RADIATION-INDUCED DEGRADATION OF WATER POLLUTANTS—STATE OF THE ART†
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Abstract—The radiation-induced decomposition of biological resistant pollutants in drinking as well as in wastewater is briefly reviewed. First, some important units, definitions etc., radiation sources, as well as dose-depth curves in water as functions of the electron energy and 6°Co-γ-rays are mentioned. Following is a schematical presentation of water radiolysis and of characteristics of primary free radicals. Then the degradation of some aliphatic and aromatic chlorinated compounds in the presence of air is presented. Some spectroscopic and kinetic data of transients resulting from chlorinated phenols are also quoted in order to illustrate and to explain the rather complicated degradation mechanisms. In this respect the synergistic effect of radiation and oxygen as well as that of ozone is also discussed. Finally, a scheme for technical application of high energy electron beam is presented.

1. INTRODUCTION
As a result of the strong development of various industries and the rapid growth of world population a rather heavy overloading of water resources is observed. In addition to this, the usage of various chlorine-containing pesticides and other chemicals, as well as fertilizer in modern agriculture, contributes to contamination of ground water. The killing of microorganisms in drinking water containing humic compounds by chlorination leads to the formation of various halogenated hydrocarbons (Rook, 1974). Such substances are carcinogenic and are usually removed by filtration through activated charcoal which is subsequently burned up. The resulting chlorine oxides contribute to the occurrence of acid rain. Due to the above mentioned pollution sources, environmental and toxicological effects have increased considerably (Hutzinger et al, 1974, 1982, Fishbein, 1979; Strobel and Dieter, 1990). This is also reflected in the health of the population in industrial areas.

Fundamental studies have shown that a complete degradation of biologically resistant compounds, disinfection of sewage sludge as well as killing of microorganisms can be achieved by ionizing radiation treatment. Abundant literature is available on this topic. This is now the basis for technical electron beam remediation in water.

In order to present a more complete picture of the subject matter and as an introduction for newcomers to this field, some basic knowledge in radiation chemistry is briefly mentioned.

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Table 1. Some useful definitions, radiation units and conversion factors.

| Output power of electron accelerator (in kW): |
| kW = mA × MeV |
| mA = electron current, MeV = electron energy |
| Radiation yield: G-value = number of produced or decomposed molecules per 100 eV absorbed energy. For conversion into Si-units multiply the G-value by 0.10364 to obtain G(x) in μmol J⁻¹. |
| Absorbed dose: |
| 1 rad = 100 erg g⁻¹ = 6.24 × 10⁻² eV g⁻¹ |
| 100 rad = 1 Joule kg⁻¹ = 1 Gray (Gy) |
| 1 krad = 10 Joule kg⁻¹ = 10 Gy |
| 1 Mrad = 10⁴ Joule kg⁻¹ = 10⁴ Gy |
| 1 kW = 3.6 × 10⁶ J kg⁻¹ = 360 Mrad kg⁻¹ h⁻¹ |

is approximately inverse proportional to the density (ρ) of the absorbing material (for water ρ ≈ 1g/ml) and roughly proportional to the electron energy (for water R₉ ≈ 0.5 cm/1 MeV penetration depth). Hence, the shape of a depth–dose curve in a material is a function of electron energy, absorber density and incidence angle of the electron beam.

The depth–dose curves (D, %) in water for ⁶⁰Co-γ-rays and 2 MeV electrons are given for comparison in Fig. 2. Obviously, the γ-rays have a much deeper penetration in water than the electrons (see also Fig. 1).

4. WATER RADIOLYSIS

As a sequence of the interaction between ionizing radiation (electrons, γ-rays) and water electronically excited and ionized molecules are formed. Subsequently this leads to the production of several very reactive primary species (OH, eaq, H) and molecular products (H₂, H₂O₂). Their yields (G-values, related to the absorbed dose) as well as the major reactions taking place in irradiated water and the corresponding rate constants (k) are presented in Table 3.

In the presence of oxygen in water the reducing species, H-atoms and the “solvated electrons” (eaq) are converted into oxidizing species, perhydroxyl radicals (HO₂⁻) and perhydroxyde radical anions (O₂⁻). The last ones together with the OH-radicals can initiate degradation of water pollutants.

For information and practical interest the absorption spectra of the primary products of water radiolysis and their initial yields (Gₚ) as function of pH are presented in Fig. 3. These data are also needed in the case when reaction mechanisms are postulated in order to get material and energy balance.

Table 2. Output power (kGy kg⁻¹ h⁻¹) of various radiation sources

<table>
<thead>
<tr>
<th>Type of radiation source</th>
<th>Dose rate (Mrad/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray source 10 mA, 250 kV</td>
<td>0.18</td>
</tr>
<tr>
<td>⁶⁰Co-γ-source: 0.5 × 10⁶ Curie</td>
<td>65</td>
</tr>
<tr>
<td>1.0 × 10⁶ Curie</td>
<td>130</td>
</tr>
<tr>
<td>Electron accelerator:</td>
<td></td>
</tr>
<tr>
<td>- Van de Graaff (1 mA, 2 MeV)</td>
<td>7.2 × 10⁴</td>
</tr>
<tr>
<td>- DYNAMITRON (40 mA, 5 MeV)</td>
<td>7.2 × 10⁴</td>
</tr>
<tr>
<td>- LINAC (50 mA, 10 MeV)</td>
<td>1.8 × 10⁴</td>
</tr>
</tbody>
</table>

Fig. 1. Depth–dose (%) distribution in water for different electron energies (see inserted Table). Insert: discharge traces of 3 MeV electrons in a plate of polymethylmethacrylate.

5. RADIATION INDUCED DECOMPOSITION OF WATER POLLUTANTS—GENERAL REMARKS

As already mentioned above the radiation induced degradation of pollutants in water is a very powerful technique. Based on the very high radiation power of the modern EA-machines this method is marked out by a great product output, high efficiency and economics in comparison to other technologies (see e.g. Kurucz et al., 1991; Cooper et al., 1992; Cooper et al., 1993 and references therein).

The outstanding ability of electron beam irradiation in respect to water remediation is demon-
strated by some examples. First, the radiation induced oxidation of chlorinated hydrocarbon mixtures in drinking water and after that this of trichlorethylene (TCE) is discussed. It follows the degradation of phenol and 4-chlorophenol (4-C1PhOH).

5.1. Steady-state radiolysis of chlorinated hydrocarbons

As already mentioned in the process of drinking water purification by chlorination a number of chlorinated hydrocarbons are formed. Hence, the effect of

![Figure 3](https://example.com/figure3.png)

**Fig. 3.** (A) Absorption spectra of H, OH, H\(_2\)O\(_2\), and O\(_2^-\) radicals as well as H\(_2\)O \((\epsilon \text{ in } \text{dm}^3 \text{mol}^{-1} \text{ cm}^{-1})\). Insert: pK-value of H\(_2\)O. (B) Absorption spectrum of e\(_{aq}\) \((\epsilon \text{ in } \text{dm}^3 \text{mol}^{-1} \text{ cm}^{-1})\). (C) G\(_{i}\)-values of the primary products of water radiolysis as a function of pH.
the radiation-induced degradation has been proven by irradiating samples containing mixtures of chlorinated methanes, ethanes and olefines in various concentrations in the presence of air (dose: 1.9 kGy). The analysis of the samples were performed by GC-method. It can be seen in Table 4 that the pollutants are completely decomposed with exception of CC14 and C13C--CH3 which show very small amounts left (Getoff, 1986b, 1989).

It should be mentioned that in the case of natural drinking water containing inorganic salts, humic compounds etc. the required radiation dose is somewhat higher than for artificial samples (e.g. Proksch et al. 1987).

In the following the radiation-induced degradation of trichloroethylene (Cl3C=CHCl; TCE) is discussed in some details. This pollutant can occur in various kinds of wastewaters and under certain conditions also in drinking water. Its radiolysis has been previously studied (e.g. Küster and Asmus, 1971; Gehringer et al., 1985; 1986; Getoff 1986a; 1987, 1989).

Figure 4 shows the formation of C1- ions from 10-3 mol dm-3 Cl2C=CHCl as a function of the absorbed dose in the presence of air (Getoff, 1989). The initial yield G1(C1-) = 19.8 is rather high indicating the involvement of a short chain-reaction. As further products were found a mixture of aldehydes (G1 = 0.02) and simple carboxylic acids. They are however, decomposed at higher doses. The required radiation dose for the total degradation of Cl2C=CHCl strongly depends on the substrate concentration. This fact is illustrated by the insert in Fig. 4, where small amounts of trichloroethylene have been irradiated under the same conditions. A complete degradation of the pollutant has been achieved at 150 Gy, at which only traces of aldehydes and carboxylic acids were observed. Similar results have been reported by Gehring et al. (1986).

In order to obtain information about the involvement of the individual primary transients of water radiolysis (OH, eaq, H), peroxide-radicals and ozone in the degradation of trichlorethylene experiments under the required conditions have been performed (Getoff, 1989). In this case the yield of C1- was taken as an indicator for the decomposition process. The obtained initial C1- yields G1(C1-) from the various experimental series are presented in Table 5.

The rather high G1(C1-) = 11.2 observed in airfree solutions seems to result partly by the specific eaq attack on the Cl-atom of TCE and on the reaction of OH forming predominantly OH-adducts which undergo a spontaneous decomposition. For the radiolysis of TCE in the absence of air the following major reactions have been suggested (Getoff, 1989).

\[
\begin{align*}
\text{Cl2C}=\text{CHCl} + \text{e}_{aq} & \rightarrow \text{Cl1C}=\text{CH} + \text{Cl}^- \quad (1a) \\
\text{Cl1C}=\text{CH} + \text{Cl}^- & \rightarrow \text{Cl0}(\text{OH}) + \text{ClHCl} \quad (2b)
\end{align*}
\]

Simultaneously with the above processes OH radicals are adding on the double bond of TCE-molecule forming OH-adducts which are unstable and decompose, e.g.

\[
\begin{align*}
\text{Cl2C}=\text{CHCl} + \text{OH} & \rightarrow \text{Cl1C}=\text{CH(CH)} + \text{OH} \quad (2a) \\
\text{Cl0}(\text{OH}) + \text{ClHCl} & \rightarrow \text{Cl0}(\text{OH}) + \text{ClHCl}
\end{align*}
\]

The initial yield of Cl- obtained from aqueous 1 x 10-3 mol dm-3 Cl2C=CHCl in the presence of different O2-concentrations at pH = 6.5 (Getoff, 1989).

<table>
<thead>
<tr>
<th>Series No.</th>
<th>Gas-content (mol dm-3)</th>
<th>G1(Cl-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>airfree</td>
<td>11.2</td>
</tr>
<tr>
<td>2</td>
<td>0.25 x 10-3 O2</td>
<td>9.1</td>
</tr>
<tr>
<td>3</td>
<td>1.25 x 10-3 O2</td>
<td>7.6</td>
</tr>
<tr>
<td>4</td>
<td>1.25 x 10-3 O2</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Fig. 4. Dose-dependence of Cl-formation from 10-5 mol dm-3 Cl2C=CHCl in the presence of air (pH 6.4). Insert: Radiation induced decomposition of 2.74 x 10-5 mol dm-3 Cl2C=CHCl in the presence of air (pH ~ 6.5) as a function of a dose (Getoff, 1989).
mean value: \( k_2 = 3.3 \times 10^8 \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \) (Köster and Asmus, 1971)

\[
\begin{align*}
\text{Cl}_2\text{C} \cdots \text{CH(Cl)OH} &\rightarrow \text{Cl}_2\text{C} \cdots \text{CHO} + \text{Cl}^- + \text{H}^+ \quad (3a) \\
\text{Cl}_2\text{(OH)C} \cdots \text{CHCl} &\rightarrow \text{ClOC} \cdots \text{CHO} + \text{Cl}^- + \text{H}^+ \quad (3b)
\end{align*}
\]

\( k_3 > 7 \times 10^5 \text{s}^{-1} \) (Köster and Asmus, 1971)

The radicals (\( \text{Cl}_2\text{C} \cdots \text{CHO} \)) are disappearing according to a second order reaction, e.g.

\[
2\text{Cl}_2\text{C} \cdots \text{CHO} \rightarrow \text{products} \quad (4)
\]

\( 2k_4 = 6.2 \times 10^8 \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \) (Köster and Asmus, 1971)

The radicals can also form adducts or abstract \( \text{Cl}^- \) or \( \text{H}^- \) atom from TCE molecule.

It has been reported earlier (Koltzenburg et al., 1982; see also Lal et al., 1987; Getoff, 1993a) that in general alkyl radicals with leaving groups on \( \beta \)-position, resulting from the reaction of \( \text{OH} \) with a halogenated compound, undergo a fast hydrolysis. As a result of this \( \text{OH} \)-group is incorporated on the place of \( \text{Cl}^- \) atom, e.g.

\[
\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{Cl}^- + \text{H}^+ \quad (5)
\]

Under airfree conditions the obtained species can disappear by dimerisation and/or disproportionation. In the presence of air (0.28 \( \times 10^{-3} \text{mol}^{-1}\text{O}_2 \) at 20°C and 760 torr) or in water saturated with pure oxygen (1.40 \( \times 10^{-3} \text{mol}^{-1}\text{O}_2 \) at 20°C, 760 torr) the above mentioned radicals can add oxygen resulting in peroxyl-radicals. Depending on the \( \text{O}_2 \) as well as on the TCE concentration in the aqueous solution a competition for \( e_\text{aq}^- \) and \( \text{H}^- \) atoms between \( \text{O}_2 \) and TCE takes place. Both \( e_\text{aq}^- \) and \( \text{H}^- \) atoms, at low pollutant concentration in aerated water, are converted into peroxyl-radicals (see Table 3). Hence, the attacking species under these conditions are \( \text{O}_2^- \) as well as \( \text{OH}^- \) which are leading to the corresponding TCE-adducts. They are unstable and can undergo a multiple hydrolysis (Koltzenburg et al., 1982; Lal et al., 1987; Getoff, 1993a) e.g.

\[
\begin{align*}
\text{Cl}_2\text{(OH)C} &\rightarrow \text{CH(Cl)O}_2^- \quad \text{(tetroxide)} \\
\text{ROO}^- + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{COOH} + \text{Cl}^- + \text{H}^+ + \text{CO}_2 \\
\text{CO}_2 &\rightarrow \text{CO}_3^- \quad \text{(oxalate)}
\end{align*}
\]

The phosgen (\( \text{Cl}_2\text{CO} \)) hydrolysing according to reaction (8). The formaldehyde is completely decomposed at higher doses.

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{OH}(pK = 11.9) \quad (11)
\]

The produced \( \text{OH}/\text{O}_2^- \) species [equations (10) and (11)] are consumed according to reaction (2).

In addition to the above reaction steps also the formation of tetroxides and oxy-radicals can be involved in the degradation process of TCE, e.g.

\[
\begin{align*}
2\text{Cl}_2\text{(OH)C} &\rightarrow \text{CH(Cl)O}_2^- \rightarrow \text{ROO}^- \rightarrow \text{OH} + 2\text{Cl}^- + \text{H}^+ \quad (12)
\end{align*}
\]

\[
\text{ROO}^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{COOH} + \text{Cl}^- + \text{H}^+ + \text{CO}_2
\]

(13)

The oxy-radical can decompose after abstracting an \( \text{H}^- \) atom from a compound in the bulk of the solution:

\[
\begin{align*}
\text{Cl}_2\text{(OH)C} &\rightarrow \text{CH(Cl)O} + \text{H}_2\text{O} \rightarrow \text{ClOC} \rightarrow \text{CHO} + \text{Cl}^- + \text{H}^+ \\
\text{Cl}_2\text{(OH)C} &\rightarrow \text{CH(Cl)O} + \text{H}_2\text{O} \rightarrow \text{ClOC} \rightarrow \text{CHO} + \text{Cl}^- + \text{H}^+ \\
\text{CO}_2 &\rightarrow \text{CO}_3^- \quad \text{(oxalate)}
\end{align*}
\]

(14)

(15)

(16)

(17)

(18)

(19)

(20)

The observed \( G(\text{Cl}) \)-values in solutions saturated with pure oxygen are somewhat lower compared to those containing air (Table 5). In this case the primary \( e_\text{aq}^- \) attack on TCE is completely excluded, but as shown above the produced \( \text{O}_2^- \) species are involved in the process.

5.2. Combined radiation-ozone processing of water

It is well known that a great number of organic pollutants in water can be decomposed just by reaction of ozone (\( \text{O}_3 \)). In the combined radiation-ozone water treatment \( \text{HO}_2^-/\text{O}_2^- \) as well as \( \text{OH}^- \) radicals act as carriers for the chain-reaction of ozone degradation (e.g. Hoigne, 1982; Sehested et al., 1983, 1984, 1991, 1992; Bühler et al., 1984; Staehelin et al., 1984). In the absence of pollutants in water the chain-mechanisms by Weiss (1935) is operative. The major reaction steps are:

\[
\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{OH} + 2\text{O}_2 \quad (20)
\]

\[
\begin{align*}
2\text{O}_2 &\rightarrow (\text{CO}_2)_2 \quad \text{(oxalate)}
\end{align*}
\]

(21)
\[ \text{O}_3 + \text{O}_2^– \rightarrow \text{O}_3^– + \text{O}_2 \]  
\[ k_{21} = 1.5 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ (Sehested et al., 1983)} \]

\[ \text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2 \]  
\[ k_{22} = 1.1 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ (Sehested et al., 1984)} \]

\[ \text{O}_3 + e_{\text{aq}} \rightarrow \text{O}_3^– \]  
\[ k_{23} = 3.6 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ (Sehested et al., 1982)} \]

\[ \text{O}_3 + \text{O}^– \rightarrow \text{O}_3^– \]  
\[ k_{24} = 2.5 \times 10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ (Adams et al., 1966)} \]

\[ \text{O}_3^– + \text{OH} \rightarrow \text{O}_3 + \text{OH}^– \text{ (30%)} \]  
\[ \substack{\text{e}^\text{aq} \rightarrow \text{HO}_2 \text{ (70%)} \end{array} \text{ (Staehelin et al., 1984)} \]

\[ \text{O}_3^– + \text{H}^+ \rightarrow \text{HO}_3 \]  
\[ k_{26a} = 5.2 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ (Staehelin et al., 1984)} \]

\[ k_{26b} = 3.3 \times 10^2 \text{s}^{-1} \text{ (Staehelin et al., 1984)} \]

The ozone intermediates \( \text{HO}_2^+ \) (\( \lambda = 350 \text{ nm, } \epsilon_{350} \approx 300 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1} \)) and \( \text{O}_3^–\) (\( \lambda = 430 \text{ nm, } \epsilon_{430} \approx 2000 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1} \)) are strongly oxidizing agents and hence they can decompose organic pollutants. The simultaneous application of radiation and ozone for water treatment leads to a very efficient degradation of pollutants (e.g. Gilbert and Gustin, 1973; Micic et al., 1975; Hashimoto et al., 1979, 1980; Takehisa and Sakumoto, 1982; Getoff and Lutz, 1985; Getoff, 1986a, 1987, 1990b, 1992; Waite et al., 1992; Lin et al., 1993).

Micic et al., (1975) reported that the decomposition of phenol in oxygenated water solutions strongly depends on its concentration and on the applied dose rate. The degradation yield, \( G(\text{–PhOH}) \) of \( 2 \times 10^{-2} \text{mol dm}^{-3} \) phenol increases from 2.6 to 250 by decreasing the dose rate from 100 to 13 Gy h \(^{-1} \). This effect is explained by a chain reaction initiated by \( \text{OH} \) and \( \text{O}_3^– \) radicals and propagated mainly by the \( \text{O}_2^– \) transients. Similar observations have been made also by Pikaev and Shubin (1984 and reference therein). At low dose-rates in aerated phenol solutions they reported \( G(\text{–PhOH}) = 250-500 \). As a main process is suggested the formation of polymers. The increase of the temperature to 80°C is leading to a two fold higher decomposition of phenol. Takehisa and Sakamoto (1982) showed that the
applied dose can be reduced 20-fold by combination of radiation and ozonation. In this case preferentially carboxylic acids (mainly oxalic acid) are produced which are subsequently decomposed to H₂O and CO₂.

As final products of oxygenated 10⁻³ mol/dm⁻³ phenol solutions Hashimoto et al., (1979) have determined by means of HPLC-method: G(pyrocatechol) = 1.42, G(hydroquinone) = 0.94 and traces of resorcinol and phloroglucinol as well as G(PhOH) = 2.66. The same authors Hashimoto et al., 1980 studied the degradation of 10⁻³ mol dm⁻³ phenol by electron beam processing in airfree as well as in solutions containing O₂ or saturated with pure oxygen in flow system. The phenol-content was reduced up to 90% at a dose of 5 kGy and a flow rate of 1.5-5 dm³/min⁻¹ and 2 mA current beam. The formation of the same products was observed as described above.

Waite et al. (1992) used high energy electron (1.5 MeV beam) and a current varied up to 50 mA (doses up to 8.5 kGy) for decomposition of phenol (0.75 x 10⁻³ mol dm⁻³) at pH 5 and 7 in addition to studies conducted to the radiolysis of trichloroethylene (6 x 10⁻⁵ mol dm⁻³ pH 7) and chloroform (6 x 10⁻³ to 1 x 10⁻⁴ mol dm⁻³, pH 5) in absence and presence of clay. In the case of phenol (no clay) a complete decomposition was observed at a dose of about 7 kGy. About the same dose was needed for the degradation of chloroform, but only 0.5 kGy were sufficient for the radiolysis of trichloroethylene. Lin et al. (1993) conducted electron beam (1.5 MeV, 50 mA) experiments for removing phenol (0.01 to 0.95 x 10⁻³ mol dm⁻³) over the pH-range of 5–9 using doses up to 7 kGy under flow stream (480) dm³ min⁻¹) in absence and presence of 3% kaolin clay. At low doses as major products were found: catechol, hydroquinone and resorcinol. However, at continued oxidative procedure the formation of formaldehyde, acetaldehyde, glyoxal and formic acid were identified. Although phenol (0.95 x 10⁻¹ mol dm⁻³) was decomposed by a recirculation experiments the total organic carbon in the solution decreased only slightly, indicating the formation of polymers.

From the above reported data it is obvious that the radiation induced-phenol degradation proceeds by rather complicated reaction mechanisms depending on many factors: substrate concentration, applied dose and dose-rate, availability of oxygen etc. The degradation of 10⁻³ to 10⁻¹ mol dm⁻³ phenol saturated with oxygen (1.25 x 10⁻³ mol dm⁻³ O₂, pH = 6.5) as well as the formation of the major products resulting from 10⁻⁴ mol dm⁻³ phenol as a function of dose (dose-rate: 70 Gy min⁻¹) is presented in Fig. 6 for illustration. Obviously, at a dose of about 1.2 k Gy the 10⁻⁴ mol dm⁻³ phenol is practically completely degraded (Fig. 6, curve B). How-

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**Fig. 5.** Utilization of the ozone formed in the air-layer between accelerator window and water surface.

*EA = Electron accelerator; P = Gas pump; GCB = Gas collecting bell.*
ever, at the same time pyrocatechol, hydroquinone and hydroxyhydroquinone are formed (Fig. 6, II).

The decomposition of phenol in aerated solutions is initiated by OH-attack \((k = 1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) resulting in the formation of OH-adducts (hydroxycyclohexadienyl radicals) on o-, m-, p- and ipso-positions (e.g. Getoff and Lutz, 1985; Getoff, 1986a, 1987, 1992b, 1993a). These transients can add \(O_2\) forming the corresponding peroxy-radicals which are leading to ring-opening and splitting of \(HO_2^{-}\)-species. The last ones are then reacting in the same manner as OH radicals. All these reaction steps are favored at low substrate concentrations and low dose-rates. At higher concentrations and dose-rates the phenol-transients react preferentially with the phenol leading to the formation of oligomers. The major reactions explaining the formation of the above mentioned products are given for illustration of some reaction steps [see equations (30–37)] on the opposite page.

The \(HO_2^{-}/O_2^{-}\) and the OH radicals resulting from the above processes are initiating chain-reactions. The observed products are attacked further by OH, \(HO_2^{-}/O_2^{-}\) species in a prolonged irradiation procedure and can be decomposed upto \(CO_2\) and \(H_2O\).

5.4. Degradation of chlorinated aromatic compounds

Chlorophenols have been often chosen as model substances for studies in respect of the irradiation-induced degradation of chlorinated aromatic compounds, e.g. pesticides used in agriculture, or basic substances applied in the chemical industry (e.g. Getoff and Solar, 1986, 1988; Draper et al., 1989 etc.).

It is of special interest to show the synergistic effect of radiation and ozone, taking \(10^{-4} \text{ mol dm}^{-3}\) 4-Cl-phenol (4-CIPhOH) as an example (Getoff and Solar, 1988). The course of its degradation has been followed as a function of dose (dose rate: \(50 \text{ Gy min}^{-1}\)) in aerated \((0.25 \times 10^{-3} \text{ mol dm}^{-3} \text{O}_2)\) as well as in solutions saturated with oxygen \((1.25 \times 10^{-3} \text{ mol dm}^{-3} \text{O}_2)\) and containing \(1.1 \times 10^{-5} \text{ mol dm}^{-3} \text{O}_3\) which are presented in Fig. 7. Obviously, in the first case (Fig. 7, A/I, curve a) a dose of above 12 kGy is needed for degradation of the pollutant, compared to a dose less than 1.5 kGy for the solutions containing even a small amount of ozone (Fig. 7, A II, curve a). The course of the \(\text{Cl}^-\) yields in respect to dose in both cases are rather similar, however the aldehyde yield is strongly effected by ozone (compare curves c in I and II inserts, Fig. 7).

The yield of the substrate degradation, \(G\) (4-CIPhOH), as well as the formation of \(\text{Cl}^-\) and aldehyde for the same substrate concentration under different conditions are presented in Fig. 7, Table B. Here again is illustrated that the highest \(G\)-values are observed in the presence of ozone.

![Fig. 7](image-url)

**Fig. 7.** (A) Radiation induced decomposition of \(10^{-4} \text{ mol dm}^{-3}\) 4-Cl-phenol (\(pH \sim 6.5\)) as a function of dose. (I) In the presence of air \((0.25 \times 10^{-3} \text{ mol dm}^{-3} \text{O}_2)\). (II) In the presence of \(1.25 \times 10^{-3} \text{ mol dm}^{-3} \text{O}_2\) and \(1.1 \times 10^{-5} \text{ mol dm}^{-3} \text{O}_3\). (a) decomposition of 4-Cl-phenol; (b) formation of \(\text{Cl}^-\) and (c) aldehyde. (b) Initial yields \((G_i)\) of the decomposition of \(10^{-4} \text{ mol dm}^{-3}\) 4-Cl phenol as well as of the formation of \(\text{Cl}^-\) ions and of aldehydes observed under various irradiation conditions at \(pH \sim 6.5\) (Getoff and Solar, 1988).
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\[ \text{Scheme 2} \]

\[ \text{C}_6\text{H}_5\text{OH} + \text{OH} \rightarrow \text{C}_6\text{H}_5\text{O}^+ + \text{H}_2\text{O} \quad (\sim 70\%) \]  

(\text{OH - adducts on p-, m-, p- and ipso - positions})

\[ 2 \text{C}_6\text{H}_5(\text{OH}) \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{OH} \quad (\sim 30\%) \]

\[ \text{C}_6\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O}_2^\bullet \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{HO}_2^\bullet \]

(pyrocatechol)

\[ \text{C}_6\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O}_2^\bullet \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{HO}_2^\bullet \]

(mucondialdehyde)

\[ \text{C}_6\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O}_2^\bullet \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{HO}_2^\bullet \]

(hydroquinone)

\[ \text{C}_6\text{H}_5\text{OH} + \text{OH} \rightarrow \text{C}_6\text{H}_5\text{O}_2^\bullet \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{HO}_2^\bullet \]

(hydroxyhydroquinone)

\[ \text{C}_6\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O}_2^\bullet \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{HO}_2^\bullet \]


\[ \text{Mucosaldehyde} \quad \text{Muconic acid} \quad \text{Maleic acid} \quad \text{Oxalic acid} \quad \text{Formic acid} \]

(30)

(31)

(32a)

(32b)

(33)

(34)

(35)

(36)

(37)
The very efficient synergistic effect of radiation and ozone is illustrated by the following reaction steps given in equation (38).

By means of pulse radiolysis technique it has been possible to gain a deeper insight in the complicated degradation mechanisms of chlorinated phenols (e.g. Getoff and Solar, 1986, 1988). The transient absorption spectra obtained at 2 μs and 100 μs after a 0.4 μs electron pulse in the case of 4-CIPhOH solution saturated with oxygen is presented in Fig. 8 (Getoff and Solar, 1988).

First, the OH-attack on the substrate takes place resulting in the formation of OH-adduct, where \( k(\text{OH} + 4\text{-CIPhOH}) = 1.5 \times 10^{10} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \). The resulting transients are represented by spectrum A, Fig. 8. Simultaneously, \( \text{e}_{\infty} \) and H-atoms are converted in the slow reacting \( \text{O}_2^- \) species (see also Table 3). The next step is addition of oxygen to the OH-adduct (\( k \approx 2 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \)) under formation of peroxyl-radicals, followed by splitting off of water and \( \text{HO}_2/\text{O}_2^- \) species. The last ones attack the substrate as well as the radicals present in the bulk of the solution. Hence, the measured absorption spectrum (B) at 160 μs after pulse expresses a mixture of transients. This fact is illustrated by the kinetic traces given as insert in Fig. 8. Finally, the reactions of \( \text{HO}_2/\text{O}_2^- \) species with substrate and with the radicals present in the bulk in the solution take place as well as opening of the aromatic ring. All these reaction steps are competing with each other. The reaction mechanisms are similar to that of phenol [see equation (30–37)] leading to the degradation of 4-CIPhOH.

A special environmental problem is the degradation of the extremely toxic polychlorinated biphenyls (PCBs). It has been found by several authors (e.g. Singh et al., 1985 and references therein) that in alkaline isopropanol solution a radiolytic dechlorination by chain-reaction takes place (\( G_i > 1000 \)). Further investigations in this respect are urgently needed.

5.5. Combination of radiation and conventional techniques

Depending upon the kind and concentration of given pollutants in water the efficiency and economy
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Fig. 9. Schemes for purification of drinking (A) and of industrial wastewater by electron processing (B).

of their decomposition can be essentially increased by combination of conventional methods and irradiation. Sakumoto and Miyata (1984) reported the purification of polluted water by combined application of radiation and conventional methods, such as biological oxidation, coagulation with $\text{Fe}_2(\text{SO}_4)_3$, and ozonation. The choice of combination of methods depends on the biological, chemical and physical properties of the pollutants and their behaviour against radiation. Water containing organic compounds having functional groups, such as hydroxyl, carbonyl, carboxyl etc. will be first irradiated and then introduced to a biological degradation procedure. Soluble monomers and polymers in water can be converted under irradiation into higher molecular weight substances. Hence, their removal can be successfully achieved by a subsequent coagulation in the presence of air. Although ozone is a powerful oxidizing agent it cannot lead in some cases to a complete destruction of pollutants without double bonds in their molecule. As shown above $\text{O}_3$ is a rather selective reagent to an unsaturated part of a pollutant molecule, however, as mentioned before, the ozone radiolysis in water results in the formation of OH and $\text{HO}_2/\text{O}_2^-$ radicals (e.g. Weiss, 1935; Taube and Bray, 1940; Alder and Hill, 1950 etc.) which are able to decompose the organic substances. This is one of the major reasons for the efficient synergistic effect of the $\text{O}_3$-radiation combination. The electron beam processing of drinking water as well as of wastewaters is schematically presented in Fig. 9 (see also Getoff, 1992a, 1993a, 1993b).

In the case of drinking water no chlorination procedure is needed before the electron beam processing (Fig. 9A). The optimal dose (and dose-rate) have to be elaborated by preliminary experiments. The scheme for electron treatment of wastewater is given in Fig. 9B. It represents a combination of radiation and conventional methods. The most efficient procedure should be developed by experiments designed for the individual purpose.

6. ECONOMICS

Concerning the economics for degradation of pollutants in water by electron beam processing in the presence of ozone or by combined methods of radiation and conventional techniques, it is difficult to give precise data in advance. This is so because of many factors involved in the process, such as kind and amount of pollutants in water, their properties (chemical, biological, physical etc.) as well as the dose, dose-rate needed and their decomposition in the presence of air, ozone etc. These parameters can be determined by laboratory and pilot-plant experiments. As an example in this respect the studies by Hashimoto et al. (1988) can be useful.

7. CONCLUSION

After a brief introduction concerning some basic data of radiation units, sources and primary products of water radiolysis, the radiation induced degradation of chlorinated pollutants in water are reviewed. The decomposition process of aliphatic, olefinic and aromatic substances under various conditions are discussed and probable reaction mechanisms are presented. The synergistic effect of radiation and ozone is also reviewed. Finally, schemes for purification of drinking water as well as of industrial wastewater are proposed.

REFERENCES


