliphatics often present in water at low concentration levels. For example, 80% of a 58 ppm of trichloroethylene (TCE) contained in a water sample (1 L) could be removed within 40 min of irradiation using a low-pressure Hg arc. The authors studied other halogenated aliphatics such as tetrachloroethylene, 1,1,2,2-tetrachloroethane, dichloromethane, chloroform, carbon tetrachloride, and ethylene bromide. Photolysis of a 53 ppm dichloromethane sample yielded only a 30% removal of the contaminant after 3 h of irradiation. In another paper, Sundstrom et al.[18] investigated the direct photolysis of some aromatic pollutants in a 3.3-L water sample irradiated under the same conditions. Of the aromatics studied, they found that 2,4,6-trichlorophenol (2×10^{-4} M) was most reactive, with a reduction of its concentration to 2% (i.e. 98% removal) within 50 min of irradiation.

Guittonneau et al.[6] studied the oxidation of a number of volatile polychlorinated hydrocarbons, such as chloromethanes ($CHCl_3$, CCl_4) and chloroethanes ($C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, C_2Cl_6) in different combinations in diluted aqueous solutions. They conducted experiments in a 4-L batch reactor equipped with a 40-W low-pressure Hg arc at 16 °C and pH 7.5. They concluded that UV-C photolysis (200–280 nm) alone does not decompose halogenated compounds and that the diminution of the concentration of some of the substrates is mainly due to evaporation. Low concentrations of volatile organic chlorides (VOC) are, in fact, rather difficult to degrade, as rather large fractions of the pollutant may be stripped by air or oxygen added permanently to the photochemical reactor. On the other hand, stripped VOC's can be efficiently degraded in the gas phase or as a condensate.[19]

In another paper,[2] the same authors published results on the direct photolysis of aromatics in water using the same experimental conditions as described above.[6] Results indicate that 90% removal of chlorobenzene (7×10^{-5} M), 1,2,4-trichlorobenzene (7×10^{-5} M), nitrobenzene (10^{-4} M), phenol (10^{-4} M), and 4-nitrophenol (10^{-4} M) is achieved within 45, 125, >60, >60, and >60 min of irradiation time, respectively. In general, chlorobenzenes are more rapidly photodecomposed than nitroaromatics. The authors also showed that no TOC reduction was observed within the first 60 min of irradiation, but mineralization of organic chloride to chloride ions occurred, and an increase of absorbance of the solutions at 253.7 nm was measured, and they concluded that photolysis of aromatics is leading to the formation of polyhydroxyl compounds. Castrantas et al.[5] provided data showing the destruction of phenols and substituted phenols by photolyzing 12 L of aqueous solution with UV light (eight low-pressure Hg lamps of 51.7 W each). Results show that 23% of initial 10 ppm phenol were decomposed within 40 min at pH 4, whereas no reduction was observed at pH 10. *m*-Cresol (11.5 ppm), 2-chlorophenol (13.6 ppm), 2,5-dimethylphenol (13 ppm), and 2,5-dichlorophenol (17.3 ppm) were found to be completely removed (>99%) within 240, 80, 30, and 210 min, respectively, at pH 7.8–8.5 and ca. 23 °C.

The reviewed results show that 253.7-nm radiation may be useful for the degradation of substituted aromatics. However this method is totally inefficient for effective removal of chlorinated aliphatics. For the latter perspective, research and development work is based on the use of light sources emitting in the spectral region of 210–230 nm where chlorinated substrates show higher absorption cross sections. Technical procedures have already been developed using specially tuned Hg arcs[20-22] or Xe-doped Hg arcs,[20] whereas the use of KrCl excimer sources emitting at 222 nm is still on a research level.[1,20] Given the fact that H_2O_2 photolysis can also be improved with such light sources, different reactor geometries must be adopted in accord with a particular procedure of oxidative degradation in mind. A brief summary of data originating from the 222-nm photolysis is given in the next section.

2.2.2. Irradiation from 210 to ca. 230 nm

Specially tuned medium-pressure Hg arcs and Xe-doped Hg arcs show a broad emission band from 210 to ca. 230 nm. The formerly known UV-C light sources[13,14] have been further developed and are currently under investigation on pilot and technical scales for the removal of chlorinated organics by direct photolysis (see section 2.1). To our knowledge, no experimental data have been published so far.

KrCl excimer sources emitting in a relatively narrow band (i.e. 222 ± 6 nm)[23] may be used for specific excitation of e.g. chlorinated aliphatics as well as for the development of a highly efficient photolysis of H_2O_2 (see section 3.2). Their monochromaticity, their radiant efficiency, and the fact that the geometry of excimer sources may be varied in accord with the results of optimal photochemical reactor design may be convincing arguments for its potential technical use. Batch-mode experiments [e.g. 3 L, KrCl (150 W)[19]] using recirculating tubular reactors have been used for the removal of a variety of chlorinated organic model compounds, such as carbon tetrachloride, 1,1,1-trichloroethane, or 1,1,1,2-tetrachloroethane dissolved in ultrapure water. So far, kinetic experiments have been undertaken in order to determine the efficiency of the 222-nm photolysis of those substrates with respect to other procedures,[19,20] and GC and IC analyses indicate that initial homolysis of the C–Cl bond is followed by electron-transfer reactions leading to chloride ion formation. To our knowledge, no data are yet published showing complete removal (DOC analysis) of the substrates.

Besides the rather abundant technical literature concerning the use of Xe/Hg arcs, we would like to draw attention to the paper of Toy et al.[24] who studied the elimination of 1,1,1-trichloroethane in aqueous solutions using a 200-W Xe-doped Hg arc. They found that a 30-min irradiation time was needed to remove 80% of the initial 3.6 ppm of pollutant. The experimental design seems, however, not optimized, as only a 4-mL quartz reaction tube was used at a temperature of 35 °C.

Comparative studies focused on energy efficiencies of the different light sources for homolysis of C–Cl bonds as well as for mineralization of different chlorinated model compounds will certainly have a strong impact on applications of photochemical water treatment processes on a technical level.

2.2.3. Irradiation from 313 to 367 nm

Halogenated alkanes and alkenes cannot be photolyzed in the spectral region of 313–367 nm, and we summarize briefly some of the work reported on the degradation of halogenated aromatics upon direct excitation in aqueous media. Dulin et al.[4] investigated the photolysis of chloroaromatic compounds in water using a 450-W medium-pressure Hg arc combined with a filter to remove incident light below 230 and above 410 nm. They studied the formation of products and determined quantum yields for the photolysis of chlorobenzene, 2- and 4-chlorobiphenyl, as well as 2- and 4-chlorobiphenyl ethers in water.

Cesareo et al.[3] reviewed data on the direct photolysis of chlorinated aromatics in aqueous media in the UV-A (320–380 nm) and UV-B (280–320 nm) spectral domains. Among the very few data referring to direct photolysis in water, we note the report of complete photohydrolysis of chlorobenzene into phenol. Concerning the direct photolysis of polychlorinated phenols in water, several papers show that photolysis in the UV-A and UV-B spectral domains is rather inefficient. For example, for a 90% removal of 4-chlorophenol 22 h of irradiation at $\lambda \geq 340$ nm were needed. Pentachlorophenol solutions exposed to light ($\lambda > 290$ nm) showed approximately 50% removal at pH 7.3 and 3 h of irradiation time.

Simmons and Zepp[25] produced results on the influence of humic substances on direct excitation of 19 nitroaromatics in aqueous systems. For the photolysis, they used a 450-W medium-pressure Hg arc fitted with a filter to isolate the 366-nm line. They found that photolysis rates are strongly dependent on the nature of the substituent on the nitroaromatic ring and that humic substances enhanced the rates. Humic substances might in fact act as an inner filter in pure photolysis procedures[26] and, hence, severely diminish degradation efficiencies. The reviewed results could be interpreted in adopting a sequence of reactions in which electronically excited chromophores of the humic substances (HS*, eq 5) may act as donors in an electron-transfer reaction reducing nitroaromatics in a first reaction step (eq 6).

$$\mathrm{HS} \xrightarrow{h\nu} \mathrm{HS}^* \qquad (5)$$

$$\mathrm{HS}^* + \mathrm{PhNO_2} \rightarrow \mathrm{HS}^{\bullet+} + \mathrm{PhNO_2}^{\bullet-} \qquad (6)$$

2.2.4. Polychromatic Irradiation

Medium-pressure Hg arcs emit particularly strongly in the spectral region between 254 and 400 nm[13,14] and are not only effective in generating hydroxyl radicals from hydrogen peroxide or ozone, for example, but also by causing electronic transitions in a large number of organic molecules. Chemical transformations of the corresponding electronically excited states (photochemical reactions) may include rearrangements, but primarily energy- and electron-transfer reactions and homolytic and heterolytic fragmentation reactions. Examples mentioned above demonstrate clearly that organic material can be photochemically degraded without the preliminary formation of hydroxyl radicals.

Photochemical treatment of contaminated effluents and groundwaters using a medium/high-pressure Hg arc with polychromatic output in the 200–400-nm range has been patented.[27] Among the examples, we note that the photolysis of a mixture of benzene, toluene, and xylene (BTX) in a 200-L water sample (approximately 20 ppm BTX, i.e. benzene 8 ppm, toluene 7 ppm, and xylene 4 ppm) lead to an approximately 70% removal within 60 min of irradiation time.

Using a medium-pressure Hg lamp, Peterson et al.[28] studied the photochemical degradation of pesticides in water. Their results show that the half-life of *m*-xylene was 5.7 min starting with an initial concentration of 22.6 ppm. This rate of degradation was enhanced only slightly by the addition of hydrogen peroxide. Photochemical remediation of captan occurred with a half-time of 1.4 min in the absence or in the presence of hydrogen peroxide. This last result might be due to spectral cutoff by the reactor or an inner filter effect caused by the aromatic compounds strongly absorbing in the UV-C region.

In experiments concerning the direct photolysis of aqueous 1,2-dibromopropane, a 100-W medium-pressure Hg lamp was used in a quartz tube reactor. The results show a 50% decrease of the initial 20-ppm substrate concentration within 4 h at 20 °C and at pH 6.9.[29] Under these experimental conditions, degradation of the brominated substrate is initiated by the homolysis of the C–Br bond which absorbs strongly at about 250 nm.

Ho[30] exposed aqueous solutions of dinitrotoluene (DNT) to the polychromatic radiation of a 450-W medium-pressure Hg arc, and more than 99.7% of the initial 75.8 ppm DNT were eliminated from the sample within 17 h of irradiation time. Khan and co-workers[31] performed photolyses of 2-chlorophenol in a 40-L semibatch reactor using a medium-pressure Hg arc with an electrical power of 5000 W. Decomposition of 200 ppm of 2-chlorophenol was achieved under these conditions within 4 h.

Table I. Oxidation Potentials of Some Oxidants[43]

species	oxidation potential (V)
fluorine	3.03
hydroxyl radical	2.80
atomic oxygen	2.42
ozone	2.07
hydrogen peroxide	1.78
perhydroxyl radical	1.70
permanganate	1.68
hypobromous acid	1.59
chlorine dioxide	1.57
hypochlorous acid	1.49
hypoiodous acid	1.45
chlorine	1.36
bromine	1.09
iodine	0.54

Summarizing the literature on organic pollutant degradation by photolysis, we may conclude that these procedures are generally of low efficiency when compared to procedures involving hydroxyl radical generation. However, photolysis of pollutants may be important in cases where hydroxyl radical reactions are known to be slow (e.g. perchlorinated aliphatics).

3. Hydroxyl Radical Generation

3.1. Introduction

Oxidation of organic pollutants by the combination of ultraviolet light and oxidants (H_2O_2, O_3, etc.) implies in most cases generation and subsequent reaction of hydroxyl radicals.

The oxidation potentials for common oxidants are listed in Table I and show that the most powerful oxidizing species after fluorine is in fact the hydroxyl radical.

The hydroxyl radical is a short-lived, extremely potent oxidizing agent, capable of oxidizing organic compounds mostly by hydrogen abstraction (eq 7). This reaction generates organic radicals which by addition of molecular oxygen yield peroxyl radicals (eq 8). These intermediates initiate thermal (chain) reactions of oxidative degradation, leading finally to carbon dioxide, water, and inorganic salts.

$$\mathrm{HO^\bullet} + \mathrm{RH} \rightarrow \mathrm{R^\bullet} + \mathrm{H_2O} \qquad (7)$$

$$\mathrm{R^\bullet} + \mathrm{O_2} \rightarrow \mathrm{RO^\bullet_2} \rightarrow\rightarrow \qquad (8)$$

$$\mathrm{HO^\bullet} + \mathrm{RX} \rightarrow \mathrm{RX^{\bullet+}} + \mathrm{HO^-} \qquad (9)$$

Besides hydrogen abstraction, electron transfer to hydroxyl radicals (eq 9) constitutes another mechanism of oxidative degradation. Reaction 9 combined with a subsequent proton transfer can hardly be differentiated from eq 7.

The reaction scheme demonstrates clearly that rate and efficiency of oxidative degradation processes, which are primarily based on the production and the reactivity of radical intermediates, depend (1) on the energy needed in order to homolyze a given chemical bond, and (2) to a large extent on the concentration of dissolved molecular oxygen.

Table II. Theoretical Amounts (mol) of Oxidants and Photons Required per Mole of Hydroxyl Radical Formed in the H_2O_2/UV and the O_3/UV Reaction Systems[33]

system	O_3	UV	H_2O_2
H_2O_2/UV		0.5	0.5
O_3/UV	1.5	0.5	(0.5)[a]

[a] Hydrogen peroxyde formed in situ.[33]

Table III. Molar Absorption Coefficients, Theoretical Stoichiometry, and Quantum Efficiency of the Formation of Hydroxyl Radicals from Photolysis of Hydrogen Peroxide and Ozone, Respectively

	ϵ(253.7 nm) ($M^{-1}\,cm^{-1}$)	stoichiometry[a]	$\Phi(HO^\bullet)$
H_2O_2	18.6[b]	$H_2O_2 \rightarrow 2HO^\bullet$	0.98[a]
HO_2^-	240[b]		
O_3	3300[a]	$3O_3 \rightarrow 2HO^\bullet$	2.00[b]

[a] Reference 32. [b] Reference 34.

Carbon–chlorine (C–Cl) bonds are relatively inert toward potential radical substitution by hydroxyl radicals, and therefore perchlorinated compounds are only slowly oxidized by degradation processes relying on hydroxyl radicals as the reactive intermediate.[1]

Advanced oxidation processes (AOP) presently under technical development rely on the generation of very reactive free radicals, such as hydroxyl radicals, to be considered as initiators of oxidative degradation. They will be reviewed in subsections 3.2–3.6.

The H_2O_2/UV, O_3/UV, and H_2O_2/O_3/UV procedures employ UV photolysis of H_2O_2 and/or O_3 in order to generate $HO^\bullet$ radicals. For the photocatalytic oxidation (TiO_2/UV), the semiconductor absorbs UV light and generates $HO^\bullet$ radicals mainly from adsorbed H_2O and hydroxide ions. The VUV photolysis uses high energy radiation interacting efficiently with water and generating primarily $HO^\bullet$ and $H^\bullet$ radicals.

3.2. H_2O_2/UV Process

Among the numerous processes of potential application for water treatment, those ensuring complete oxidation of organic pollutants are of particular interest, where the lowest levels of pollution are desired. AOP involve the generation of $HO^\bullet$ radicals in relative high steady-state concentrations in order to affect dissolved and/or dispersed organic contaminants with high efficiency. These processes imply such simple reactions as the UV photolysis of H_2O_2, O_3, and other photoactive oxidants.

3.2.1. H_2O_2 Photolysis

The mechanism most commonly accepted for the photolysis of H_2O_2 is the cleavage of the molecule into hydroxyl radicals with a quantum yield of two $HO^\bullet$ radicals formed per quantum of radiation absorbed (Table II).[32] The rate of photolysis of aqueous H_2O_2

$$H_2O_2 \xrightarrow{h\nu} 2HO^\bullet \qquad (10)$$

has been found to be pH dependent and increases when more alkaline conditions are used.[6,32,35] This might be primarily due to the higher molar absorption coefficient (ϵ) of the peroxide anion at 253.7 nm (Table III).

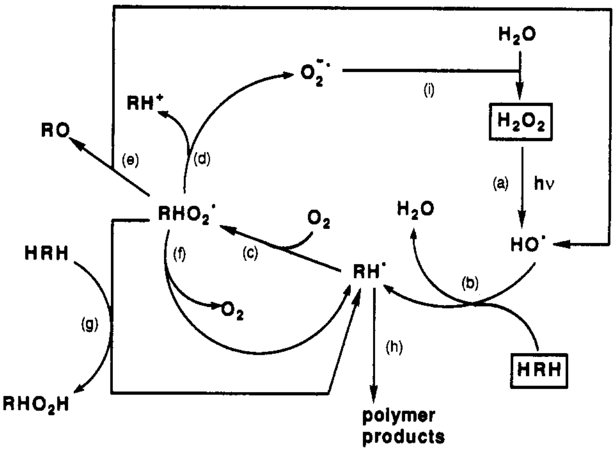


Figure 1. Reaction system for the H_2O_2/UV process. (See also ref 36.)

On the other hand, hydrogen peroxide is known to decompose by a dismutation reaction (eq 11) with a maximum rate at the pH of its pK_a value (11.6).

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + HO^\bullet \qquad (11)$$

Reactions of hydroxyl radicals generated in presence of an organic substrate may be differentiated by their mechanisms into three different classes:

hydrogen abstraction

$$HO^\bullet + RH \rightarrow R^\bullet + H_2O \qquad (7)$$

electrophilic addition

$$HO^\bullet + PhX \rightarrow HOPhX^\bullet \qquad (12)$$

electron transfer

$$HO^\bullet + RX \rightarrow RX^{\bullet+} + HO^- \qquad (9)$$

Radical–radical recombination must also be taken into account.

$$2HO^\bullet \rightarrow H_2O_2 \qquad (13)$$

3.2.2. Hydrogen Abstraction

The sequence of reactions occurring during the H_2O_2/UV process used for the oxidation of organic substrates is shown in Figure 1. Hydroxyl radicals generated by hydrogen peroxide photolysis (a, see also eq 10) react with organic compounds (HRH) primarily by hydrogen abstraction to produce an organic radical ($RH^\bullet$) (b, see also eq 7). This radical reacts quickly with dissolved oxygen to yield an organic peroxyl radical ($RHO_2^\bullet$) (c, see also eq 4), initiating subsequent thermal oxidation reactions. Peyton et al.[36] proposed three different reaction paths to be followed by either peroxyl radicals or their tetraoxide dimers: (1) heterolysis and generation of organic cations as well as superoxide anion (d), (2) 1,3-hydrogen shift and homolysis into hydroxyl radicals and carbonyl compounds (e), and (3) back reaction to $RH^\bullet$ and O_2 (f).

Nevertheless, hydrogen abstraction by $RHO_2^\bullet$ should not be discarded as a process of initiating a chain of thermal oxidation reactions (g). In aqueous systems, cations will further react by solvolysis, and superoxide anion will readily disproportionate to yield H_2O_2 (i). This is in contrast to the fate of superoxide anion in advanced oxidation processes utilizing ozone where it reacts primarily with ozone to produce hydroxyl radical.

Figure 1 reflects the importance of oxygen saturation in oxidative degradation processes. In cases of lack of oxygen, organic radicals will initiate polymerization of unsaturated organic substrate present in the reaction system or generated by dismutation.

3.2.3. Radical–Radical Reactions

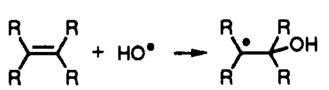
Generated at high (local) concentration, hydroxyl radicals will readily dimerize to H_2O_2 (eq 14). If an excess of H_2O_2 is used, $HO^\bullet$ radicals will produce hydroperoxyl radicals (eq 15) which are much less reactive and do not appear to contribute to the oxidative degradation of organic substrates. The concentration of $HO_2^\bullet$ is controlled by the pH of the reaction system, the latter controlling, therefore, the efficiency of superoxide dismutation.

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \qquad (14)$$

$$H_2O_2 + HO^\bullet \rightarrow H_2O + HO_2^\bullet \qquad (15)$$

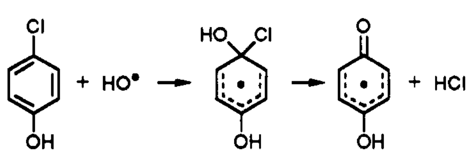
3.2.4. Electrophilic Addition

Electrophilic addition of $HO^\bullet$ radicals to organic π-systems will lead to organic radicals (eq 16) the subsequent reactions of which are quite similar to those mentioned in Figure 1.



(16)

Electrophilic addition is of particular interest for a mechanistic interpretation of the rapid dechlorination of chlorinated phenols yielding chloride ions. One possible pathway could in fact consist of an electrophilic addition of the hydroxyl radical to the arene system and of a subsequent fragmentation of the intermediate chlorohydrol (eq 17).



(17)

3.2.5. Electron-Transfer Reactions

Reduction of hydroxyl radicals to hydroxide anions by an organic substrate (eq 9) is of particular interest in the case where hydrogen abstraction or electrophilic addition reactions may be disfavored by multiple halogen substitution or steric hindrance.

$$HO^\bullet + RX \rightarrow HO^- + RX^{\bullet +} \qquad (9)$$

3.2.6. H_2O_2/UV Process: Advantages and Limits of Applications

This subsection summarizes more recent investigations using the H_2O_2/UV process for the oxidative degradation of organic pollutants dissolved or dispersed in aqueous systems.

The use of hydrogen peroxide as an oxidant brings a number of advantages in comparison to other methods of chemical or photochemical water treatment: commercial availability of the oxidant, thermal stability and storage on-site, infinite solubility in water, no mass-transfer problems associated with gases, two hydroxyl radicals are formed for each molecule of H_2O_2 photolyzed, peroxyl radicals are generated after $HO^\bullet$ attack on most organic substrates, leading to subsequent thermal oxidation reactions, minimal capital investment, very cost-effective source of hydroxyl radicals, and simple operation procedure.

There are, however, also obstacles encountered with the H_2O_2/UV process. In fact, the rate of chemical oxidation of the contaminant is limited by the rate of formation of hydroxyl radicals, and the rather small absorption cross section of H_2O_2 at 254 nm is a real disadvantage, in particular, in the cases where organic substrates will act as inner filters. Higher rates of $HO^\bullet$ radical formation may, nevertheless, be realized by the use of Xe-doped Hg arcs exhibiting a strong emission in the spectral region of 210–240 nm, where H_2O_2 has a higher molar absorption coefficient.

Special care in process and reactor design must be taken in order to ensure optimal oxygen concentration in and near the irradiated reactor volume.

The main disadvantage of all oxidative degradation processes based on the reactivity of hydroxyl radicals exists, however, in the efficient trapping of $HO^\bullet$ radicals by HCO_3^- and CO_3^{2-} ions (eq 18 and 19, respectively).[32]

$$HO^\bullet + HCO_3^- \rightarrow H_2O + CO_3^{\bullet -} \qquad (18)$$

$$HO^\bullet + CO_3^{2-} \rightarrow HO^- + CO_3^{\bullet -} \qquad (19)$$

Although, the generated carbonate radical anion has been shown to be an oxidant itself, its oxidation potential is less positive than that of the $HO^\bullet$ radical, introducing, hence, selectivity as far as the compounds to be degraded are concerned.[1]

3.2.7. Review of Recent Literature

During the last few years, several interesting studies concerning the H_2O_2/UV process used as a method of degrading organic compounds in aqueous systems (contaminated groundwater and industrial wastewaters) have been reported. A review of data and experimental conditions and results is listed in Table IV. Most of the authors are aware of the importance of parameters ensuring the possibility of experiment duplication and of comparison of process efficiencies. Most vital parameters for any kind of evaluation are the overall liquid volume used in the treatment system, true quantum yields in the case of monochromatic irradiation and homogeneous reaction systems, or electrical energy consumed, specific data on substrate concentration and/or results concerning dissolved or total organic carbon (DOC or TOC) analysis during the experiment.

In fact, in most of the H_2O_2/UV process studies, authors fail to include one or all of the above mentioned parameters and data, hence, rendering comparisons of results of different photochemical AOP impossible (Table IV). A brief summary of experiments mostly based on TOC analysis is presented below.

Table IV. Review of Experimental Conditions and Results of the H_2O_2/UV Process

substrate	light	reactor, vol (L)	H_2O_2	T (°C)	pH	[c_0]	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	$-TOC$[b] (%)	parameters[c]	ref
benzene	G10T5 LP[d] Hg 5.3 W at 254 nm	RSR,[e] 3.3	1.32×10^{-3} [f]	25	6.8	0.2×10^{-3} [f]	90	98	–	–	H_2O_2 to benzene molar ratio, pH, UV power	17
trichloroethylene	LP[d] Hg 3 × 13 W EP[g]	CSTR, 70	10[h]	–	–	500 [i]	25	84	–	–	–	34
hexachlorobenzene	LP[d] Hg 15 W at 254 nm	RSR,[e] 4	5×10^{-3} [f]	16	7.5	1.4×10^{-7} [f]	60	50	–	–	–	2
chlorobenzene			10^{-3} [f]			8×10^{-5} [f]	4	90				
1,2,4-trichlorobenzene			10^{-3} [f]			7×10^{-5} [f]	6	90				
nitrobenzene			10^{-3} [f]			10^{-4} [f]	36	90				
phenol			10^{-3} [f]			10^{-4} [f]	7	90				
4-nitrophenol			10^{-3} [f]			10^{-4} [f]	18	90				
(mixture of)	LP[d] Hg 15 W at 254 nm	RSR,[e] 4		16	7.5				–	–	–	2
chlorobenzene			10^{-3} [f]			8×10^{-5} [f]	30	≥98				
1,3-dichlorobenzene			10^{-3} [f]			7.5×10^{-5} [f]	35	≥98				
1,2,4-trichlorobenzene			10^{-3} [f]			7×10^{-7} [f]	40	≥98				
(mixture of)												
chlorobenzene			10^{-3} [f]			8.4×10^{-5} [f]	5	≥98				
nitrobenzene			10^{-3} [f]			8.5×10^{-5} [f]	8	≥98				
4-chloronitrobenzene			10^{-3} [f]			8×10^{-5} [f]	10	≥98				
methanol	LP[d] Hg 15 W total UV radiant power	2	0.7 mL[j]	–	–	200[h]	30		75	84	–	15
methylene chloride		1.8	0.15 mL[k]			100[h]	25	83				50
dimethylhydrazine (UDMH)		2	76 mM[l]			5000[h]	180	60				
1,2-dibromopropane	MP[m] Hg 100 W EP[g]	(quartz tube)	8.24×10^{-1} [f]	20	7	1.14×10^{-4} [f]	115	100	–	–	hydrogen peroxide addition	29
(mixture of)	LP[d] Hg 15 W at 254 nm	4		16	7.5				–	–	UV power, H_2O_2 conc, bicarbonate conc	6
carbon tetrachloride			19.7×10^{-5} [f]			63×10^{-8} [f]	50	0				
chloroform						75×10^{-8} [f]	50	100				
(mixture of)												
1,1,1-trichloroethane			19×10^{-5} [f]			38×10^{-8} [f]	50	75				
1,1,2-trichloroethane						50×10^{-8} [f]	20	>95				
(mixture of)												
pentachloroethane			96×10^{-5} [f]			79×10^{-8} [f]	50	70				
hexachloroethane						80×10^{-8} [f]	50	0				
1,1,2,2-tetrachloroethane						100×10^{-8} [f]	50	≥90				
(mixture of)												
1,1,2-trichloroethane			94×10^{-5} [f]			50×10^{-8} [f]	50	85				
pentachloroethane						65×10^{-8} [f]	50	92				
1,1,2,2-tetrachloroethane						58×10^{-8} [f]	50	>98				
1,1,2-trichloroethane			15×10^{-5} [f]			10^{-6} [f]	60	≥98				
trichlorophenol	MP[m] Hg 198 W/L	FR,[n] PS,[o] 7.6 L/min	100[h]	–	7.5	0.6[h]	2	50	–	–	–	51
2,4-dichloro-4-nitroaniline						1.4[h]	2	>30				
3,3-dichlorobenzidine						1[h]	2	75				
tetrachloroethylene	MP[m] Hg 160 W/L	FR,[n] TS[p] (Peroxpure)	7 mg/min			704[i]	2.5	100				
1,1-dichloroethylene						263[i]	2.5	100				
Freon-TF						71[i]	2.5	0				
trichloroethylene						54[i]	2.5	100				
1,1,1-trichloroethane						?	2.5	0				

Table IV (Continued)

substrate	light	reactor, vol (L)	H_2O_2	T (°C)	pH	[c_0]	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	$-TOC$[b] (%)	parameters[c]	ref
benzene	LD[d] Hg 5.3 W at 254 nm	RSR,[e] 3.3	1.4×10^{-3} [f]	25	6.8	2×10^{-4} [f]	90	>98	–	–	H_2O_2 to substrate molar ratio	18
phenol						2×10^{-4} [f]	50	≥98				
toluene						2×10^{-4} [f]	60	99				
chlorobenzene						2×10^{-4} [f]	60	95				
2-chlorophenol						2×10^{-4} [f]	60	95				
2,4-dichlorophenol						2×10^{-4} [f]	40	96				
2,4,6-trichlorophenol						2×10^{-4} [f]	40	>98				
dimethyl phthalate						2×10^{-4} [f]	120	>98				
diethyl phthalate						2×10^{-4} [f]	120	>98				
phenol	LP[d] Hg 16 W EP[g]	0.100	1 mL[a]	16	6.5	–	180	–	60	95	initial H_2O_2 conc	37
catechol							180		60	95		38
trichloroethylene							180		2.5	≥80		
trichloroethylene	LP[d] Hg 15 W total UV radiant power	0.250	24×10^{-4} [f]	20	6.8	2×10^{-4} [f]	40	>99	–	–	initial H_2O_2 conc, reactor depth, UV power, pH, T, [c_0]	52
phenol	MP[m] Hg 1000 W EP[g]	FR[n] TS[p] (Peroxpure)	1000 mg	–	–	100[h]	5	100	–	–	UV power	43 53
trichloroethylene	MP[m] Hg 30 kW EP[g]	FR[n] PS,[o] 227 L/min	50[h]	–	–	3700–4000[i]	0.833	>99	–	–	–	54
1,2-dichloroethane	MP[m] Hg 0.0375 W/L total UV radiant power	1	1[h]	22	2	0.4[h]	20	51	–	–	–	55
carbon tetrachloride	MP[m] Hg 100 W EP[g] 5.76 W/L total UV radiant power	CSTR, 1	1.55[h]			0.5[h]	45	30	–	–	[c_0], UV power, initial [H_2O_2], pH, bicarbonate conc	41
1,2-dichloroethane			2.16[h]			0.5[h]	60	≥99				42
trichloroethylene			1.97[h]	23	5.8	0.58[h]	45	>99				
1,1,2,2-tetrachloroethylene			1.81[h]			0.32[h]	30	≥99				
benzene			2.22[h]			0.53[h]	30	>99				
1,1,1-trichloroethane			2.62[h]	23	5.9	0.53[h]	15	83				
1,4-dichlorobenzene			0.53[h]	24	6.4	0.82[h]	20	>99				
carbon tetrachloride	MP[m] Hg 100 W EP[g] 5.54 W/L total UV radiant power	1	215.4[h]	–	–	39.2[h]	125	41	–	–	[c_0], UV power, initial [H_2O_2], pH, bicarbonate conc	41
1,2-dichloroethane			215.4[h]			31.0[h]	168	>99				
trichloroethylene			234.1[h]			36.2[h]	120	>99				
benzene			451.7[h]			43.4[h]	63	95				
1,1,1-trichloroethane			224.8[h]			33.0[h]	185	85				
1,1,1-trichloroethane	MP[m] Hg 100 W EP[g]	1	224.8[h]	–	–	33.0[h]	25	40	–	–	UV power, [c_0]	41
	450 W EP[g]	1	212.8[h]			40.8[h]	25	93				
phenol	8 × LP[d] Hg 51.7 W EP[g] each	12	30.0[h]	22	4	10.0[h]	16	94	–	–	pH, UV power, [c_0], initial H_2O_2 conc	5
m-cresol			25.0[h]	22	8	11.5[h]	60	>99				
2-chlorophenol			20.0[h]	22	8	13.6[h]	40	>99				
2,5-dimethylphenol			20.0[h]	24	8	13.0[h]	30	>99				
2,5-dichlorophenol			20.0[h]	23	8	17.3[h]	30	>99				
4-chloronitrobenzene	LP[d] Hg 90 W EP[g]	FR,[n] 60 L/h	5×10^{-5} [f]	16	7.5	2.5×10^{-6} [f]	4	75	–	–	[c_0], bicarbonate conc	50

Table IV (Continued)

substrate	light	reactor, vol (L)	H_2O_2	T (°C)	pH	[c_0]	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	$-TOC$[b] (%)	parameters[c]	ref
4-chloronitrobenzene	LP[d] Hg 90 W EP[g]	4	10^{-3} [f]	16	7.5	9×10^{-5} [f]	35	95	–	–	initial H_2O_2 conc, bicarbonate conc	50
phenol	MP[m] Hg 0.32 W/L 5.8 W at 253.7 nm	0.140	42×10^{-4} [f]	–	6.3	28×10^{-5} [f]	80	≥85	–	–	initial H_2O_2 conc, pH, UV power	56
2-chlorophenol			69×10^{-4} [f]		6.3	46×10^{-5} [f]	80	80				
2,4-dichlorophenol			98×10^{-4} [f]		6.3	20×10^{-5} [f]	120	70				
nitrobenzene	4 × LP[d] Hg 25 W EP[g] each, 0.48 W/L at 254 nm	AOP's reactor	408[h]	15–20	–	50[h]	120	80	–	–	–	57
m-xylene	MP[m] Hg 5000 W EP[g]	FR,[n] TS[p] (Peroxpure Model SQ-5)	115[h]	52–57	5.4	56.7[h]	4	50	–	–	[c_0]	28
captan			115[h]		5.4	1[h]	1.4	50				
chlordane			115[h]		5.4	1[h]	3.9	50				
pentachloronitro benzene			100[h]	35		1[h]	1.3	50				
methylene chloride	24 × LP[d] Hg 65 W EP[g] each	PS[o] (Ultrox), 567	13.0[h]	–	–	100[h]	25	83	–	–	–	58 59
methanol			13.0[h]			75[h]	30	0				60
trichloroethylene			48.0[h]			1.3[h]	16	100				
(mixture of) benzene			88.77[h]			4.4[h]	30	96				
toluene						3.8[h]		97				
ethylbenzene						0.185[h]		60				
xylene						3.200[h]		97				
fatty acids				80	–	–	480	–	33300	62	T	61
naphtenic acids				80			120		430	90		
(mixture of VOC)	MP[m] Hg 100 W EP[g]	1							–	–	–	42
1,1-dichloroethylene			88[h]	20	7	0.14[h]	90	>99				
trichloroethylene						61.5[h]	90	99				
1,1,2,2-tetrachloroethylene						0.06[h]	90	>99				
(mixture of)	MP[m] Hg	FR[n] (Peroxpure)		–	–				–	–	[c_0]	62
benzene			100[h]			6.850[h]	5	>99				
toluene						50.900[h]	5	>99				
chlorobenzene						22.500[h]	5	>99				
ethylbenzene						6.000[h]	5	>99				
xylenes(*p*-, *m*-)						36.000[h]	5	>99				
o-xylene						45.700[h]	5	>99				
4-chlorophenol	2 × 100-J Xe flash lamps	quartz cell	0.07[f]	–	4.7	6.4×10^{-4} [f]	900 μs	>80	–	–	–	63
dioxane	LP[d] Hg 25 W EP[g]	RSR[e] 10	100[h]	–	3	100[h]	60	88	–	–	reactor volume, UV power	27
dioxane	MP[m] Hg 200–400 nm	200	100[h]	–	3	100[h]	60	94	–	–	–	27
BTX (benzene, toluene, xylene)	MP[m] Hg 200–400 nm	200	30[h]	–	3	8[h] 7[h] 4[h]	60	70	–	–	–	27
trinitrotoluene (TNT)	MP[m] Hg 1000 W EP[g] 200–300 nm	200	400[h]	–	3	93[h]	60	79	–	–	–	27
TNT	LP[d] Hg 25 W EP[g]	10	400[h]	–	3	109[h]	60	24	–	–	–	27
atrazine	LP[d] Hg 16 W EP[g]	0.100	2.5% v/v 0.24[f]	16	6	–	180	–	1.5	≤80	initial H_2O_2 conc, [c_0]	38
1,2-dimethyl-3-nitrobenzene	MP[m] Hg 125 W EP[g] Phillips HPK	0.220	1% v/v 0.05[f]	40	6.5	120–130[h]	40	–	–	>90	initial H_2O_2 conc	39

Table IV (Continued)

substrate	light	reactor, vol (L)	H_2O_2	T (°C)	pH	[c_0]	t (min)	−c[a] (%)	TOC_0 (ppm C)	−TOC[b] (%)	parameters[c]	ref
nitro-*o*-xylenes (industrial wastes)	MP[m] Hg 125 W EP[g] Phillips HPK	0.220	1% v/v 10% v/v	50 50	2 2	–	120 475	–	800 4500	>90 90	TOC_0 initial H_2O_2 conc	40
diethyl malonate	MP[m] Hg 5.5 W at 254 nm	CSTR, 8.5	35×10^{-5} [f]	23	5.5	3×10^{-5} [f]	50	100	–	–	humic acid and polyethylene glycols	64
chloroform (mixture of)	MP[m] Hg, 5000 W EP[g], high intensity lamp	FR,[n] 75 L/min 230		–	–	20[h]	80	97	–	–	–	65
trichloroethylene						40[h]						
chloroform (mixture of)						40[h]						
benzene						20[h]	16	≥99				
trichloroethane						50[h]	50	≤40				
2,4-dinitrotoluene (DNT)	MP[m] Hg 450 W EP[g]		13[r]	27–35	6–6.8	75.8[h]	45	100	–	–	H_2O_2 to DNT molar ratio, [c_0]	30
trichloroethylene	LP[d] Hg	1	4.5[s]	20	6.8	58[h]	45	≥98	–	–	H_2O_2 to substrate molar ratio, pH, T, [c_0]	8
dichloromethane			3[t]			53[h]	180	80				
carbon tetrachloride						53[h]	180	45				
tetrachloroethane						53[h]	180	50				
ethylene dibromide						53[h]	180	52				
chloroform						53[h]	180	93				
tetrachloroethylene						53[h]	180	≥98				
trichloroethylene	LP[d] Hg	1	9×10^{-4} [f]	25	6.8	3×10^{-4} [f]	40	>90	–	–	H_2O_2 conc, [c_0], mixing	66
benzene			9×10^{-4} [f]	25	6.8	10^{-4} [f]	50	>90				
benzene	MP[m] Hg 125 W EP[g] Phillips HPK >290 nm		0.025[h]	–	–	2×10^{-4} [f]	186	50	–	–	–	67
toluene						2×10^{-4} [f]	108	50				
o-xylene						2×10^{-4} [f]	102	50				
m-xylene						2×10^{-4} [f]	66	50				
p-xylene						2×10^{-4} [f]	114	50				
cumene						2×10^{-4} [f]	24	50				

[a] Substrate concentration removed. [b] TOC removed. [c] Parameters studied. [d] LP, low pressure. [e] RSR, recirculating flow reactor. [f] M. [g] EP, electrical power. [h] mg/L. [i] μg/L. [j] 0.7 mL of 30% H_2O_2 were supplied at 5-min intervals over 20 min. [k] 0.15 mL of 30% H_2O_2 were supplied at start (t = 0). [l] 76 mM (2.580 mg) H_2O_2 per hour per 2 L or 8.6 mL of 30% H_2O_2 per hour. [m] MP, medium pressure. [n] FR, flow reactor. [o] PS, pilot scale. [p] TS, technical scale. [q] 1 mL of 30% H_2O_2 in 100 mL of solution. [r] H_2O_2 to dinitrotoluene molar ratio. [s] H_2O_2 to trichloroethylene molar ratio. [t] H_2O_2 to dichloromethane molar ratio.

Yue et al. studied the TOC degradation rate for the oxidative removal of several organic compounds.[37,38] Results show that conversion (diminution of TOC) of trichloroethylene, phenol, 4-chlorophenol, and catechol[10,33] is higher if the initial H_2O_2 concentration in increased. For all organics studied, TOC removal rate follows first order kinetics.

Legrini et al.[39] and Jakob et al.[40] investigated the oxidative degradation of 1,2-dimethyl-3-nitrobenzene (120–130 mg/L) and nitro-*o*-xylenes containing industrial wastewaters (800 and 4500 ppm C) by the combination of H_2O_2 and a 125-W medium-pressure Hg arc. In the model case, 95% TOC removal (initial substrate concentration 120 mg/L) was observed within 40 min of irradiation time using 1% v/v H_2O_2 (30% wt/v). Diluted industrial waste water (800 ppm C) was completely mineralized within 3 h of irradiation under the same experimental conditions.

In their technical report, Sundstrom et al.[7] investigated the efficiency of the H_2O_2/UV process with a variety of aliphatic and aromatic compounds, including trichloroethylene (TCE), chloroform, dichloromethane, benzene, chlorobenzene, chlorophenol, and diethyl phthalate. The reactions were conducted in batch and flow reactors equipped with low-pressure Hg lamps. The authors found that the rates of degradation increased with increasing hydrogen peroxide concentration and UV light intensity and were highly dependent on the chemical structure of the substrates. The reactivities for volatile aromatic halocarbons were found to be PCE > TCE > $CHCl_3$ > $CHCl_2$ > tetrachloroethane, ethylene dibromide, carbon tetrachloride. The order of reactivity for aromatic compounds (determined in a flow reactor) was found to be trichlorophenol > toluene > benzene > dichlorophenol, phenol > chlorobenzene > chlorophenol > diethyl phthalate, dimethyl phthalate. The reacted chlorine (chlorinated aliphatics) was found in all cases to be converted into chloride ion, indicating that the chlorinated structures were destroyed.

In another paper, Weir et al.[17] found that benzene was more slowly oxidized at alkaline pH and that the temperature effect on the reaction rate was minimal.

Glaze et al.[34] investigated the destruction of trichloroethylene by the H_2O_2/UV procedure in which H_2O_2 was added into a 70-L CSTR reactor at a rate of 10 mg/min while photolyzing the solution with three 13-W low-pressure Hg lamps. They observed that TCE decomposed at a reasonable rate, but hydrogen peroxide accumulated to unacceptable levels.

Guittonneau et al.[2] studied the oxidative degradation of phenol, some chloroaromatic (hexachlorobenzene, chlorobenzene, 1,2,4-trichlorobenzene) and nitroaromatic compounds (nitrobenzene, 4-chloronitrobenzene, 4-nitrophenol) in water by the H_2O_2/UV process. Results show that substituents influence the rate of oxidation of these aromatic compounds. In particular, chlorobenzenes are more rapidly decomposed than nitroaromatic compounds. In another publication, the authors focus their interest on the degradation of aliphatic halogenated compounds by the H_2O_2/UV system.[6] They found that chloromethanes and chloroethanes containing at least one H atom may be eliminated; however, perchlorinated substrates were not affected, and process efficiency decreased in the presence of bicarbonate and carbonate ions.

Symons et al.[41,42] studied eight industrial solvents regulated by the U.S. Environmental Protection Agency using a nominal 1-L continuously stirred quartz batch reactor and two medium-pressure Hg lamps of 100 and 450 W. Starting with an initial concentration of 0.5 mg/L, the overall rate of disappearance decreases in the order 1,4-dichlorobenzene > 1,1,1-trichloroethane > benzene, tetrachloroethylene > trichloroethylene > 1,2-dichloroethane > carbon tetrachloride. Hager[43] reported results quantifying the effect of the incident radiant power on the destruction rate of phenol by the H_2O_2/UV procedure. The reaction time for phenol degradation was inversely proportional to the relative radiant power being applied (75–1000 W/L). Rates of removal using the H_2O_2/UV Perox-pure process were found to decrease from vinyl chloride, trichloroethylene > chlorophenol > benzene, toluene, xylene > methylene chloride > acetone.

Hager et al.[44,45] treated ground waters contaminated with mixtures of hazardous aliphatic compounds in pilot scale equipment. They found that for trichloroethylene in the concentration range of 2000–10000 μg/L, optimum treatment conditions included a liquid flux of 230 L/min, addition of 50 mg/L of hydrogen peroxide, and irradiation by a medium-pressure Hg arc of 30000 W of electrical power. Under these conditions, removal of TCE from 3700–4000 μg/L to 0.7–0.8 μg/L was achieved in 50 s of irradiation time. In cases where pollutant concentrations must be decreased by several orders of magnitude, relatively high permanent concentrations of H_2O_2 seem to be needed. This is probably due to the increasingly successful competition for hydroxyl radicals by other components of the irradiated aqueous solution.

3.2.8. Addition of Fe Salts

Among conventional procedures of chemical water treatment, Fenton-type catalyzed generation of hydroxyl radicals from H_2O_2[46,47] has found technical application. In general, electronic excitation of solvated or complexed Fe^{3+} cannot be used for the homolysis of hydrogen peroxide. However, depending on the organic compounds present in the aqueous system, photochemical reduction of Fe^{3+} to Fe^{2+} [13,14,48,49,221] may be favored, hence, producing a relative high concentration of Fenton catalyst. Consequently, besides UV-C photolysis of hydrogen peroxide, UV-B, UV-A, and visible light contribute to the acceleration of the catalyzed hydrogen peroxide dismutation. Applying UV irradiation to a procedure based on a Fenton-type catalyzed reaction of H_2O_2 may then yield a most effective system for oxidative degradation.[27]

3.3. Ozone/UV Process

3.3.1. Introduction

Aiming for decontamination in drinking water production as well as for treatment of strongly contaminated residual waters, the use of ozone in conjunction with UV light as a method of removal of organic material has been technically developed.

The O_3/UV process seems at present to be the most frequently applied AOP for a wide range of compounds. This is mainly due to the fact that ozonization is a well-known procedure in water technology and that ozonizers are therefore in most cases readily available in drinking water treatment stations. From the photochemists point of view, the absorption spectrum of ozone provides a much higher absorption cross section at 254 nm than H_2O_2, and inner filter effects by e.g. aromatics are less problematic. There remain, however, many questions related to mechanisms of free radicals production and subsequent oxidation of organic substrates. In fact, the literature contains many conflicting reports on the efficiency of this oxidation method which may be linked to mechanistic problems as well as to the difficult tasks of dissolving and photolyzing ozone with high efficiency. Finally, linked to the problem of quantifying rates of absorbed photons in heterogeneous (gas/liquid) media and to the reactivity of ozone toward most unsaturated organic compounds, procedures for the determination of quantum efficiencies still remain to be worked out.

3.3.2. O_3 Photolysis

Numerous investigations deal with the light-induced decomposition of ozone in aqueous systems.[33,34,68–70] A two-step process has been proposed involving the light-induced homolysis of O_3 and the subsequent production of $HO^•$ radicals by the reaction of $O(^1D)$ with water (eqs 20 and 21).[34] However, it has been observed that

$$O_3 \xrightarrow{h\nu < 310\text{ nm}} O_2 + O(^1D) \quad (20)$$

$$O(^1D) + H_2O \rightarrow HO^• + HO^• \quad (21)$$

photolysis of ozone dissolved in water leads to the production of hydrogen peroxide (eq 22) in a sequence

$$O_3 + H_2O \xrightarrow{h\nu} \rightarrow H_2O_2 + O_2 \quad (22)$$

of reactions, where hydroxyl radicals, if formed at all, do not escape from the solvent cage.[34]

Recently, Peyton and Glaze[33,69] have added proof that hydrogen peroxide is in fact the primary product of ozone photolysis. A summary of the chemistry involved

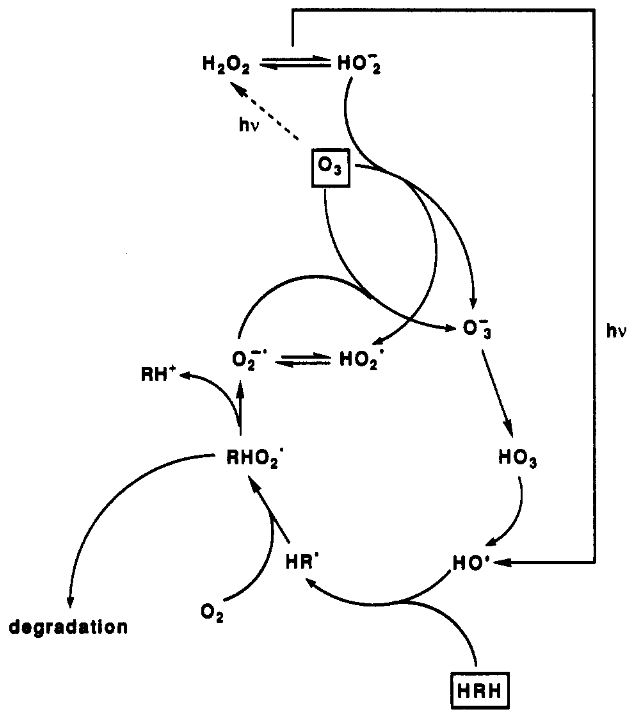


Figure 2. Reaction pathways in the ozone/UV and ozone/peroxide systems.[36]

in the generation of HO• radicals by the O_3/UV process is shown in Figure 2, where a sequence of reactions is proposed including the interaction of organic substrates present in water.[36]

The authors suggest that initiation can occur by the reaction of ozone with HO^- or HO_2^-, or by photolysis of hydrogen peroxide. The latter is formed by ozone photolysis as well as from the reaction of ozone with many unsaturated organic compounds. As already described above, HO• radicals react with organic substrates to produce organic radicals, which efficiently add molecular oxygen to yield organic peroxyl radicals. These peroxyl radicals may be considered as the true propagators of the thermal chain reactions of oxidative substrate degradation and oxidant consumption.[36]

3.3.3. O_3/UV Process: Examples of Applications

The O_3/UV process is an advanced water treatment method for the effective oxidation and destruction of toxic and refractory organics, bacteria, and viruses in water. The process has also been used in the decolorization of bleaching waters in the paper industry.[71]

Staehelin and Hoigné[72] may be considered the pioneers in investigating ozone decomposition in aqueous systems containing model pollutants to be oxidized. Basically, aqueous systems saturated with ozone are irradiated with UV light of 254 nm in a reactor convenient for such heterogeneous media. Corresponding rates of oxidative degradation (e.g. evolution of CO_2) are much higher than those observed in experiments where either UV light or ozone have been used separately. The efficiency of the process has been proven on a pilot and technical scale with the destruction of toxic or refractory organic pollutants from the ppm or ppb range to acceptable or nondetectable limits without generation of hazardous waste.

Like other HO• radical generating degradation processes, O_3/UV oxidizes a wide range of organic compounds including partially halogenated (e.g. chlorinated) and unsaturated halogenated hydrocarbons. This process can be operated in a batch intermittent or continuous mode and does not need special monitoring.

Techniques and safety rules of large scale ozone production and use are known from sterilization procedures applied to the production of water for public consumption. The low ozone solubility in water and consequent mass transfer limitations represent one of the most serious and rather specific problems in the technical development of the O_3/UV process.[31,73] Prengle et al., as well as Glaze et al., have recommended and used stirred-tank photochemical reactors in order to obtain better results in mass transfer and to solve some of the remaining technical problems encountered in scale-up.[34,41,42] However, other geometries of photochemical reactors (tubular, internal loops, etc.) have also shown promising results. Other problems which may impair the efficiency of contaminant removal are mostly linked to potential secondary reactions of the oxidative intermediates depending on the particular experimental conditions of a water treatment project (e.g. free radical scavenging by natural water components, such as bicarbonates[74-76] and humic substances.[64]

A large number of papers have been published dealing with the oxidation of organic compounds in aqueous systems by ozone and UV radiation. Here again, in most of the studies, authors omit parameters, in particular TOC values, in their reports, making comparison with pilot or semipilot plant data rather difficult (Table V).

Table V summarizes experimental conditions and results of a selection of references. Most papers reviewed here are related to the removal of total organic carbon (TOC) from waters.

Sierka et al.[74] studied the TOC removal of humic acid (4.3 ppm C) in a 3.8-L semibatch reactor, continuously fed with ca. 8 mg/min of ozone, and found that 87% TOC reduction occurred at pH 7 and at 20 °C in 20 min of irradiation time. The destruction of 2-chlorophenol initially at 200 mg/L in a 40-L semibatch reactor using a 5000-W medium-pressure Hg lamp was also studied. The removal of 99% of the initial substrate occurred within 50 min of irradiation time.[31]

TOC degradation of a mixture of phenol and methylene chloride (5310 ppm C), and naphthenic acids (340 ppm C), using eight 40-W low-pressure Hg lamps as an irradiation source, has been patented.[61] Examples describe the effect of temperature and initial TOC content on the efficiency of the O_3/UV process and results indicate that 55% TOC removal of organic mixture and 82% TOC removal of naphthenic acids occurred in 260- and 120-min irradiation time, respectively, at a temperature of 80 °C.

Francis[77] studied the O_3/UV reaction system by using model compounds in deionized water. These experiments were conducted in a 300-L immersion-type reactor irradiated with a 2000-W doped medium-pressure Hg lamp. The following TOC degradation rates were found, for ethylene glycol (4.4 ppm C), 50 ppb C/min; for glycol (5.2 ppm C), 90 ppb C/min; and for chloroform (15 ppm C), 33 ppb C/min, and 100% removal of 1,1,2-trichloroethylene was found within 20 min of irradiation time. The removal of carbon

Table V. Review of Experimental Conditions and Results of the O_3/UV Process

substrate	light	reactor, vol (L)	O_3	T (°C)	pH	$[c_0]$	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	−TOC[b] (%)	parameters[c]	refs
humic acid	LP[d] Hg	3.8	8.2[e]	20	7		20	–	4.31	87	$NaHCO_3$	74
2-chlorophenol	MP[g] Hg 5000 W EP[h]	40	$(6–8) \times 10^{-2}$ [i]	23	6.5–7.5	200[f]	50	>99	–	–	–	31
1,2-dichloroethane	0.0375 W/L	semibatch, 1	590[j]	21	2	0.4[f]	20	>90	–	–	UV radiant power, additives (acetate), pH	55
1,2-dichloroethane			3[j]	22	2	0.4[f]	27	50				
trichloroethylene			2.3[j]	21	6.9	0.4[f]	0.5	>99				
ethylene glycol	MP[g] doped Hg 2000 W EP[h]	300	20[k]	–	–		80		4.4	50[l]	methods of ozone injection	77
glycerol							50		5.2	90[l]		
trichloroethylene							20		7.7	100[l]		
chloroform							40		15	33[l]		
carbon tetrachloride						13[f]	80	110[l]	0.25			
tetrachloroethylene	LP[d] Hg 13W EP[h]	CSTR, 70	0–16[e]	–	–	–	–	–	–	–	ozone dose, UV dose	34
trichloroethylene			0–16[e]									
halogenated organics ($CHCl_3$, CCl_4, $CHBr_2Cl$, $CHBr_3$, C_2HCl_3, C_2Cl_4, 1,1,1-$C_2H_3Cl_3$)	MP[g] Hg 30 W EP[h] 9.2 W at 254 nm	semicont, 72 or 0.9	12[m]	20	–	<0.5[f]	–	–	–	–	ozone dose, UV dose, pH	75
hexachlorobenzene	MP[g] Hg	20 (Ultrox-system)	–	–	–	40[n]	60	≥96	–	–	–	84
1,2-dibromo-3-chloropropane						50[h]	30	≥98				
pentachlorophenol						50[n]	5	>98				
lindane						60[n]	15	≥98				
(mixture of)	16 × LP[d] Hg 2.2 W each at 254 nm	4	3.8[f]	20	7						pH	78
phenol						50[f]	140	>99	–	–		
p-cresol							140	>99	–	–		
3,4-xylenol							140	>99	–	–		
catechol							100	100	–	–		
(mixture of) phenols							100	–	200	≥90		
trihalomethane (lake water)	LP[d] Hg 6 W EP,[h] 0.67 W/L at 254 nm	9	30[f] (33.6[e])	–	7	–	60	≥45	3	–	ozone dose	85
methanol	MP[g] Hg 40 W EP[h] UV output 14.3 W	2	70[o]	–	–	200[f]	30		75	65	ozone dose	15
methylene chloride		1.8	10 mM[p]			100[f]	25	84				16, 58
1,4-dioxane		2	205[e]			700[f]	120	72				59, 60
dimethylhydrazine (UDMH)	MP[g] Hg 40 W EP[h] UV output 14.3 W	2	76.5[q]	–	–	5000[f]	180	96	–	–	–	15, 16
2-methylisoborneol	LP[d] Hg 6[r]	14[s]	4[f]	–	–	150[t]	20	90	–	–	ozone dose	86
geosmin			4[f]			32[t]	30	100				
diethyl malonate	G10T5 5.5 W 254 nm	CSTR, 8.5	1.3×10^{-5} [u]	23	5.5	3×10^{-5} [v]	30	100	–	–	humic substances, polyethylene glycols	64
o-nitrotoluene	LP[d] Hg 50 W EP[h]	3	10[f]	40	8	216[f]	90	100	140	≥42	pH, carbonate, bicarbonate	79
p-nitrotoluene-2-sulfonic acid			10[f]	40	8	410[f]	180	100	125	≥76		
p-methylaniline-3-sulfonic acid			10[f]	40	8	298[f]	50	100				
formic acid			11.5[f]	40	8	210[f]	60		47	≥95		

Table V (Continued)

substrate	light	reactor, vol (L)	O_3	T (°C)	pH	[c_0]	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	$-TOC$[b] (%)	parameters[c]	refs
4-chloronitrobenzene	LP[d] Hg 90 W EP[h]	60 L/h 4	2×10^{-5} [v]	16	7.5	2.2×10^{-6} [v]	4	78	–	–	ozone dose, bicarbonate, reactor volume, UV power	50
4-chloronitrobenzene	LP[d] Hg 15 W EP[h]	200 L/h 0.82	2×10^{-5} [v]	16	7.5		0.25	70				
(mixture of)	24 LP[d] Hg 65 W EP[h] each	flow reactor, 19 L/min 570	68.76[f]	–	–				–	–	ozone dose, [c_0]	58
benzene						2250[n]	30	>99				
toluene						520[n]	30	>99				
ethylbenzene						70[n]	30	>99				
xylene						1115[n]	30	>99				
phenol, methylene chloride	8 × LP[d] Hg 40 W EP[h] each	flow reactor, 11.4 L/min		80	–	–	260		5310	55	T, TOC_0	61
naphthenic acids				80			120		340	82		
humic acid	LP[d] Hg 20 W EP[h]	RSR,[w] 0.30	0.27[x]	20	6.9		200		100	95	ozone dose, UV power	87
chloroform		0.012				30[f]	200	>99				
phenol	LP[d] Hg 120 W EP[h]	10	15[f] in feed gas (O$_3$ dose 7.8 mg L^{-1} min^{-1})	20	6.7	16×10^{-4} [v]	180	100	124	≥95	[c_0], functional groups, molecular weight	80
							60	100	124	22		
ethylene glycol							60			24		
glycol aldehyde										35		
glyoxal										65		
glyoxylic acid										93		
oxalic acid										98		
methyl alcohol							60			90		
ethyl alcohol										37		
n-propyl alcohol										15		
n-butyl alcohol										7		
n-amyl alcohol										6		
formaldehyde	LP[d] Hg 120 W EP[h]	10	15[f] in feed gas (O$_3$ dose 7.8 mg L^{-1} min^{-1})	20	6.7	16×10^{-4} [v]	60	100	124	97	[c_0], functional groups, molecular weight	80
acetaldehyde								100	124	33		
propionaldehyde										16		
formic acid							60			100		
acetic acid										28		
propionic acid										22		
n-butyric acid										10		
n-valeric acid										8		
oxalic acid							60			98		
malonic acid										44		
succinic acid										23		
glutaric acid										14		
adipic acid										12		
methanol	0.75 W/L		5.26×10^{-5} [y]	–	–	3.4×10^{-3} [v]	120	≥75	–	–	UV dose	88
1,1,1-trichloroethane (also TCE, PCE)	LP[d] Hg 60 W EP[h]	thin channel continuous flow	0.10[x]	20	6.9	100–600[f]	0.66	>80	–	–	ozone dose, T	89
pesticide	LP[d] Hg 15 W EP[h]	2.7	0.8[k]	–	–	–	120	–	2	≥90	[c_0], radiant power, ozone dose	81
humic acid							85		1.22	≥90		
pesticide	5 × LP[d] Hg 40 W EP[h] each	RSR,[w] 240	2[z]	–	–	–	180	–	1.3	>60	ozone flow rate, water flow rate	82
pesticide	LP[d] Hg 16 W EP[h]	0.1	1.1[aa]	18	6–7	–	60	–	1.4	≥99	ozone dose, UV power	38
1,1-dichloroethylene	LP[d] Hg	3.78 L/min (Ultrox-UV/OX), 304	–	–	–	25[n]	–	>76	–	–	residence time, oxidants	90
trans-1,2-dichloroethylene						200[n]		>95				
						20[n]		>25				
1,1-dichloroethane						3.9[h]		>48				
1,1,1-trichloroethane						230[n]		>56				
trichloroethylene						130[n]		>96				
tetrachloroethylene						190[n]		>97				

[a] Substrate concentration removed. [b] TOC removed. [c] Parameters studied. [d] LP, low pressure. [e] mg/min. [f] mg/L. [g] MP, medium pressure. [h] EP, electrical power. [i] mM. [j] mL/min. [k] g/h. [l] ppb C/min. [m] g/m^3 per h. [n] μg/L. [o] 70 mM O_3 supplied per 30 min or 2.2 L/min. [p] 10 mM O_3 supplied per 25 min. [q] 3660 mg or 76.5 mM of O_3 supplied per hour per 2 L or 2 L/min. [r] mW/cm^2. [s] m^3/day. [t] ng/L. [u] mol/L per min. [v] M. [w] RSR, recirculating flow reactor. [x] mol/m^3 (in reactor). [y] M/min. [z] L/min. [aa] g/L.

tetrachloride, initially at 13 ppm C, was observed with a rate of 110 ppb C/min during 80 min.

Gurol et al.[78] studied the oxidative degradation of mixtures of phenolic compounds by the O_3/UV procedure using a 16-W low-pressure Hg lamp and a 4-L semibatch reactor. Complete substrate removal (>99%) of mixtures of phenol, *p*-cresol, 3,4-xylenol, and catechol (50 mg/L) occurred within 140 min. The authors also reported the effect of pH on the rates of oxidation of the organic compounds investigated and found decreasing reactivity in the orders catechol > 3,4-xylenol > *p*-cresol > phenol at pH 2.5, catechol > 3,4-xylenol ≥ *p*-cresol = phenol at pH 7.0 and the same reactivity at pH 9.

Xu et al.[79] published results on TOC removal by the O_3/UV process for a variety of organic pollutants (*o*-nitrotoluene, ONT; *p*-nitrotoluene-2-sulfonic acid, NTS; *p*-methylaniline-3-sulfonic acid, MAS; and formic acid). Experiments were carried out with 3-L water samples continuously sparged with ozone (ca. 10 mg/L) and irradiated with a 50-W low-pressure Hg lamp. They found that ONT, NTS, and MAS were completely removed from water within 90, 180, and 50 min of irradiation time, respectively. Results also include TOC removal rates of ONT, NTS, and formic acid of ≥42% (90 min), ≥76% (180 min), and ≥95% (60 min), respectively.

Takahashi[80] studied the degradation of several groups of organic compounds, including alcohols, aldehydes, carboxylic acids, dicarboxylic acids, phenols, and other organic pollutants of low molecular weight (see Table V for experimental conditions). Degradation of phenol was shown to be enhanced by the simultaneous use of ozone and UV light; however, the synergistic effect decreased as the concentration of phenol increased. This result could be interpreted as a consequence of competitive light absorption. Within 3 h of irradiation, lowest TOC values were attained with organic substrates containing 1–6 carbon atoms. The rate of removal of TOC in the same group of compounds decreased with increasing molecular weight. No difference between TOC removals was observed with alcohols, aldehydes, and carboxylic acids having the same number of carbon atoms.

Yue et al.[38] studied pesticide degradation. TOC removal by the use of ozone in combination with UV light was better than 99% for a 60-min irradiation time. In another study, the authors investigated the effect of reactor volume, UV radiant power, ozone addition, and initial TOC concentration on the rate of removal of a pesticide and of humic substances.[81] Yet unpublished results indicate that ≥90% TOC was mineralized within 120 and 85 min of irradiation for pesticide and humic acid, respectively. The same authors used a 240-L pilot reactor for the degradation of trichloroethylene and pesticides, and more than 60% of TOC was removed within 3 h of reaction time.[82]

3.4. O_3/H_2O_2/UV Process

3.4.1. Introduction

The chemistry of the thermal O_3/H_2O_2 process[91–94] has recently been reviewed by Peyton[36] and the reaction pathways leading to the generation of $HO^\bullet$ radicals are summarized in eqs 23–27.

$$H_2O_2 + H_2O \rightleftarrows H_3O^+ + HO_2^- \tag{23}$$

$$O_3 + H_2O_2 \rightarrow O_2 + HO^\bullet + HO_2^\bullet \text{ (very slow)} \tag{24}$$

$$O_3 + HO_2^- \rightarrow HO^\bullet + O_2^{\bullet-} + O_2 \tag{25}$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \tag{26}$$

$$O_3^{\bullet-} + H_2O \rightarrow HO^\bullet + HO^- + O_2 \tag{27}$$

Again $HO^\bullet$ radicals are considered to be the most important intermediate, initiating oxidative degradation of organic compounds by one of the four mechanisms listed earlier. Corresponding rate constants are usually in the order of 10^8 to 10^{10} M^{-1} s^{-1}.[93] Compared to the rates of oxidative degradation observed in thermal reactions of ozone with organic pollutants, addition of hydrogen peroxide results in a net enhancement due to the dominant production of $HO^\bullet$ radicals. This process is further enhanced by the photochemical generation of $HO^\bullet$ radicals.[15,16,85]

New data suggest that experimental work related to the O_3/H_2O_2/UV process is mainly devoted to industrial development. Pilot scale reactors have been built for the exploitation of this method on a technical scale.[58–60,90,95,96]

3.4.2. Review of Recent Data

Experimental conditions and parameters of recent investigations of the O_3/H_2O_2/UV process are summarized in Table VI. References since 1985 show that the process is principally commercialized by Ultrox International (previously Westgate Research).[58–60,90,95,96]

Zeff et al. have obtained patents on the oxidation of a variety of organic compounds.[15,16] Under conditions listed in Table VI, 97% of the DOC of an aqueous methanol solution (200 ppm, 2 L) were removed within 30 min of irradiation time, at ambient temperature. Under similar experimental conditions, methylene chloride (100 ppm, 1.8 L) and dioxane (700 ppm, 2 L) were almost completely oxidized within 25 and 120 min, respectively. The authors also investigated the oxidative treatment of groundwaters of a chemical plant containing mainly vinyl chloride, methylene chloride, 1,1-DCE, 1,1-DCA, 1,2-DCA, *trans*-1,2-DCE, TCE, PCE, chloroform, chlorobenzene, benzene, toluene, ethylbenzene, and xylene at a TOC of 400 ppm. The O_3/H_2O_2/UV process was found to remove more than 98% of the TOC within 60 min of irradiation (optimum conditions are listed in Table VI). Control experiments confirm that the combination of UV, H_2O_2 and O_3 is more efficient than the treatment by UV, H_2O_2 or O_3 alone or in combination of two.

Wallace et al.[85] performed semibatch degradation studies with settled and filtered surface waters looking

Table VI. Review of Experimental Conditions and Results of the $H_2O_2/O_3/UV$ Process

substrate	light	reactor, vol (L)	H_2O_2	O_3	T (°C)	pH	$[c_0]$	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	$-TOC$[b] (%)	parameters[c]	ref
methanol	LP[d] Hg	2	0.7[f]	62[f]	15–20	–	200[i]	30		75	≥97	O_3 to H_2O_2	15
methylene chloride	40 W	1.8	0.15[g]	5.2[g]			100[i]	25	≥92			molar	16
1,4-dioxane	EP[e]	2	35[h]	205[h]			700[i]	120	≥92			ratio	58
													59
													60
dimethylhydrazine	LP[d] Hg	2	76 mM/h	76.5 mM/h	15–20	–	5000[i]	180	≥98	–	–	–	15
(UDMH)	40 W EP[e]		per 2 L[j]	per 2 L[j]									16
(mixture of)	total UV		28 mM or	14 mM or			400[i]	60	≥98				
vinyl chloride, methylene chloride, chloroform, chlorobenzene, benzene, xylene, 1,1-DCE, 1,1-DCA, 1,2-DCA, TCE, PCE	output 14.3 W	2	32 mL, (30%)	11 mg/min									
trihalomethanes	LP[d] Hg 6 W EP[e]	9	20[i]	30[i,k]	–	7	–	60	≥60	3	–	ozone dose	85
(VOCs mixture)	24 × LP[d] Hg	continuous flow	13[i]	110[i]	15–20	7.2	170[i]	40	91	–	–	O_3 to H_2O_2 molar	58 96
trichloroethylene	65 W EP[e]	(Ultrox-					60–70[i]		98			ratio,	
1,1-dichloroethane	each	system)					10–12[i]		54			UV	
1,1,1-trichloroethane		570					4–5[i]		83			power	
(mixture of)	24 × LP[d]	continuous	44.39[i]	49.14[i]	–	–		30		–	–	O_3 to H_2O_2	58
benzene	Hg	flow					2250[i]		100			molar	
toluene	65 W EP[e]	(Ultrox-					520[i]		>99			ratio,	
ethylbenzene	each	system)					68[i]		100			UV	
xylene		570					1100[i]		100			power	
trichloroethylene		19 L/min 140 L/min	18[i]	18.3[i]			3.3[i]	16	100				

[a] Substrate concentration removed. [b] TOC removed. [c] Parameters studied. [d] LP, low pressure. [e] EP, electrical power. [f] 70 mM O_3 supplied per 30 min or 2.2 L/min (62 mg/min) and 0.7 mL of H_2O_2 30% supplied at 5-min intervals over 20 min. [g] 10 mM O_3 supplied per 25 min or 0.5 L/min (5.2 mg/min) and 0.15 mL of H_2O_2 30% v/v. [h] 205 mg/min O_3 and 35 mL of H_2O_2 30% added within 90 min. [i] mg/L. [j] 76.5 mM (3660 mg) O_3 supplied per hour per 2 L and 76 mM (2.58 mg) H_2O_2 per hour per 2 L (8.6 mL of H_2O_2 30% per hour). [k] concentration in gas flow.

at the "trihalomethane formation potential" (THMFP). Under conditions listed in Table VI, THMFP decreasedto levels lower than 40% of the initial value within 60 min. The authors have also shown that the combination of hydrogen peroxide, UV radiation, and ozone increased the fraction of added ozone which has been consumed and deduced that the rate of ozone mass transfer into the bulk liquid must be higher under these conditions than in a treatment process based on ozone alone. Furthermore, their report strongly advocates the use of a stirred-tank photochemical reactor as a means to ensure efficient ozone mass transfer which, in combination with the enhanced consumption of ozone, leads to its more economical use.

Lewis et al.[96] and other investigators[58–60,90,95] performed pilot scale work on the treatment of groundwater, contaminated with volatile organic chlorides (VOC) and mixtures of benzene, toluene, ethylbenzene, and xylene, investigating the effects of ozone and hydrogen peroxide flow rates and UV radiant power on the efficiency of the $O_3/H_2O_2/UV$ process. The "Ultrox system" achieved VOC removals up to 98% and almost complete degradation of the aromatic compounds[58] (Table VI). However, oxidation of 1,1-dichloroethane and 1,1,1-trichloroethane seems rather difficult. In general, very low TOC removals were observed, indicating that only partial oxidation of those halogenated organic compounds could be achieved. By investigating these VOC and semivolatile organic pollutants, such as PCB and pesticides, GC analysis did not reveal the production of new compounds, a result not to be expected for progressive oxidation degradation.

3.5. TiO_2/UV Process

3.5.1. Introduction

The degradation of organic pollutants present in wastewaters using irradiated dispersions of titanium dioxide is a fast growing field in basic and applied research. The development of this process in order to achieve complete mineralization of organic pollutants has been widely tested for a large variety of chemicals.[39,40,97–112] Nevertheless, it remains surprising that only a very few experiments have been performed on a pilot scale.[98]

Carey et al.[113] first reported the photocatalytic degradation of biphenyl and chlorobiphenyls in the presence of titanium dioxide. Since Carey's paper in 1976, many applications using the TiO_2/UV process have been investigated.[97,114–140] Titanium dioxide[113–126,141] and platinized titanium dioxide[131–135,141,142] powders have both demonstrated their ability to decompose various organics in water. Platinized titanium dioxide is in most cases more efficient due to a faster electron transfer to dissolved molecular oxygen.[143] Other semiconductor dispersions have also been used for the photocatalytic degradation of pollutants.[141,142,144,145]

Heterogeneous photocatalytic techniques have also been used to transform and recover inorganic materials (e.g. precious metals) from the environment.[141,146–149]

Many investigators have demonstrated that the use of aqueous TiO_2 suspensions may improve the efficiency of sunlight detoxification of hazardous wastewaters.[107,144,146,150–153]

A review of the photocatalytic degradation of chlorinated benzenes, phenols, naphthalenes, dibenzofurans, and dibenzo-*p*-dioxins in aqueous media was published a few years ago.[3] Data on the complete mineralization of a number of common contaminants of water supplies, such as halogenated alkanes, alkenes, and aromatics using photocatalytic degradation have also been reported.[103,148,154]

3.5.2. Mechanism of the TiO_2-Photocatalyzed Oxidative Degradation

For a mechanistic explanation of the semiconductor-catalyzed oxidative degradation of organic material in aqueous systems, the band-gap model has proven to be very useful.[155–158]

Spectral absorption characteristics of TiO_2 allow its excitation in the UV-C, UV-B, and UV-A regions. Therefore, the use of medium-pressure mercury arcs of high electrical power is of considerable interest. Electronically excited TiO_2 exhibits strong oxidation potentials of the electron-depleted valence band (hole (h^+), eq 28). Two oxidation reactions have been experimentally observed: electron transfer from adsorbed substrate RX (eq 29)[159] and electron transfer from adsorbed solvent molecules (H_2O and HO^-) (eqs 30 and 31).[160]

$$TiO_2 \xrightarrow{h\nu} TiO_2\,(e^- + h^+) \qquad (28)$$

$$TiO_2\,(h^+) + RX_{ad} \rightarrow TiO_2 + RX_{ad}^{\bullet +} \qquad (29)$$

$$TiO_2\,(h^+) + H_2O_{ad} \rightarrow TiO_2 + HO_{ad}^{\bullet} + H^+ \qquad (30)$$

The second reaction mechanism appears to be of greater importance in oxidative degradation processes, most probably due to the high concentration of H_2O and HO^- molecules adsorbed at the particle surface. Molecular oxygen which must be present in all oxidative degradation processes is the accepting species in the electron-transfer reaction from the conduction band of the photocatalyst to oxygen (eq 32). Superoxide anion and its protonated form subsequently dismutate to yield hydrogen peroxide or peroxide anion.[1]

$$TiO_2\,(h^+) + OH_{ad}^- \rightarrow TiO_2 + HO_{ad}^{\bullet} \qquad (31)$$

$$TiO_2\,(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \qquad (32)$$

It has also been shown that the addition of hydrogen peroxide[148,152,153,161–165] considerably enhances the rate of photodegradation, most probably via reaction 33, or by surface-catalyzed dismutation of H_2O_2. Organic pollutants adsorbed onto the surface of the titanium dioxide particles will then be oxidized by $HO^{\bullet}$ radicals.

$$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + HO^{\bullet} \qquad (33)$$

This heterogeneous photoprocess has been found to be pH dependent,[111,147,166–170] the properties of the solid–liquid interface (e.g. the electrical double layer) being modified as the pH of the solution is varied. Consequently, the efficiency of the adsorption–desorption processes and, hence, the separation of the electron–hole pairs are also significantly affected. Recent investigations have shown that for the degradation of phenols and nitrophenols, photoreactivity increases in alkaline medium.[166]

3.5.3. Equipment Requirements

In numerous investigations, highly turbulent aqueous suspensions of TiO_2 particles in immersion type photochemical reactors have been used. However, the particle size of the added photocatalyst requires (ultra)centrifugation or microfiltration techniques for its separation from the treated liquid and therefore serious technical and economical problems for a further development of this procedure. These difficulties can be overcome by the use of TiO_2-covered supports in fluidized-bed-type reactors,[98] or by means of catalyst immobilization on beads,[171] inside tubes of either glass[172] or teflon,[173] fiberglass,[174,175] or woven fibers.[176]

3.5.4. TiO_2/UV Process Efficiency

The TiO_2/UV process is known to have many important advantages, in particular: a large number of organic compounds dissolved or dispersed in water can be completely mineralized; the rate of reaction is relatively high if large surface areas of the photocatalyst can be used; TiO_2 is available at a relative modest price and would be recycled on a technical scale; UV lamps emitting in the spectral region required to initiate the photocatalytic oxidation are well known and are produced in various sizes; improvements to increase the absorption cross section and to widen the spectral domain of absorption are sought by surface modifications and transition metal ion doping. Grätzel et al. could in fact show very high rates of absorbed photons on rough TiO_2 surfaces.[177] On the other hand, research work with metal ion doped TiO_2 aiming at a higher efficiency of oxidative degradation is not conclusive so far.

The quantum yield of the TiO_2/UV process is relatively low ($\Phi \leq 0.05$);[178] this method of water treatment has, however, the advantage of being operational in the UV-A domain with a potential use of solar radiation.[179] The nonlinear behavior[168] (half-power dependence[141,142,148,180]) of the photocatalytic oxidative degradation rate versus the rate of absorbed photons will nevertheless limit the effect of light amplification by solar collectors.

3.5.5. Problems in the Development of the TiO_2/UV Process

The development of a practical treatment system based on heterogeneous photocatalysis has not yet been successfully achieved, because there are many operating parameters which must be considered, in particular, type and geometry of photoreactor, the photocatalyst, the optimal use of energy, and wavelengths of the radiation. The central issue in the design of commercial units is the irradiation field in a scattering and absorbing heterogeneous medium. In addition, rates of reaction seem rather slow, but combinations of catalysts (e.g. TiO_2/Pt) show some potential, as the overall rate of oxidative degradation seems to be governed by the electron-transfer reaction from the conduction band of the semiconductor. Finally, experimental data from kinetic investigations are needed in order to evaluate the efficiency of fluidized- and fixed-bed reactors. Moreover, inhibiting factors in the photocatalytic treatment system should be investigated in more detail, as data on passivation and contamination are favorable but too scarce.[181]

In general, the photocatalyzed oxidative degradation process is, at its present state of development, too slow to be desirable as an alternative procedure to existing wastewater treatments. The process may, however, already find technical applications in small- to medium-sized units for the treatment of contaminated groundwaters and for the production of ultrapure water for pharmaceutical and microelectronic industries.

3.5.6. TiO_2/UV Process: Review of Recent Literature

Experimental data and results of recent publications on the TiO_2/UV process are summed up in Table VII. The table shows that in quite a number of reports and publications, the authors do not disclose TOC values, a vital parameter in wastewater treatment.

Okamoto et al.[97,99] studied the effects of several parameters, such as pH, O_2 partial pressure, initial phenol concentration, concentration of TiO_2, and additives (e.g. Cu^{2+}) to various semiconductor dispersions, on the removal of phenol under conditions listed in Table VII. Results indicate that the substrate was completely removed, but that reduction of TOC was $\leq$35% for 90 min of irradiation time.

Matthews[100,101,104,105,107,110] investigated the degradation of a variety of organic pollutants by the TiO_2/UV process using a spiral glass tube reactor loaded with a thin layer of TiO_2 (e.g. ref 100) as well as a noncoated spiral glass tube reactor (e.g. ref 110). A black-light fluorescent lamp (20 W) was used as the light source. The effects of substrate concentration, flow rate, temperature, TiO_2 loading, radiant power, total volume of substrate solution and geometry of reactor on the efficiency were investigated. For kinetic investigations, the formation of carbon dioxide and of ions, such as ammonium and nitrate, were monitored. In another publication, the author investigated the diminution of TOC in aqueous solutions of several common organic contaminants (acetic acid, benzoic acid, formic acid, ethanol, methanol etc.). Results, under experimental conditions listed in Table VII, indicate a high degree of TOC removal ($\geq$96%) within the first 10 min of irradiation. The author concludes that the TiO_2/UV process might be further developed as a means of TOC analysis for low initial substrate concentrations.

Abdullah et al.[111] investigated the degradation of salicylic acid, aniline, and ethanol using a reactor similar to that described in ref 109. They studied the effect of pH and other additives (chlorides, perchlorates, nitrates, sulfates, and phosphates) on the removal of organic material, determining the removed TOC by monitoring the CO_2.

Legrini et al.[39] used an annular semibatch reactor and a 125-W medium-pressure Hg lamp for their investigation of the complete mineralization of 1,2-dimethyl-3-nitrobenzene and of nitro-*o*-xylene contained in industrial wastewaters. They studied the effects of various semiconductor dispersions, wavelength, and initial hydrogen peroxide concentration on the rate of TOC diminution. Yet unpublished results show that more than 95% TOC removal was achieved within 50 min of irradiation time for initial model substrate concentrations of 120–130 mg/L. Results on the removal of nitro-*o*-xylenes from industrial wastewaters indicate that, under conditions shown in Table VII, TOC degradation rates were found to be approximately 0.9 ppm C/min.[40] The authors found that the TOC removal rate is significantly enhanced by the addition of hydrogen peroxide.

Jakob et al.[40,102] worked on the photocatalytic degradation of contaminated industrial wastewater using a multilamp semipilot plant reactor continuously sparged with gas (air, oxygen). Several parameters, including initial substrate concentration, TiO_2 loading, gas and liquid flow rates, and temperature, were studied in order to optimize the process. Results show that the photocatalytic treatment of a 20-L water sample loaded with 900 ppm C of nitro-*o*-xylenes was found to remove more than 95% of the initial TOC content.

In summary, the literature has established the capability of the photocatalytic oxidation to mineralize organic contaminants dissolved or dispersed in water. Furthermore, the process may be used as a photochemical procedure for the recovery of precious metals and for total organic carbon analysis within some concentration limits. Nevertheless, we believe that in a next step, technical development of the TiO_2/UV process will depend on new ideas for TiO_2 fixation and, consequently, on new designs of photochemical reactors.

3.6. Vacuum Ultraviolet (VUV) Process

3.6.1. Introduction

The vacuum ultraviolet consists of the UV spectral domain where air (oxygen) strongly absorbs radiation; its border with the UV-C is at 190 nm, and spectroscopic work at shorter wavelengths can only be performed in vacuum or in nonabsorbing gases. Excitation in the VUV spectral domain leads in most cases to the homolysis of chemical bonds.

VUV photochemical processes are becoming possible with the development of excimer light sources[23] emitting in this domain. Some years ago, the production of low-pressure Hg arcs emitting at 185 nm was abandoned by major lamp producers.

For applications in environmental protection engineering, degradation of organic material in condensed and gaseous phases are most interesting. For example, chlorinated and/or fluorinated hydrocarbons are readily attacked and such a procedure may initiate further oxidative degradation by means indicated above.

Besides being used for the photohomolysis of the target substance, VUV photolysis of H_2O is a means of highly efficient generation of hydroxyl radicals (eq 34),[192] which then attack the dissolved or dispersed substrate (e.g., eq 7).

$$H_2O \xrightarrow{h\nu} {}^1/_2H_2 + HO^\bullet \tag{34}$$

Xe excimer lamps now available can be used for water photolysis on a preparative scale without any attenuation, as far as filter effects by dissolved pollutants are concerned, and suitable photochemical reactors are at present developed for the purpose of ground- and wastewater decontamination, as well as for the pro-

Table VII. Review of Experimental Conditions and Results of the TiO_2/UV Process

substrate	light	reactor, vol (L)	TiO_2	Gas	T (°C)	pH	$[c_0]$	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	$-TOC$[b] (%)	parameters[c]	ref
4-chlorophenol	>310 nm		2[d]	O_2		3	6[e]	14	50	–	–	catalyst dispersions	129, 144
3,4-dichlorophenol	>330 nm					3	18[e]	45	50				
2,4,5-trichlorophenol	>330 nm					3	20[e]	55	50				
pentachlorophenol	>310 nm					3	12[e]	20	50				
sodium pentachlorophenolate	>330 nm					10	12[e]	15	50				
chlorobenzene	>330 nm					2.5	45[e]	90	50				
1,2,4-trichlorobenzene	>330 nm					3	10[e]	24	50				
pentachlorophenol	>310 nm	0.02	2[d]	O_2	45	3	4.5×10^{-5} [f]	8	50	–	–	catalyst dispersions; pH, wavelength	128; 129
phenol	MP[h] Hg 100 W EP[i]	0.4	2.5[g]	O_2	25	3.5	10^{-3} [f]	90	100	62	≤35	catalyst dispersions O_2 partial pressure, additives, solar irradiation, pH, $[c_0]$, TiO_2 quality, UV power	97, 99
trichloroethylene	MP[h] Hg 100 W EP[i] 4 W at 365 nm	0.4	0.2[g]	O_2	25	2.9–4.4	10^{-3} [f]	–	–	–	–	$[c_0]$, pH, TiO_2 quality, solar irradiation, (CO_2 monitoring)	182
chlorobenzenes							10^{-3} [f]						
nitrobenzene							10^{-3} [f]						
chlorophenols							10^{-3} [f]						
phenol, benzene							10^{-3} [f]						
benzoic acid							10^{-3} [f]						
dichloroethane							10^{-3} [f]						
chloroform							10^{-3} [f]						
atrazine	≥340 nm 1500-W Xenon lamp		0.1[d]	–	–	–	5[e]	10; 50	50; 100	–	–	$[c_0]$, TiO_2 quality	151
salicylic acid	Hg 20 W EP[i] black light fluorescence	0.5[j]	85[k,l]	no gas	24–29	–	10^{-5} [f]	7.11	50	–	–	type of reactor (spiral, annular), flow rate, $[c_0]$	100
phenol							10^{-5} [f]	9.72	50				
4-chlorophenol							10^{-5} [f]	8.74	50				
2-chlorophenol							10^{-5} [f]	8.22	50				
salicylic acid	Hg 20 W EP[i] black light fluorescence	0.5[j]	85[k,l]	no gas	25	–	10^{-5} [f]	7.11	50	–	–	TiO_2 loading, flow rate, T, $[c_0]$	101, 105
phenol							10^{-5} [f]	7.17	50				
4-chlorophenol							10^{-5} [f]	8.22	50				
2-chlorophenol							10^{-5} [f]	8.73	50				
benzoic acid							10^{-5} [f]	6.92	50				
2-naphthol							10^{-5} [f]	8.53	50				
naphthalene							10^{-5} [f]	4.33	50				
fluorescein							10^{-5} [f]	6.41	50				
phenol	MP[h] Hg 500 W EP[i] 44.7 W at 385 nm	2	1[d]	O_2	36	3	80[e]	–	60[m]	–	–	semiconductor type, pH, $[c_0]$, TiO_2 loading, O_2 partial pressure, radiant power, solar irradiation, anion addition, He, He/O_2	130
phenol	Hg 20 W EP[i] black light fluorescence	n	1.2 g per 70 g SiO_2[o]	atm	–	–	10^{-5} [f]	6	≥99.9	–	–	$[c_0]$, TiO_2 loading, flow rate, type of reactor, radiant power	104
salicylic acid	20-W lamp	0.5[p]	1.2 g per 70 g SiO_2[o]	no gas	20–25	–	10^{-5} [f]	3.68	50	–	–	$[c_0]$, TiO_2 loading flow rate, type of reactor, radiant power	104
phenol							10^{-5} [f]	4.91	50				

Table VII (Continued)

substrate	light	reactor, vol (L)	TiO_2	Gas	T (°C)	pH	[c_0]	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	$-TOC$[b] (%)	parameters[c]	ref
phenol	40-W lamp	annular reactor single pass[q]	0.15 g per 60 g SiO_2[o]	atm	–	–	10^{-5} [f]	8	99.9	–	–	[c_0], TiO_2 loading, flow rate, type of reactor, radiant power	104
salicylic acid							10^{-5} [f]	8	99.9				
fluorescein							10^{-5} [f]	8	99.9				
2-chlorophenol							10^{-5} [f]	8	99.8				
4-chlorophenol							10^{-5} [f]	8	99.2				
2-naphthol							10^{-5} [f]	8	99.9				
catechol							10^{-5} [f]	8	99.6				
sodium salicylate	100 W	0.4	0.2[g]	–	–	4.5	5×10^{-5} [f]	14	85	–	–	–	125
o-dichlorobenzene	K 40 W 09 N 300–430 nm	1[r]	–	–	–	–	20[e]	180	≥60	–	–	–	183
m-dichlorobenzene							20[e]	180	≥60				
p-dichlorobenzene							20[e]	360	≥25				
2,3,4-trichlorobiphenyl							10[s]	180	≥45				
methylene blue	Hg 20 W EP[i] black light fluorescence	0.5[t]	85[l]	atm	–	–	10^{-5} [f]	11.8	50	–	–	[c_0], flow rate, volume, solar irradiation	107
theophylline	Hg 20 W EP[i] black light fluorescence	*u*	85[l]	–	–	–	1.8×10^{-4} [f]	–	–	–	–	CO_2, NH_4^+, nitrate ion monitoring	106
proline							6×10^{-4} [f]						
pyridine							4×10^{-4} [f]						
piperidine							5.4×10^{-4} [f]						
trichloroethylene	MP[h] Hg 500 W EP[i]	0.5	1.2[d]	atm	–	3–4	4.5×10^{-4} [f]	60	70	–	–	H_2O_2 addition, volume, semiconductor type	161
		0.025					3.5×10^{-4} [f]	25	50				
Kraft lignin	MP[h] Hg 500 W EP[i]	0.02	rutile 0.5[g]	atm	–	–	0.02[v]	180	≥99	–	–	TOC, color, product monitoring	184
4-chlorophenol	6 × Hg 15 W EP[i] black light fluorescence	0.25[w]	440[l]	atm	30	5.8	6.3×10^{-5} [f]	120	92	–	–	[c_0], HCl addition, mixtures of substrates	108
(mixture of) 4-chlorophenol							6.3×10^{-5} [f]	180	≥70				
2,4,5-trichlorophenol							6.3×10^{-5} [f]	180	≥70				
2,4-dichlorophenol							6.3×10^{-5} [f]	180	≥70				
benzene	7 × Hg 15 W EP[i] black light fluorescence	RSR,[x] 0.6	1[d]	O_2	20	–	2.8×10^{-4} [f]	40	≥99	–	–	TiO_2 loading, binary reactant	185
perchloroethylene							2.07×10^{-4} [f]	40	≥99				
2-chlorophenol	MP[h] Hg HPK 125 W EP[i]	0.02	2.5[d]	atm	–	4.5	20[e]	120	99	–	–	[c_0], pH, volume, radiant power, mixtures of substrates	186
3-chlorophenol						4.7	20[e]	110	99				
4-chlorophenol							20[e]	80	99				
phenol	MP[h] Hg 1000 W EP[i]	2	1[d]	O_2	36	3	1.2×10^{-3} [f]	75	≥83	–	–	additives (H_2O_2), He	162
acetic acid	Hg 20 W EP[i] black light fluorescence	0.04[y]	85[l]	O_2	–	3.5	–	10		120[z]	99.2	TOC analysis	109
benzoic acid								10		168[z]	98.2		
ethanol								10		144[z]	95.8		
formic acid								10		119[z]	100		
methanol								10		144[z]	96.5		
nitrobenzene								10		144[z]	97.9		
propan-2-ol								10		158[z]	99.4		
salicylic acid								10		168[z]	101.2		
sucrose								10		144[z]	99.3		
4-nitrophenol								10		72[z]	100.8		
2,4-dichlorophenol	300–400 nm	3[aa]		atm			10[e]	12	95	–	–	[c_0], flow rate, O_2	175
pentachlorophenol							100[e]	≤15	99.5				

Table VII (Continued)

substrate	light	reactor, vol (L)	TiO_2	Gas	T (°C)	pH	[c_0]	t (min)	$-c$[a] (%)	TOC_0 (ppm C)	$-TOC$[b] (%)	parameters[c]	ref
dichloromethane	MP[h] Hg 500 W EP[i]	0.025	2.8[d]	–	–	–	5×10^{-4} [f]	80	50	–	–	H_2O_2 addition	163
chloroform							5×10^{-4} [f]	65	50				
carbon tetrachloride							5×10^{-4} [f]	480	50				
1,1-dichloroethane							5×10^{-4} [f]	97	50				
1,2-dichloroethane							5×10^{-4} [f]	53	50				
1,1,1-trichloroethane							5×10^{-4} [f]	125	50				
1,1,2-trichloroethane							5×10^{-4} [f]	68	50				
1,1,1,2-tetrachloroethane							5×10^{-4} [f]	69	50				
1,1,2,2-tetrachloroethane							5×10^{-4} [f]	55	50				
1,2-dichloroethylene							5×10^{-4} [f]	51	50				
trichloroethylene							5×10^{-4} [f]	63	50				
tetrachloroethylene							5×10^{-4} [f]	48	50				
phenol 2-chlorophenol 3-chlorophenol 4-chlorophenol acetic acid benzoic acid ethanol formic acid methanol nitrobenzene salicylic acid	Hg 20 W EP[i] black light fluorescence	0.04[ab]	0.04[g] (1[d])	atm	40	3.5	1–50[e]	–	–	–	–	flow rate, TiO_2 loading, [c_0], solar irradiation, (CO_2 monitoring)	110
acetic acid monochloroacetic acid dichloroacetic acid trichloroacetic acid	MP[h] Hg 100 W EP[i]	0.4	0.4[g] (1[d])	O_2	25	–	10^{-3} [f]	–	–	–	–	type of gas (N_2, O_2, N_2O), H_2O_2 addition (CO_2, Cl^- monitoring)	187
phenol	MP[h] Hg 1000 W EP[i]	2	1[d]	O_2	36	3	0.1[d]	60	≥95	–	–	He, H_2O_2, Ag^+, TiO_2 type (rutile, anatase)	164
atrazine (in soil)	1500-W Xe lamp ≥340 nm	pyrex cell, 0.005	0.5[d]	–	–	–	25[e]	15	>99	–	–	semiconductor type, TiO_2/soil slurries, ZnO/soil slurries, type of soil	188
phenol	MP[h] Hg 400 W EP[i] ≥300 nm	1	2.5[d]	O_2	35	2	1000[e]	480	24	–	–	H_2O_2 addition, Fe^{3+}, Cu^{2+}, pH, type of gas	165
phenol	MP[h] Hg 1600 W EP[i]	test tube, 0.015	0.15[g]	O_2	25	7	10^{-3} [f]	300	≥95	–	–	O_2, N_2 pH, T, [c_0], TiO_2	167
salicylic acid aniline ethanol	Hg 20 W EP[i] black light fluorescence	0.02[ac]	85[l]	air	50	4.1	–	–	–	5 5 5	–	Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, pH	111
4-chlorophenol	MP[h] Hg HPK 125 W EP[i] ≥ 340 nm	0.02	0.04[g]	air	20	7	80[e] 20[e]	150 60	99.9 99.9	–	–	semiconductor type, TiO_2 loading, [c_0], pH, T, radiant power	142
amines, nitrogen or sulfur-containing organic compounds	Hg 20 W EP[i] black light fluorescence	0.04[ad]	85[l]	–	–	–	–	–	–	–	–	[c_0], radiant power, (NO_3^-, NH_4^+, CO_2 monitoring)	112
ethanol	RH 400–10 W	0.002	0.03 3[g]	O_2	25	–	3.43×10^{-2} [f]	–	–	–	–	type of catalyst, O_2, Ar, air, product monitoring	189
chromium [Cr(VI)]	MP[h] Hg HPK 125 W EP[i]	annular flow reactor, 0.2	0.5[d]	Ar	41	1	35.5[e]	105	95	–	–	flow rate, gas flow, [c_0], TiO_2 loading, pH, T, semiconductor type	147
phenol	MP[h] Hg 400 W EP[i]	1	2.5[d]	O_2	35	6.5	2[d]	360	18	–	–	[c_0], TiO_2 loading, pH, O_2 flow, radiant power	168

Table VII (Continued)

substrate	light	reactor, vol (L)	TiO_2	Gas	T (°C)	pH	$[c_0]$	t (min)	$-c^a$ (%)	TOC_0 (ppm C)	$-TOC^b$ (%)	parameters^c	ref
chloroform trichloroacetate chloroethyl-ammonium	Xe lamp 450 W EP^i	0.1	0.5^d	air	23	–	–	–	–	–	–	$[c_0]$, pH, O_2, radiant power	169
o-cresol *m*-cresol *p*-cresol	MP^h Hg/Xe 900 W EP^i	0.05	2^d	air	30	3	20^e 20^e 20^e	180 180 180	$\geq 80^{ae}$ $\geq 80^{ae}$ $\geq 80^{ae}$	–	–	$[c_0]$, pH, O_2, radiant power	170
2-nitrophenol 3-nitrophenol 4-nitrophenol	Xe 1500 W EP^i	0.05	1^d	O_2	40	3	0.08^d 0.08^d 0.08^d	360 360 360	≥85 ≥50 ≥80	–	–	TiO_2 loading, O_2, $[c_0]$, reactor volume, anions	190
2-nitrophenol 3-nitrophenol 4-nitrophenol	MP^h Hg 500 W EP^i	1.5	$0.2–2^d$ 2^d	O_2 or He/O_2	27	–	$0.03–0.3^d$	–	–	–	–	TiO_2 loading, O_2, $[c_0]$, reactor volume	190
methylene blue salicylic acid rhodamine methyl orange	MP^h Hg 100 W EP^i	RSR,^{x} 0.250	0.5^{af}	–	21 –27	6	$9 \times 10^{-6\,f}$ $8 \times 10^{-6\,f}$ $8 \times 10^{-6\,f}$ $8 \times 10^{-6\,f}$	26 13.6 29.6 38.7	50 50 50 50	–	–	$[c_0]$, TiO_2 loading, volume, flow rate, solar irradiation, H_2O_2 addition	153
2-chlorophenol 2,7-dichloro-dibenzodioxine atrazine	Xe 1500 W EP^i	pyrex cell, 0.005	0.5^d	O_2	60	–	$1.5 \times 10^{-4\,f}$ $1.56 \times 10^{-4\,f}$ $1.16 \times 10^{-4\,f}$	9 120 30	66 87 ≥99	–	–	O_2, $S_2O_8^{2-}$, IO_4^-, ClO_3^-, H_2O_2	191
1,2-dimethyl-3-nitrobenzene	MP^h Hg HPK 125 W EP^i >320 nm	0.220	5^d	air	40	7	120^e	50	>99	–	>95	various catalysts, H_2O_2, wavelength	39
nitro-*o*-xylenes (industrial wastes)	MP^h Hg HPK 125 W EP^i	0.220	5^d	air	50	2	–	540	–	800	≥60	H_2O_2	40
nitro-*o*-xylenes (industrial wastes)	5 × 700 W EP^i MP^h Hg	20	5^d	air	–	1.7	–	2400	–	900	>95	$[c_0]$, TiO_2 loading, gas flow rate, T, type of gas	102
benzene toluene *o*-xylene *m*-xylene *p*-xylene cumene	MP^h Hg HPK 125 W EP^i		0.25^d	–	–	–	$2 \times 10^{-4\,f}$ $2 \times 10^{-4\,f}$ $2 \times 10^{-4\,f}$ $2 \times 10^{-4\,f}$ $2 \times 10^{-4\,f}$ $2 \times 10^{-4\,f}$	18 78 42 12 30 <6	50 50 50 50 50 50	–	–	–	67

[a] Substrate concentration removed. [b] TOC removed. [c] Parameters studied. [d] g/L. [e] mg/L. [f] M. [g] g. [h] MP, medium pressure. [i] EP, electrical power. [j] Coated spiral glass tube, coil volume 90 cm^3, continuous recirculation mode. [k] TiO_2 (Degussa-P25) coating inner surface of spiral glass. [l] $\mu g/cm^2$. [m] mg/L h. [n] Spiral glass tube, single pass, open system mode, flow rate 20 mL/min. [o] Supported colloidal TiO_2 photocatalyst. [p] Closed system, continuous recirculation mode, flow rate 120 mL/min. [q] Spiral glass tube, single pass, open system mode, flow rate 10 mL/min. [r] Nutile's photoreactor, commercial prototype reactor, recirculation mode. [s] $\mu g/L$. [t] TiO_2 (Degussa P25) coating inner surface of spiral glass, liquid flow rate 100 mL/min. [u] Coated spiral glass tube, coil volume 90 cm^3, continuous recirculation mode, flow rate 184 mL/min. [v] % wt. [w] Spiral glass coil, volume 75 cm^3, flow rate 250 mL/min. [x] RSR, recirculating flow reactor. [y] Coated spiral glass tube, solution volume 40 cm^3, continuous recirculation mode. [z] Mass of carbon (μg) added to the solution (40 mL). [aa] Nutile's reactor. [ab] Spiral glass tube not coated with TiO_2, flow rate 270 mL/min. [ac] Coated spiral glass tube, coil volume 90 cm^3. [ad] Coated spiral glass tube, coil volume 90 cm^3, flow rate 180 mL/min. [ae] Complete mineralization to CO_2 and water in air-equilibrated TiO_2 suspensions takes place in 7–8 h at pH 3 (with O_2, degradation is faster, ≤ 2.5 h). [af] Grams per 100 g of sand.

duction of ultrapure water for the use in the pharmaceutical and microelectronic industries. Recent data show that this procedure for the generation of hydroxyl radicals is competitive with the other processes mentioned so far.

3.6.2. VUV Process: Equipment Requirements, Process Efficiency, and Development Problems

Preparative scale experiments involving environmental aspects were made possible by the development of Xe excimer VUV sources with a wavelength of 172 ± 12 nm and with up to 1000-W electrical power. Braun et al. have been carrying out water decontamination experiments and corresponding kinetic investigations using excimer lamps of 150-W electrical power placed along the axis of a cylindrical photochemical reactor.[19,40,193,194] Such reactors may be used as recirculating batch or flow-through reactors.

Technical applications are so far limited to aqueous systems containing relatively low concentrations of organic pollutants; however, concentration limits depend on the chemical structure of the compound to be oxidized. In such a reactor geometry, the irradiated annular volume is reduced to a thin layer (ca. 70-μm thickness) located around the light source. This volume is rapidly depleted of oxygen depending on the number of $HO^•$ radicals produced per unit of time and on the efficiency of reaction 7 mentioned above, as the addition of oxygen to the intermediate organic radicals (eq 8) is highly competitive. Already at the electrical powers mentioned, the Xe excimer lamp produces high local concentrations of hydroxyl radicals and, consequently, of organic radicals which under conditions of insufficient oxygen supply may polymerize. For high TOC concentrations, reactor designs must be changed in order to improve the oxygen logistics in the irradiated reactor volume.

In general, the VUV process is very simple and has the particular advantage that no chemicals need to be added. The process represents a real challenge to other photochemical water treatment processes.

3.6.3. VUV Process: Review of Recent Work

Due to the yet very limited availability of the excimer light sources, only a small number of research groups are active in this field (e.g. Glaze et al.,[195] Braun et al.) and results have been presented so far only in symposia proceedings. Our work in this domain has been focused so far on the degradation of a number of model substrates, such as 4-chlorophenol, xylidines, 3-methylisoxamine, and dimethyl-3-nitrobenzene in aqueous solution.[102,193,194,196,197] Experiments were performed in a 1-L batch reactor in a recirculating mode using a 172-nm Xe excimer lamp, and effects of several reaction parameters, such as substrate concentration, volume of solution, temperature, liquid flow rate, added chemicals and gases on the rates of degradation have been investigated. For example, some results show that a 90% TOC removal of 4-chlorophenol and of a mixture of xylidine isomers (initial concentrations approximately 5×10^{-4} M) occurred within 120 min of irradiation of solutions of 750 and 1000 mL, respectively. For a given set of experimental conditions, a degradation efficiency of approximately 70 (mg C) per kWh has been determined. Potential improvements depend entirely on the implementation of new reactor geometries which take into account the extremely high absorption cross section of water.[102,193,194]

4. Photochemical Electron-Transfer Processes

Photochemical electron-transfer processes of current interest in environmental research comprise: electron-transfer reactions upon electronic excitation of the organic contaminant in the aqueous medium; photocatalyzed electron-transfer processes; and electron-transfer processes upon electronic excitation of natural components of the aquatic system, such as humic materials. This classification is at present of pure academic interest, as practical examples are scarce or nonexistent.

Taken from the vast literature on photoinduced electron transfer,[198] a large number of electronically excited organic molecules could transfer an electron to acceptors present in its complex environment (e.g. eq 2). Oxidation could also take place by photoionization. However, the concentration of reductive agents in a natural environment cannot be very important, as such pollutants would be degraded rapidly by microbial processes or in abiotic thermal reactions involving e.g. activated oxygen species.

Under reductive conditions, aliphatic halogenated hydrocarbons may be transformed in a series of reaction steps to the corresponding alkanes. Such conditions can for instance be generated by photoredox catalysis, involving reaction systems thoroughly investigated for the hydrogen production from water.[199] Wang et al. reported the dehalogenation of chloroform, bromoform, chlorodibromoethane, and TCE using the well-known $Ru(bipy)_3^{2+}$/methyl viologen system for the production of the required electrons.[200] The rate of photohydrogenolysis is considerably enhanced by the addition of Zn, and the authors interpret their results by postulating a metal–hydrogen bond as the reactive center for subsequent dehalogenation of the substrate.

Recently, Bolton et al. presented patent examples for the reductive dehalogenation of chlorinated aliphatics in aqueous solution.[65]

A number of examples show that light-induced electron-transfer reactions using chromophore aggregates as donors are more efficient than corresponding reactions with isolated molecules. Humic acids are macromolecules of yet unknown structure but act as multichromophoric systems. The hypothesis of intramolecular chromophore interactions has found support in photochemical experiments resulting in the production of solvated electrons.[201] Humic substances present in surface waters may hence play an important role in the (photochemical) production of superoxide anion and hydrogen peroxide in our aquatic environment.

5. Energy-Transfer Processes

Energy-transfer processes may occur between a large number of organic compounds present in surface waters. However, we would like to focus on the generation of singlet molecular oxygen, as this activated oxygen species is thought to be of some importance in abiotic self-purification processes taking place in surface waters. Several authors have shown that humic and fulvic acids may act as singlet oxygen sensitizers,[202–210] the quantum yield of singlet oxygen production being ca. 3% and depending on the nature of the sensitizer.[211,212] However, the reactivity of singlet oxygen and, hence, its impact as an oxidizing species in natural waters seems overestimated. Singlet oxygen is known to react rather specifically with π-systems of relatively high electron density, sulfides and amines.[13,14] The specificity of singlet oxygen reactions has recently been shown by Frimmel et al. in investigations involving EDTA complexes and atrazine derivatives.[26,213,214] The importance of singlet oxygen reactions in aquatic systems is reduced by its efficient physical deactivation by H_2O; additional deactivation may take place by transition metals present in surface waters.[26,214]

6. Summary and Outlook

This review concentrates on the experimental work in view of a technical development of AOP's. Mechanistic interpretations and corresponding fundamental investigations have been included in as much detail as seems necessary for an evaluation of the technical potential of the different processes. These parts of the overview lead to the conclusion that, for a given case of water treatment, the most efficient procedure or combination of procedures has to be determined, with pollutant nature, absorption spectrum, concentration, and reactivity, as well as inhibitory effects of pollutant mixtures[185] and the presence of radical trapping agents being the most important parameters. Possible technical solutions may then be found in modular installations which can be adapted and/or combined in accord with the fundamental rules of photochemical technology[215] and substrate reactivity.

In checking the vast selection of experimental results, the lack of pertinent information which would allow evaluation of their efficiency and up-scaling potential, as well as comparisons of different procedures for the same type of pollutant is evident and seems to plague most of this literature. Besides information concerning make and electrical power of the light source, reactor volume, initial concentration of model pollutants, and times of irradiation which in general is included in experimental parts, details on reactor geometry and material, initial absorption spectrum and its dependence on irradiation time, procedure of addition of reagents and catalysts, temperature, pH of the reaction system, presence of radical traps (e.g. carbonate, bicarbonate) or UV filters (e.g. nitrates), flow of substrate solution and purging gas should be included.

For process efficiency evaluations, we would like to stress again the importance of the quantification of the energy consumed, e.g. by using an appropriate energy meter.[102]

The UV energy efficiency

$$\phi_e = Q_{UV}/\Delta(\text{mg C}) \qquad (35)$$

where Q_{UV} is the absorbed energy[188] in the UV spectral domain, has been proposed in order to express the absorbed energy in the UV region per milligram of carbon oxidized.[83] In practice, a somehow compromised quantum yield determination is made by taking the emitted energy. In fact, absorbed energies are very difficult to determine in multichromophore reaction systems with considerable spectrum and absorbance variations. In contrast, approximate emitted energies can be calculated from product specifications published by the lamp producers, and corresponding UV energy efficiency calculations lead to maximum values which are, however, of limited usefulness.

The efficiency of the oxidative degradation by O_3/UV is sometimes expressed by the ratio of ΔTOC to the quantity of ozone consumed (efficiency ratio, eq 36). Assuming that one atom of oxygen in each ozone molecule is used in the process, the two other oxygen atoms being lost as molecular oxygen, the efficiency ratio is defined as the ratio of TOC oxidized to carbon dioxide to the molar equivalent of ozone fed into the process.

$$\text{efficiency ratio} = \frac{\Delta\text{TOC} \times \text{total volume}}{{}^1/_8 \times [O_3] \times \text{volume of gaseous } O_3 \text{ used}} \qquad (36)$$

where ΔTOC is expressed in mg C/L, the volumes in L, and the concentration of O_3 in mg/L of gas. The factor $^1/_8$ is to account for molar ratio requirement of 2 mol of ozone (96 g) per 1 mol of organic carbon to be oxidized (12 g).

For comparisons of process efficiencies, the use of these results would imply that energy costs of light production are negligible in comparison to those of ozone generation.

Of more pragmatic use and independent of the difficulties to determine radiant energies or photonic rates in complex media, the ratio of ΔTOC to energy consumption seems most useful for the comparison of different AOP's for the same model substrate, as well as for optimal reactor design and cost effectiveness for a given procedure from laboratory to technical scale.[98,216] Efficiencies are expressed as the ratio of ppm TOC destroyed to electrical power consumed during the same time of irradiation. By multiplication with the total volume of solution treated, eq 37 yields a value independent of the size of the equipment used.

$$\phi = \frac{\Delta\text{TOC} \times \text{total volume}}{\text{power (kWh) consumed}} \qquad (37)$$

The diminution of the concentration of a model compound as a function of irradiation time is not a sufficient argument for a potential technical application. Oxidative degradation should also be analyzed by TOC or DOC measurements in order to quantify the degree of oxidation. On one hand, ratios of substrate depletion rate to energy consumption may lead to optimistic interpretations as far as times of irradiation, lamp size, and power consumption are concerned. On the other hand, complete mineralization of dissolved or dispersed organic material would make technical applications of AOP's impossible for economical reasons, as the rate of organic carbon depletion slows down at lower TOC values. Practical solutions will be found in most cases in aiming for a predefined degree of oxidation (incomplete oxidation) where the chemical treatment can be stopped and the treated solution led to a biological treatment station or directly into an effluent without any toxicologic hazard.

In general, TOC diminution is following apparent zero-order kinetics for a large fraction of the irradiation time, leading to complete mineralization. Under conditions of substrate photolysis, pseudo-first-order regime is found when initial substrate concentrations are very low and absorbance variations negligible. In mediated processes, the rate of all oxidative degradation reactions depends on the concentration of hydroxyl radicals acting as initiator and on the concentration of dissolved molecular oxygen. For TiO_2-photocatalyzed processes, apparent zero-order kinetics of TOC diminution is observed under conditions, where saturation coverage of the active surface sites by organic molecules is achieved, or where a steady-state concentration of hydroxyl radicals is generated at the surface of the irradiated TiO_2. Therefore, determination of TOC depletion rates may be achieved without difficulty in applications focusing on incomplete degradation processes of aqueous systems of high initial pollutant concentration.

The situation is different for experiments using model compounds, the concentration of which decreases rather rapidly by 1 or 2 orders of magnitude. An apparent zero-order kinetics of depletion might then change rapidly to a first, second, or mixed order regime at low concentrations depending on the process investigated. In the case of the TiO_2-photocatalyzed degradation, the kinetics of substrate degradation has been successfully modeled by the Langmuir–Hinshelwood equation modified for competitive adsorption of solvent and substrate molecules on the active sites of the photocatalyst.[101,108,114,125,130,141,217-220]

Taking into account the importance of light-driven reactions for the existence of life on this planet, it is rather astonishing that only a relatively small number of research groups is consistently investigating the vast pool of photochemical reactions with which nature makes use of the debris of synthesis and destruction. On the other hand, applications of photochemical reactions in the domain of environmental techniques attract considerable interest. The present situation is similar to that observed in the early days of photochemical solar energy conversion; in both cases, laboratory results were hastly extrapolated to a technical scale and many of the basic rules acquired in technical development ignored. From the reviewed literature, qualitative interpretations and generalizations may be made, but for an evaluation of the technical and economical feasibility of a given procedure, series of experiments under defined and reproducible conditions are necessary, the results of which will not appear in the literature until technical implementation has been reached.

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