

Purification of drinking water by irradiation. A review

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Abstract. The present review deals with the possibilities of water purification by UV-light, solar energy in combination with catalysts (e.g. $n\text{-TiO}_2$), as well as by using ionizing radiation (e.g. high energy electrons or γ -rays). The various methods are illustrated by typical examples concerning the degradation of aliphatic and aromatic halogenated pollutants in water. Some probable reaction mechanisms initiated by light or ionizing radiation are also given.

Keywords. Water purification; pollutants; degradation; photolysis; radiolysis.

1. Introduction

Water is the most important life factor for all living systems. As a consequence of the rapid development of various industries, the application of fertilizer, pesticides etc. in modern agriculture, the production and combustion of fossil fuels etc., there has been a strong overloading of water resources. On the other hand, the chlorination of drinking water (containing humic substances) for the purpose of disinfection leads to the formation of a number of toxic compounds (Rock 1974; Hutzinger *et al* 1982; Getoff 1986a). Hence, a subsequent purification of the water, e.g. by filtration through activated carbon, is necessary.

Careful investigations by various laboratories in the recent years proved that biological resistant pollutants in water can be decomposed by UV-light, solar energy in the presence of special catalysts, e.g. $n\text{-TiO}_2$, and ionizing radiation. All these three possibilities are later illustrated by examples and critically discussed. Based on the present state-of-the-art a comparison between them is made with respect to their technical application.

2. Photoinduced degradation of water pollutants

2.1 Using VUV- and UV-light

In the last decades, a number of papers have been published about the photoinduced decomposition of water pollutants. Only some of them will be briefly mentioned in the frame of this review, since further papers on nearly the same topics are also on the programme.

Naturally, a *direct photochemical degradation* can be achieved only when the incident light (vacuum-UV-quanta: $\lambda < 200$ nm or UV-light: $\lambda > 200$ nm) is absorbed by the

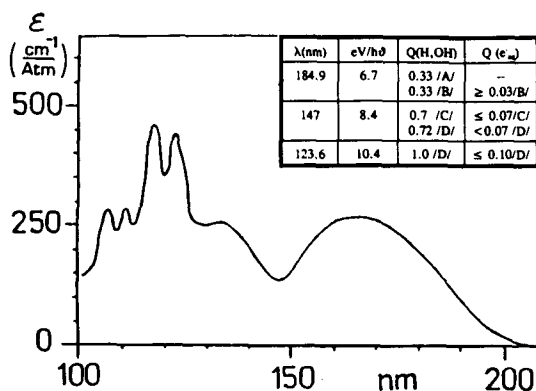


Figure 1. Absorption spectrum of water (Watanabe and Zelikoff 1953). Inset: Quantum energy (eV/h ν) and quantum yields (Q) of the primary products of water photolysis with VUV-light at 123.6, 147 and 184.9 nm. (A) Dainton and Fowles 1965b; (B) Getoff 1968b; (C) Sokolov and Stein 1966; (D) Getoff and Schenck 1968.

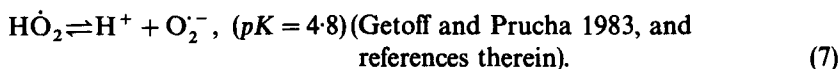
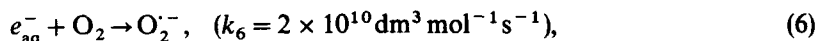
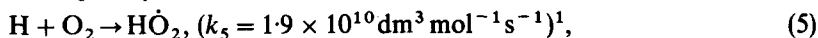
pollutant in question. As sources for VUV-light, low pressure Hg-lamps emitting simultaneously $\lambda = 184.9$ nm (10%) and 253.7 nm (100%) are mostly used. For UV-light the same lamps were equipped with a Vycor-filter for absorption of the 184.9 nm-line, as well as medium pressure Hg-lamps, emitting several lines in the range of 250 to 578 nm.

2.1a *Water photolysis*: Figure 1 shows the absorption spectrum of water as well as the quantum yield (Q) of H, OH and e_{aq}^- of the primary products of water photolysis for three VUV-lines. The light at 123.6 and 147 nm can be produced by electrodeless special lamps (Getoff 1968a; Getoff and Schenck 1968). The VUV-light at these two wavelengths is at present of no practical interest, but is rather important with respect to the ozone chemistry in the upper atmosphere.

As can be seen from figure 1, the VUV-line at 184.9 nm is absorbed by water and hence it can be photolytically decomposed:



The free radicals so produced, OH, H and e_{aq}^- (solvated electrons), can initiate the decomposition reactions of water pollutants. In the presence of air, both H and e_{aq}^- are converted into peroxy-radicals.



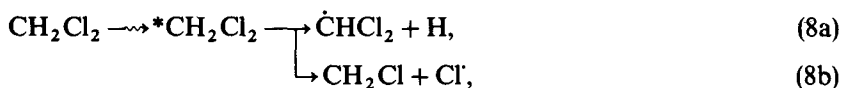
¹ If not otherwise specified, the constants used (k) are taken from Buxton *et al* (1988).

The HO_2 species are in general more reactive than the O_2^- ones. The absorbed energy per quantum at 184.9 nm is: $E = 6.7 \text{ eV}/h\nu$, which was taken as basis for calculation of the "photochemical" G -values² of: $G_{\text{ph}}(\text{H}, \text{OH}) = 4.92$ and $G_{\text{ph}}(e_{\text{aq}}^-) \leq 0.45$ at pH 7.

In the following the photoinduced decomposition of *dichloromethane* and *tetrachloroethylene* in aqueous solution as representatives of halogenated aliphatic pollutants are briefly discussed.

2.1b Dichloromethane: This compound is studied in the presence of air in neutral aqueous solutions as a model for the halogenated, simple aliphatic compounds (Getoff 1991, and references therein). Its major absorption lies in the VUV-range (see figure 2). Hence, using VUV-light of 184.9 nm, both processes – direct electronic excitation of the substrate as well as photolysis of water – take place simultaneously. The yield of the photoinduced Cl-cleavage is determined as a function of the absorbed light energy and is taken as an indicator of the decomposition process. This dependence is shown in figure 2. It is obvious that upto a VUV-dose of about $3.9 \times 10^{16} \text{ hv}\cdot\text{ml}^{-1}$ the formation of Cl^- ions is linear with absorbed energy and later on tends to a saturation value.

In addition to the photolysis of water (reactions (1) to (4)), a direct excitation of CH_2Cl_2 by the 184.9 nm VUV-light also takes place:



The H-atoms are scavenged by O_2 , according to reaction (5), resulting in HO_2 radicals which are converted into O_2^- species (see reactions (5) to (7)). Both transients, $\dot{\text{C}}\text{HCl}_2$ and $\dot{\text{C}}\text{H}_2\text{Cl}$ react with oxygen and the resulting peroxy-radicals subsequently lead

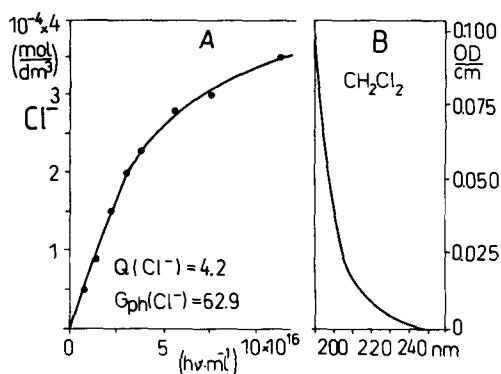


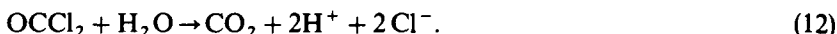
Figure 2. (A) Photoinduced Cl-cleavage from aqueous air-saturated $2 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ CH_2Cl_2 using $\lambda_{\text{exc}} = 184.9 \text{ nm}$. (B) Absorption spectrum of $10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ CH_2Cl_2 in water (pH ~ 7).

² G -value = number of formed or decomposed molecules per 100 eV absorbed energy. For conversion to SI-units multiply the G -value by 0.10364 to obtain $G(x)$ in $\mu\text{mol}\cdot\text{J}^{-1}$. Initial G -value (G_i) = yield before the degradation of final product occurs.

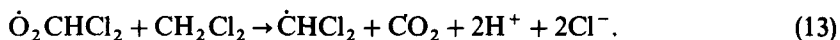
to degradation of the pollutant (Getoff 1991):



Phosgene (OCCl_2) is formed as an intermediate, but it is not stable in aqueous solution and hydrolyzes (Asmus *et al* 1985; Getoff 1989b):



It has been shown (Packer *et al* 1980; Alfassi *et al* 1987) that by increasing the number of halogen atoms in the molecule also, the reactivity of the peroxy radical is enhanced. Therefore, it is expected that the $\dot{\text{O}}_2\text{CHCl}_2$ species are stronger in reacting with organic compounds than $\dot{\text{O}}_2\text{CH}_2\text{Cl}$:

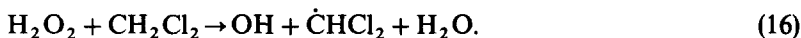
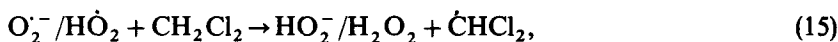


The OH radicals from the water photolysis at 184.9 nm (reactions (1) and (4)) as well as those from reactions (9) to (11) can also react with CH_2Cl_2 , whereas the H atoms resulting from reactions (1) as well as e_{aq}^- from reaction (3) are converted into O_2^- species (reactions (5) to (7)). Hence,



$$k_{14} = 0.9 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The two species, $\dot{\text{C}}\text{HCl}_2$ and $\dot{\text{C}}\text{H}_2\text{Cl}$, are involved in the above reactions (10) and (11) followed by reactions (12) and (13). Finally, the peroxy radicals, O_2^- and/or HO_2 as well as H_2O_2 also contribute to the decomposition process of the substrate, e.g.:



OH and $\dot{\text{C}}\text{HCl}_2$ radicals are consumed as discussed above. Based on the yield of Cl^- ions the quantum yield, (Q), as well as the "photochemical" G -value of the Cl^- ions were calculated and are given in figure 2 as an insert. The very high degradation yield obtained is due to the chain reactions initiated by the OH radicals which are generated in reactions (9) to (11) and then converted into $\dot{\text{C}}\text{HCl}_2$ and $\dot{\text{C}}\text{H}_2\text{Cl}$ transients, (14a) and (14b). The propagation reactions are (10), (11), (13), (14a) as well as (14b).

2.1c Tetrachloroethylene: This pollutant has been chosen as representative of the halogenated ethylenes. Its absorption spectrum with $\lambda_{\text{max}} = 203 \text{ nm}$ is shown in figure 3, B. Obviously the 253.7 nm line makes a rather small contribution to the photoinduced decomposition process. Using $2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \text{Cl}_2\text{C}=\text{CCl}_2$ and a low pressure Hg-Lamp (184.9 and 253.7 nm) it has been calculated that about 90% of the VUV-light is absorbed by the water. Hence, the primary products of the water photolysis initiate the degradation process. The rest of the absorbed energy is consumed by the substrate, leading to its decomposition (Getoff 1991).

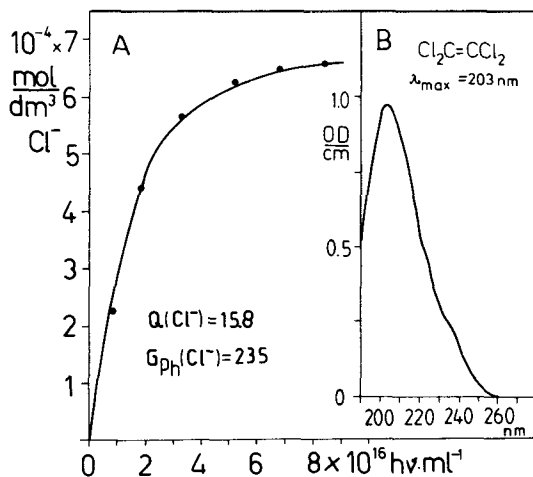


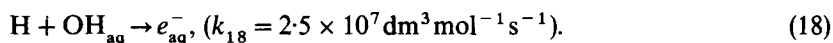
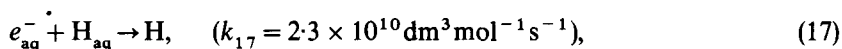
Figure 3. (A) Photoinduced Cl-cleavage of $2 \times 10^{-4} \text{ mol dm}^{-3}$ tetrachloroethylene in the presence of air at 30°C ($\text{pH} \sim 6.4$). (B) Absorption spectrum of $10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ $\text{Cl}_2\text{C} = \text{CCl}_2$ in water ($\text{pH} \sim 6.4$); $\epsilon_{203} = 9870 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

The formation of the Cl⁻ ions from tetrachloroethylene as a function of the absorbed VUV-dose (184.9 nm) is presented in figure 3A. In this case also, chain reactions are operative, similar to the above described for the CH_2Cl_2 -system, leading to a very high Q - and G_{ph} -yields (see figure 3). As decomposition products, in addition to Cl⁻ ions, small amounts of aldehydes, formic and oxalic acids were detected. However, these substances are also decomposed at higher VUV-doses.

It should be mentioned that the photoinduced degradation of various halogenated substances e.g. of trihalomethanes is investigated by various authors (e.g. Nicole *et al* 1991, and references therein).

2.2 Photoinduced formation of e_{aq}^- as promotor for pollutant degradation

The solvated electrons (e_{aq}^-) represent the basic form of the reducing primary species of water photolysis. In acid solution they can be transformed into H-atoms and vice-versa in alkaline media:



Both, H and e_{aq}^- are strong reducing transients and in the presence of air they are converted into peroxy radicals, (5) to (7). Each of their forms (H, e_{aq}^- , HO_2 , O_2^-) can initiate the degradation of pollutants. The e_{aq}^- can originate by photoexcitation of certain inorganic or organic substances in aqueous solution. Hence, for completeness their photoinduced formation is mentioned very briefly.

2.2a Formation of e_{aq}^- from inorganic ions: Some photoexcited inorganic ions can lead to the formation of e_{aq}^- . It has been found for the first time that Fe^{2+} can be oxidized by illumination to Fe^{3+} by ejection of e_{aq}^- (Getoff *et al* 1960; Getoff 1962). The same observation has been made for halide ions (e.g. Jortner *et al* 1962) and for

Table 1. Quantum yield (Q) of photoinduced e_{aq}^- formation from some inorganic and organic compounds in aqueous solution.

Substrate	λ_{exc} [nm]	Energy [eV/hv]	$Q(e_{\text{aq}}^-)$	References
OH ⁻	184.9	6.7	0.11	Dainton and Fowles (1965a)
Br ⁻	184.9	6.7	0.34	
Cl ⁻	184.9	6.7	0.43	
SO ₄ ²⁻	184.9	6.7	0.71	
Fe ²⁺	253.7	4.9	0.07	Airey and Dainton (1966)
Fe(CN) ₆ ³⁻	253.7	4.9	0.66	
Fe(CN) ₆ ⁴⁻	214 to 228	5.79 to 5.4	~0.9	Shirom and Stein (1971)
Fe ²⁺	292 to 314	4.2 to 3.9	0.0038	Solar and Getoff (1979)
C ₆ H ₅ OH	253.7	4.9	0.03	Zechner <i>et al</i> (1976)
C ₆ H ₅ OH	228.8	5.4	0.06	
C ₆ H ₅ O ⁻	253.8	4.9	0.17	Grabner <i>et al</i> (1977)
C ₆ H ₅ O ⁻	228.8	5.4	0.27	Getoff (1989a)
C ₆ H ₅ NH ₂	276.7	4.5	0.06	Köhler <i>et al</i> (1977)
C ₆ H ₅ NH ₂	253.7	4.9	0.27	
C ₆ H ₅ NH ₂	228.8	5.4	0.28	
C ₆ H ₅ NH ₂	213.9	5.8	0.34	
C ₆ H ₅ OPO ₃ ²⁻	253.7	4.9	0.028	Getoff and Solar (1974)
C ₆ H ₅ OPO ₃ ²⁻	213.9	5.8	0.23	Köhler and Getoff (1978)

other inorganic ions (Matheson *et al* 1963; Dainton and Fowles 1965b), e.g.:



The quantum yields (Q) of the photoinduced e_{aq}^- resulting from some inorganic ions are given in table 1.

2.2b Photoejection of e_{aq}^- from organic compounds: It has been established that photoinduced electron ejection and formation of e_{aq}^- from certain electronically excited organic substances in aqueous solution, having substituents such as $-\text{OH}$, $-\text{O}^-$, $-\text{OCH}_3$, $-\text{OPO}_3\text{H}_2$, $-\text{OPO}_3\text{H}^-$, $-\text{COO}^-$, $-\text{NH}_2$, $-\text{NHCH}_3$, $-\text{N}(\text{CH}_3)_2$ etc., can take place (Grossweiner *et al* 1963; Getoff 1989a, and references therein).

The ejection of electrons occurs from the singlet state (S_1 or S_2), where the energy input is much lower than the ionization potential of a given compound in its gas phase. To explain this process, therefore, it is suggested that the dipole-dipole interaction between the polarized excited substrate molecules and the surrounding water molecules as well as the solvation energy of the resulting charged species contribute energetically and enable e_{aq}^- formation (Getoff 1989a).

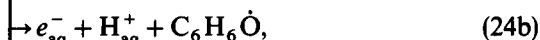
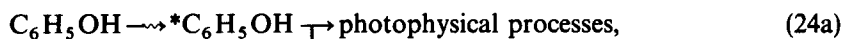
The formation of e_{aq}^- is also observed by illumination of dyes in aqueous solution, e.g. methylene blue (Vonach and Getoff 1983), a number of flavins (Getoff *et al* 1978), aromatic amines (Köhler *et al* 1977) etc.

The $Q(e_{\text{aq}}^-)$ -value strongly depends on several factors: *excitation energy* (see table 1), *the structure of the substrate molecule* as well as on the *pH and temperature of the solution* (Getoff 1989a, and references therein). It has also been established that the formation of e_{aq}^- takes place at the expense of the fluorescence (Köhler and Getoff 1974, 1976; Zechner *et al* 1976, 1981; Grabner *et al* 1977, 1980). This proves that the electron photoejection process occurs from the singlet state.

2.3 Photoinduced decomposition of phenol

Phenol is frequently observed as a pollutant in water. Its photoinduced degradation has been investigated in the presence of oxygen and small amounts of ozone (Getoff 1987). The reactivity of ozone with olefinic and aromatic compounds (without irradiation) can be designated as an electrophilic addition to the double-bond of the molecule (e.g. Bühler *et al* 1984, Sehested *et al* 1984, Hoigne 1985, Getoff 1989b, 1992, Gehringer *et al* 1992, and references therein).

As already mentioned above, the electronically excited aqueous phenol leads to the formation of e_{aq}^- in addition to other processes (Grossweiner *et al* 1963; Jortner *et al* 1963; Grabner *et al* 1977, 1980; Getoff 1989b) e.g.:



The quantum yields (Q) of the primary products (e_{aq}^- , resulting from S_1 - and S_2 -states are given in table 1. As already mentioned, in the presence of air e_{aq}^- is converted

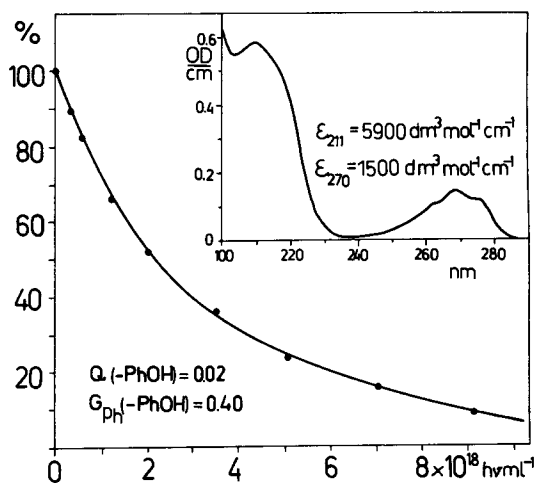
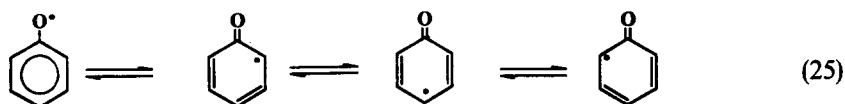


Figure 4. Photoinduced degradation (%) of aqueous $10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ phenol in the presence of $1.25 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_2$ and $1.1 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_3$ (pH = 7.5) as a function of the absorbed UV-dose ($\lambda = 253.7 \text{ nm}$). Inset: absorption spectrum of $10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ phenol.

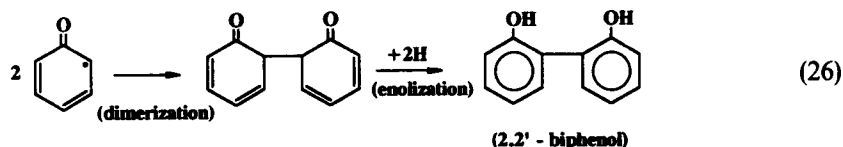
into peroxy radicals (see reactions (5) to (7)), which are subsequently involved in the decomposition process.

The photoinduced degradation of phenol using UV-light (253.7 nm) in the presence of oxygen and small concentrations of ozone in neutral solutions is shown in figure 4. The achieved Q - and G_{ph} -values, as well as the absorption spectrum of phenol are given as inserts in figure 4.

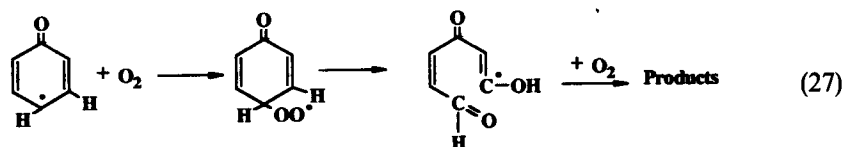
The major reaction steps leading to the decomposition of phenol may start with the formation of phenoxyl radicals (reactions (24b) and (24c)), which exist in several resonance structures.



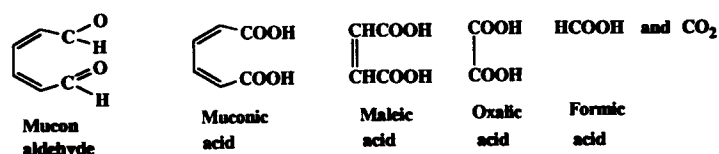
Each of them can result in different final products or add on oxygen as shown below.



Naturally, the above-mentioned peroxy radicals can also attack phenol and initiate its decomposition. In addition to this, each of the resonance structures can be scavenged by O_2 as follows.



In the presence of sufficient oxygen in the solution, the pathway (27) will proceed preferentially, however, the exact reaction mechanism of the photoinduced phenol decomposition is not yet known. The yield and the kind of the products depend on the applied UV-dose, $p\text{H}$ and the oxygen concentration. As final products of an incomplete degradation of the substrate, the following compounds were observed (Getoff 1987).



It might be mentioned that in addition to the OH , H and e_{aq}^- resulting in the VUV-water photolysis, the triplet state of the pollutant as well as the singlet oxygen ($^1\text{O}_2$) can be involved in the photochemical decomposition process in the presence of air.

3. Semiconductor-promoted pollutant degradation using solar energy

3.1 General remarks

Since the discovery by Fujishima and Honda (1971) of water splitting to H_2 and O_2 using solar energy by means of an n - TiO_2 -photoanode and metal cathode, separated by a membrane, a new pathway for research in photochemistry and photoelectrochemistry was found (Getoff *et al* 1977, Hantala *et al* 1979, etc.). The n -type semiconductors (e.g. TiO_2 , $SrTiO_3$, $GaAs$ etc.) have an excess of electrons (e^-) and, hence, are used as photoanodes or as suspensions (e.g. Izumi *et al* 1980, Vonach and Getoff 1981) or colloids (Hsiao *et al* 1983, Ahmed and Ollis 1984, Ollis 1985, 1990, Matthews 1985, 1988, Okamoto *et al* 1985, Al-Ekabi and Serpone 1988, Grabner *et al* 1991 etc.) for promoting the oxidation reaction. The p -type semiconductors ($CdTe$, GaP etc.) possess positive holes (p^+) in excess and serve as photocathodes in photoelectrochemical cells or for instance in the form of small particles and act as reduction photocatalysts (Bart 1979, Schiavello 1988, and references therein). Semiconductors can be also coated on glass (Dislich 1984) or on other carrier materials.

The application of semiconductors for photocatalyzed oxidation of aqueous pollutants is very recently discussed in an excellent review by Halmann (1992). Further, it might be mentioned that many papers dealing with TiO_2 photocatalytic purification and treatment of polluted water are presented at the 1st International Conference in London, Canada (Al-Ekabi *et al* 1992).

On illuminating a TiO_2 particle immersed in aqueous media with light of 315 to 450 nm, band-bending takes place and electrons rise from the valence band (E_v) to the conductivity band (E_c) and, hence, a charge separation takes place (see figure 5). Based on this fact, each individual particle represents a redox-system and can promote reduction or oxidation processes depending on the experimental conditions. Each semiconductor has a characteristic band-gap (in eV; 1 eV = 23 kcal/mol), e.g. for TiO_2 , $E_G = 3$ eV. Knowing the wavelength (λ in nm) of the light, one can calculate the energy per quantum: (E in eV/hv) and vice versa.

$$E = [1240/\lambda(\text{nm})](\text{eV}/h\nu) \quad (28)$$

The relative energy levels for some semiconductors are shown in figure 6. Silicon has the lowest energy-gap ($E_G = 1.1$ eV) but is not stable in aqueous solution.

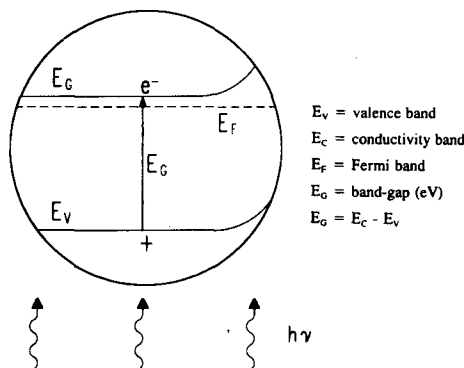


Figure 5. Simplified scheme of the energy levels of an illuminated n -type semiconductor particle.

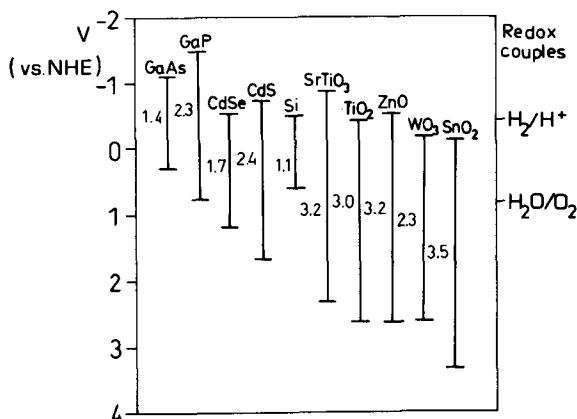


Figure 6. Relative energy levels (E_G in eV) of some semiconductors (after Nozik 1980).

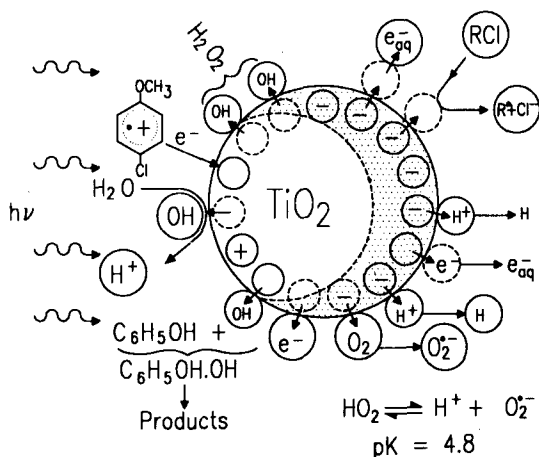


Figure 7. Some possible photoinduced processes on the surface of TiO_2 particles in polluted water.

3.2 Primary processes on semiconductor surfaces

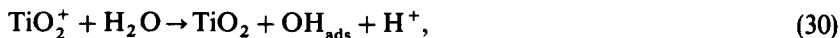
The photoinduced degradation of pollutants on the surface of e.g. TiO_2 is not a simple process. In order to visualize the possible redox-reactions, a simplified scheme is presented in figure 7. The illuminated part of the TiO_2 -particle absorbs the light-energy in 10^{-16} s and the electrons are moved from the E_v to the E_c (shadow side of the particle) bands. As a consequence of this charge separation, the illuminated part (positively charged holes, h^+) is able to decompose the adsorbed H_2O molecules to OH radicals and H^+ ions. Also, an e^- can be transferred from a pollutant (having a suitable redox-potential) to h^+ of the TiO_2 particle (see figure 7). On the other hand, the e^- can be also transferred to adsorbed H^+ , O_2 or the chlorinated pollutant initiating various reactions. It cannot be ruled out that some electrons can diffuse away from the TiO_2 surface and become "solvated electrons" (e_{aq}^-) as demonstrated by Walker (1967) on anode surfaces.

3.3 Photocatalytic degradation of pollutants

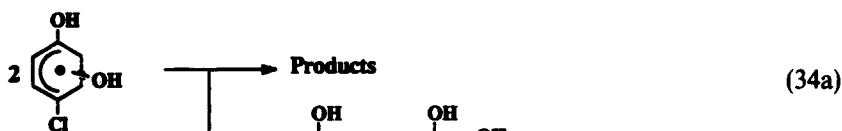
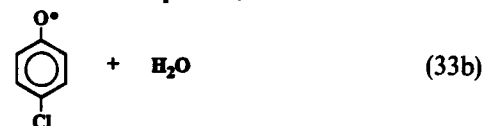
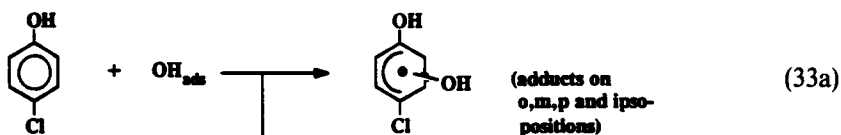
For illustration of photocatalytic degradation, some major reactions taking place on the TiO_2 surface in slightly acidic solution, are presented.



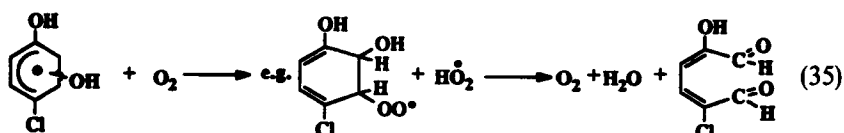
On the illuminated side of TiO_2 particles (figure 7) a number of reactions can take place:



In the presence of a pollutant, e.g. 4-Cl-phenol, similar reactions can take place as studied by pulse radiolysis (Getoff and Solar 1988) as below.

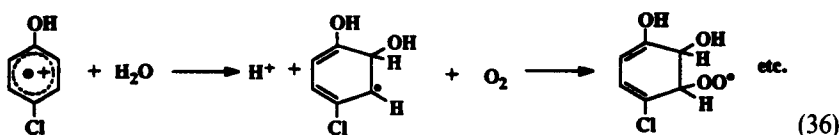


In competition with these processes, O_2 can be scavenged as below resulting in peroxy-radicals.



As a consequence of further OH attack and addition of oxygen, the resulting dialdehyde (35) can be decomposed to CO_2 and H_2O (see also reactions (25) to (27)).

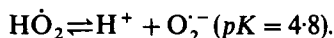
Another pathway for $\text{ClC}_6\text{H}_4\text{OH}$ degradation is the formation of a radical cation on the surface of TiO_2 particles as indicated in figure 7 which can react further.



On the shadow side of the TiO_2 -particles (see figure 7) in slightly acid media some reactions can be initiated by the electrons in the presence of oxygen:



and from (7)



The $\text{H}\dot{\text{O}}_2^-$ and $\text{O}_2^{\cdot-}$ species can attack the water pollutants in the same way as the OH radicals followed by O_2 addition (see reaction (35)).

As mentioned above, a number of papers have been published in recent years in the field of pollutant degradation assisted by semiconductors. Figure 8 shows some data concerning the oxidation rates of some pollutants in water (Mathews 1988). TiO_2 (Degussa, P25 grade) was coated on the inside of a 7-m long 65-turn spiral of borosilicate glass ($\varnothing 6$ mm, 40 ml solution was circulated through the spiral) illuminated with a 20-W lamp.

It has been also found that the TiO_2 -assisted photodecomposition of 4-Cl-phenol is temperature-dependent (Hofstadler *et al* 1992). By studying the kinetics of the laser-induced phenol oxidation, it was observed that the Cl_2^- species essentially contribute to the process (Grabner *et al* 1991; Li *et al* 1991). Further, it should be mentioned that TiO_2 particles or colloids can also mediate the transformation of CO (Park *et al* 1988) as well as CO_2 (Halmann 1978) into simple organic substances: In the absence of oxygen in the solution, the polymerisation of pollutants can also take place on the semiconductor surface.

With respect to photocatalytic water purification, there are still a number of problems to be solved. Although sunlight is free of cost and is readily available in many parts of the world, its intensity is rather low and it has to be collected and concentrated by appropriate means for the purpose of water purification on a technical scale.

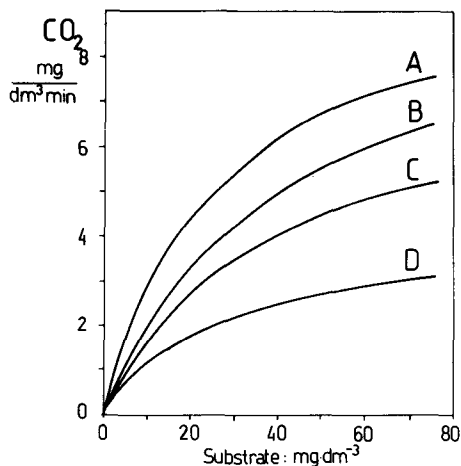


Figure 8. CO_2 rates observed by TiO_2 oxidation of various substrates as a function of their initial concentrations: (A) 4-Cl-phenol, (B) phenol, (C) acetic acid, and (D) 2-propanol (after Mathews 1988).

Further problems which have to be overcome are:

- to increase the low quantum yield of photocatalytic pollutant degradation.
- to improve the corrosion resistance and to reduce inhibition by poisoning of the semiconductor,
- the solvation of peculiar features of semiconductor coating on various support materials,
- lowering of the costs for semiconductor regeneration, water pumping etc.

Therefore, further investigations in this area are needed.

4. Pollutant decomposition by ionizing radiation

4.1 General remarks

In the last two decades, a relatively large number of papers have been published concerning radiolytic degradation of harmful substances in water. Hence, only some characteristic data for comparison with the above discussed photochemical methods will be presented. Gamma-rays as well as high-energy electrons can be used for production of reactive transients from water which can initiate the desired decomposition processes. Preference is given to high-energy electrons for several reasons: no manipulation with radioactive isotopes (e.g. ^{60}Co) or their disposal required, easy regulation of the output power and simple handling in case of repair work as well etc. The modern electron accelerators (EA-machines) provide electrons with variable

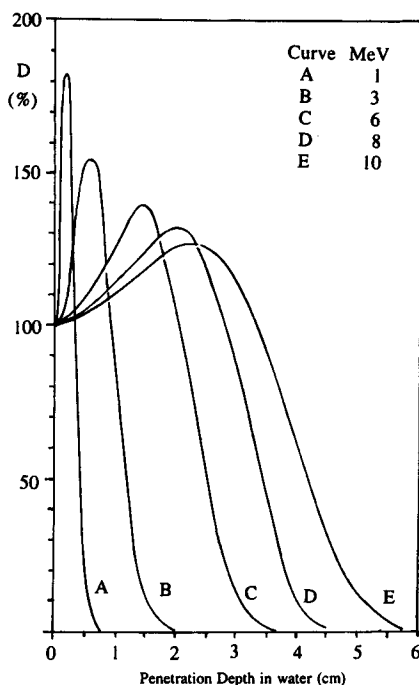


Figure 9. Depth-dose (D %) distribution in water at different electron energies.

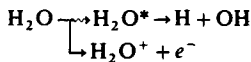
energy (e.g. from 0.5 to 2.8 MeV) and a rather high output power (80 to 100 kW) with a conversion factor (η = electron power/electricity power) of about 80%. EA-machines delivering electrons with energies of 4.5–5 (output power > 400 kW) or 10 MeV (25–50 kW) can be also used for water purification. The electron penetration in water depends on their energy. Figure 9 shows the depth dose distribution (D in %) in water for different electron energies (in MeV). The depth dose of the applied electrons and the output power (kW) of the EA-machine are determining factors for the quantity of purified water.

4.2 Water radiolysis

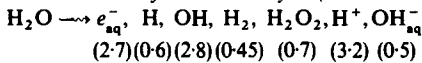
As a consequence of the interaction between the ionizing radiation and water, several transients and molecular products are formed. Their yields (G -values) and major

Table 2. Radiolysis of water and some primary reactions.

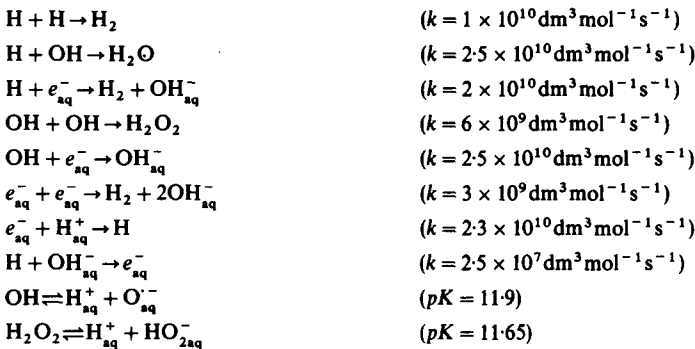
Primary reactions:



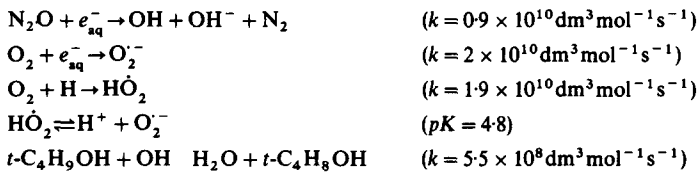
Gross reaction of water radiolysis (the G -values at pH 7 are given in brackets):*



Major primary reactions:

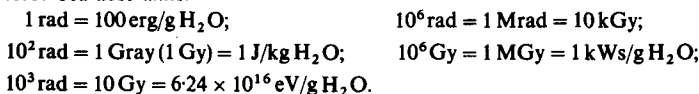


Scavenger reactions:



* G -value = number of changed molecules per 100 eV (1.60×10^{-17} J) absorbed energy. For conversion in SI-units: multiply the G -value by 0.10364 to obtain $G(x)$ in $\mu\text{mol} \cdot \text{J}^{-1}$.

Absorbed dose units:



primary reactions are summarized in table 2. The common units for absorbed radiation dose are also given for convenience.

As shown above, in the presence of air ($0.25 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_2$ at 20°C) both e_{aq}^- and H atoms are converted into peroxy radicals which, together with the OH species, attack the available pollutants and initiate their degradation.

4.3 Decomposition of chlorinated hydrocarbons

Chlorinated hydrocarbons have been studied extensively by various research groups (e.g. Balkas *et al* 1970, 1971, Köster and Asmus 1971, Neumann-Spallart and Getoff 1979, Pikaev and Shubin 1984, Gehringer *et al* 1985, 1986, 1988, 1990, 1992, Getoff and Lutz 1985, Mönig *et al* 1985, Getoff 1986, 1989–1991, Proksch *et al* 1988, Draper *et al* 1989, etc.). Some data concerning radiation-induced degradation of several chlorinated aliphatic and olefinic hydrocarbons are presented in table 3 (Getoff 1989b). These pollutants frequently appear in drinking water. Obviously, their complete decomposition is achieved at a relatively low dose. In aerated water containing olefins or aromatic pollutants, the presence of ozone strongly enhances the degradation process (Masschelein 1982, Rice and Netzer 1984, Gehringer *et al* 1992, Getoff 1992 etc.).

The following major reaction can explain the ozone effect:

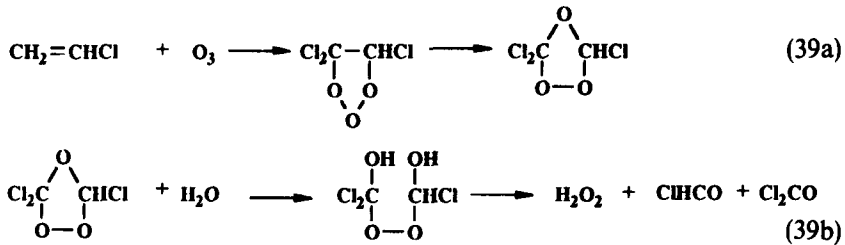
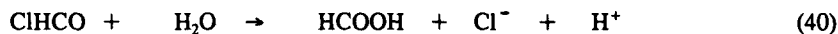


Table 3. Radiation induced decomposition of some chlorinated hydrocarbons in aerated water*. Applied dose: 1.9 kGy.

Sample No.	Treatment†	Pollutants in water/ $\mu \cdot \text{dm}^{-3}$					
		CH_2Cl_2	CHCl_3	CCl_4	$\text{Cl}_3\text{C}-\text{CH}_3$	$\text{Cl}_2\text{C}=\text{CHCl}$	$\text{Cl}_2\text{C}=\text{CCl}_2$
1	U	—	32	—	0.7	—	—
	I	—	nd	—	nd	—	—
2	U	—	—	25	0.2	—	—
	I	—	—	1	nd	—	—
3	U	48	—	—	107	1.1	—
	I	nd	—	—	0.8	nd	—
4	U	23	2.3	1.1	0.2	—	—
	I	nd	nd	0.1	nd	—	—
5	U	—	2.5	0.2	4.5	361	0.2
	I	—	nd	nd	nd	nd	nd

† U-unirradiated; I-irradiated; * the GC-analysis was performed by Dr U Bauer. Traceable limit: $< 0.1 \mu\text{g} \cdot \text{dm}^{-3}$

Abbreviations: nd = non-detectable; $\text{Cl}_3\text{C}-\text{CH}_3$ = 1,1,1-trichloroethane; CH_2Cl_2 = dichloromethane; $\text{Cl}_2\text{C}=\text{CHCl}$ = trichloroethylene; CHCl_3 = chloroform; $\text{Cl}_2\text{C}=\text{CCl}_2$ = tetrachloroethylene; CCl_4 = carbon-tetrachloride.



These reactions can also occur without irradiation. They take place in the case of aromatic pollutants likewise.

4.4 Decomposition of aromatic substances

Steady state as well as pulse radiolysis studies of various aromatic pollutants in water have been published (e.g. Schuler *et al* 1976, Getoff and Solar 1986, 1988, Draper *et al* 1989, Getoff 1990b, 1992, Nickelsen *et al* 1992 etc.). For comparison with the above discussed photochemical methods, radiation-induced phenol decomposition is discussed in brief. As shown in figure 10, at a dose of about 1.2 kGy in the presence of oxygen the initial phenol is practically decomposed. However, due to competition reactions certain amounts of pyrocatechol, hydroquinone and hydroxyhydroquinone are formed. The initial G -values (G_i) are given as an insert in figure 10 (Getoff 1986b). At higher doses these compounds and the resulting aldehydes and acids are decomposed to CO_2 and H_2O . The major reactions taking place in this case are given below, (42) to (50) In addition to these, reactions (25) to (27) are also involved.

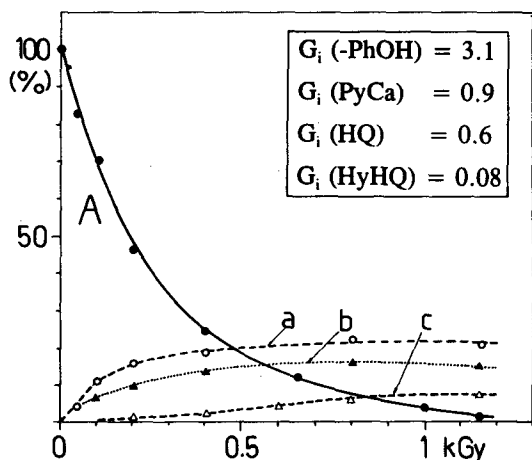
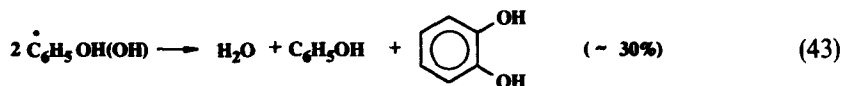
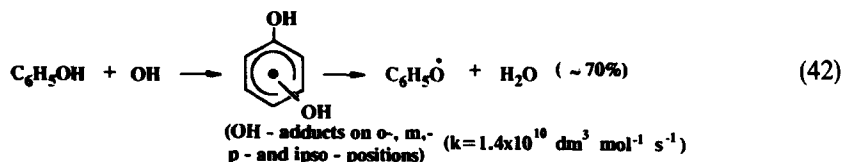
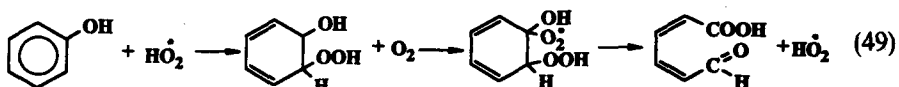
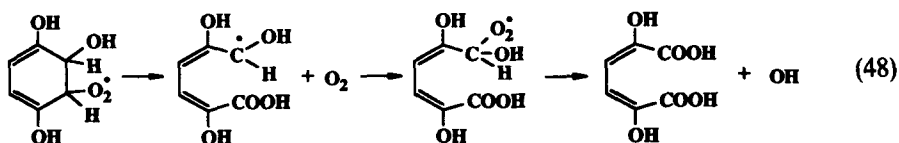
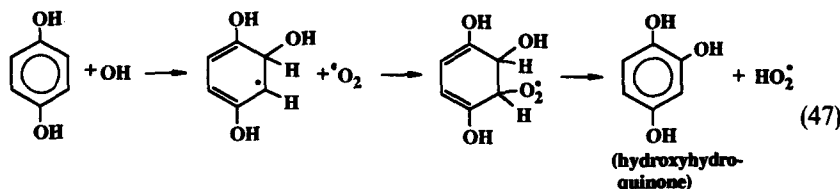
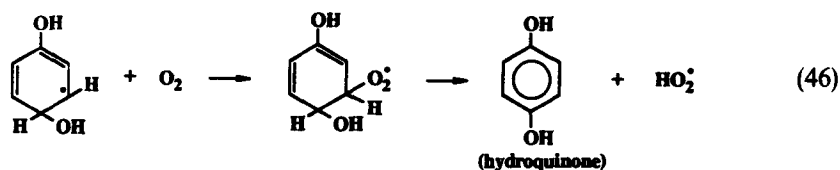
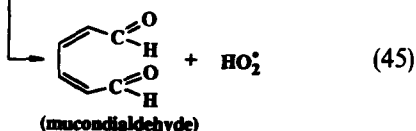
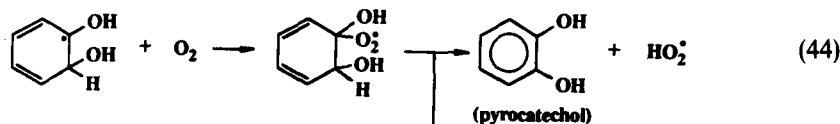


Figure 10. Decomposition of $10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ phenol (A) in the presence of $1.25 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_2$, as well as formation of pyrocatechol (a), hydroquinone (b) and hydroxyhydroquinone (c) as a function of the absorbed dose at pH 7; dose rate: 3kGy/h. Insert: Initial G -values (G_i) of phenol decomposition and of the major products.



Based on the above data, it is now calculated that for a 50% decomposition of $10^{-4} \text{ mol.dm}^{-3}$ phenol by UV-light ($\lambda = 254 \text{ nm}$, $E = 4.85 \text{ eV/hv}$), an energy of 1.56 kGy is needed. Using γ -rays or electrons in order to achieve the same decomposition degree, an energy of 0.2 kGy is necessary. Obviously, the ionizing radiation is much more efficient than the UV-light in this case.

Finally, it should be mentioned that by means of pulse radiolysis of pollutant transients, their absorption spectra and the kinetics of their formation and decay, in addition to their chemical analysis, we can essentially elucidate their reaction mechanisms.

5. Conclusion

An attempt has been made to investigate the photochemical, photocatalytic and radiation-induced decomposition of pollutants in water. Special attention has been made to explain the primary processes initiating their degradation. On the other hand, a relationship is also established between the above-mentioned three pathways.

Although a great deal of research work has been done concerning the degradation of water pollutants, further experiments are needed on a pilot scale in order to gain technical experience for construction of industrial plants for water purification.

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