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Chapter 5

Radiation-Induced Degradation of Organic Compounds and Radiation Technologies for Purification of Aqueous Systems

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Additional information is available at the end of the chapter

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Abstract

Environmental application of radiation technologies is an important part of radiation processing. Radiation treatment of aqueous systems contaminated with organic compounds is a promising method of water and wastewater purification and corresponding technologies are being developed. In this chapter, the following aspects of radiation treatment process are considered: sources of contamination and major contaminants of water and wastewater; primary processes in aqueous systems initiated by ionizing radiation; principal ways of contaminant conversion as consequences of primary processes (complete mineralization of organic compounds, partial decomposition of organic molecules resulted in detoxification, decolorization, disinfection of polluted water, and improvement in biological degradation of contaminant, polymerization of monomers' contaminants, oxidation-reduction processes, and coagulation of colloids); sources of ionizing radiation; and main equipment applied in radiation technologies of aqueous system purification.

Keywords: radiation chemistry, radiation technology, wastewater, electron accelerators, organic compounds

1. Introduction

Changes in a matter resulted from reformation of chemical bonds structure under the action of ionizing radiation gave rise to implementation of various radiation technologies. At present, an overwhelming majority of the latter represent modification of materials, that is, polymers curing, grafting, production of thermo-shrinkable plastics, improvement of semiconductor circuits, and so on [1, 2]. At the same time, there exists an important area of radiation technologies application, namely environment conservation, where those technologies are not widespread as yet, or just are at the stage of development. One of the problems in environment

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conservation is purification of flue gases and wastewater, and radiation technologies possess a high potential in the direction providing for higher purification degree, unachievable in some cases by conventional purification technologies.

Traditionally, radiation treatment (by gamma/X-rays or accelerated electrons beams) for the purification of water and wastewater is attributed to the so-called Advanced Oxidation Processes (AOPs) and corresponding technologies—to Advanced Oxidation Technologies (AOTs) (see, e.g., books [3, 4]). The reason is that initially new processes, appeared in addition to routine purification processes, such as biological treatment, coagulation, sedimentation, and filtration, have been based on the oxidation of organic impurities by strong oxidizing agent—hydroxyl radicals, produced firstly in chemical reactions with participation of hydrogen peroxide, then with the use of physical methods, and irradiation of aqueous systems produces hydroxyl radicals as one of the main intermediates. However, the attribution of radiation treatment to AOPs seems to be not quite correct, since ionizing radiation initiates in irradiated media not only oxidizing processes but also reducing ones. Though the formation of reducing particles under radiolysis, as well as under photolysis, sonolysis, electrolysis, and so on, has been mentioned earlier repeatedly [3–5], the role of reductive processes in the purification of water and wastewater was not considered as specific and important one, partly due to comparatively low importance of the processes in the decomposition of organic compounds.

A significant advantage of radiation-induced processes over other AOPs consists in sufficient knowledge of mechanism of the processes including available qualitative and quantitative data on primary events of energy absorption, intermediates formation ways and properties, and reactions of organic compounds conversions. Nowadays, new research and review articles on radiation treatment are being published which demonstrate high interest to the problem of environmental application of radiation technologies.

The aim of this chapter is to show interrelation between well-established primary radiation-chemical processes and the main ways of organic contaminants conversions, as well as to present the current state of radiation equipment being used at present or proposed to be used in radiation technologies of water and wastewater purification.

2. Types of aqueous systems to be purified

The application of radiation technologies to the purification of aqueous systems to a certain extent is determined by a subject of radiation treatment, that is, composition of the system. There are several types of aqueous systems to be purified commercially which differ considerably in qualitative and quantitative composition. The latter is usually expressed either chemically as a concentration of components (in units of moles or mass of the component per volume or mass of solution) or in units characteristic of water/wastewater purification technologies, that is, COD (Chemical Oxygen Demand), BOD (Biological Oxygen Demand), and TOC (Total Organic Carbon).

TOC is determined as the total mass of carbon atoms in dissolved organic compounds per unit solution volume and expressed usually in mg/L (mg/dm^3) or in ppm (parts per million, i.e.,

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mass of carbon per mass of solution), the latter being numerically almost the same, as far as a mass of 1 dm^3 of diluted aqueous solution is close to 1 kg. COD is a mass of oxygen necessary for complete oxidation of organic compounds, present in unit volume of the solution, into carbon dioxide (and other inorganic compounds), while the BOD is a mass of oxygen, consumed in the process of biological oxidation of organic compounds, present in unit volume of the solution. Since biological oxidation is a long-term process, instead of BOD the notation BOD_5 is often used, which means BOD measured after 5 days of biological oxidation. Like TOC, both COD and BOD are expressed in the same units and do not relate to the kind of organic compounds polluting water or wastewater, but rather reflect the total organic matter content and its part that can be degraded in biological processes [6].

The main types of aqueous systems to be purified are considered to be water (from different sources) and wastewater.

2.1. Water

Water, consumed in the course of human activity, besides municipal water, that is, water of potable quality offered by water companies, has two natural sources: (1) groundwater, that is, water, seeped through from the surface and present in porous rocks below the surface, shallow wells, or deep aquifers, and (2) surface water, that is, water from a source that is exposed to the environment like rivers, canals, lakes, and open wells [7].

Contamination of water may occur due to following reasons: municipal water—from pipelines, fittings, biofouling; groundwater—due to failing of septic systems, leaking sewer lines, and from land discharge by passage through soils and fissures or interaction with surface water; surface water—by treated wastewater, discharge of raw sewage, municipal wastewater, storm-water runoff, runoff from urban and agricultural areas, also animals and humans are both indirect and direct contributors to the contamination.

The level of water contamination usually is not high to use it for many purposes. Thus, most pristine rivers will have a 5-day carbonaceous BOD below 1 mg/L. Moderately polluted rivers may have a BOD value in the range of 2–8 mg/L. Rivers may be considered severely polluted when BOD values exceed 8 mg/L [8].

Groundwater from depth and confined aquifers is usually microbially safe and chemically stable in the absence of direct contamination; however, shallow or unconfined aquifers can be subject to contamination from discharges or seepages associated with agricultural practices (e.g., pathogens, nitrates, and pesticides), on-site sanitation and sewerage (pathogens and nitrates), and industrial wastes.

Both groundwater and surface water have natural impurities including inorganic salts and, particularly—surface water, NOM (natural organic matter), represented mainly by humic and fulvic acids, cellulose, lignin) which have to be removed, or reduced in concentration, when using the water for drinking purposes [9, 10]. Quality specifications for drinking water are subject of policies, regulations, and standards on both national and international levels [11–14]. Guidelines are being established that determine the limit concentration of chemical compounds

contaminating potable water. Now, there are more than 100 compounds for which guideline values have been established (see **Table 1**, data compiled from [11]).

Guideline values for the chemicals listed in **Table 1** are in the range of 10^{-1}–10^{-4} mg/L [15], and real contamination of water exceeds these values only in extraordinary cases when special purification is needed.

Much more significant problem of water purification is microbial contamination [11, 15]. **Table 2** shows the ranges of microbial contamination of surface and groundwater.

Exact guideline values for microbial contamination are not established, in [15] being just noted that "*E. coli* or thermotolerant coliform bacteria must not be detectable in any 100 ml sample." However, report [16] quotes data that for tolerable drinking water densities of Enteric virus, *Giardia*, and *Cryptosporidium* are equal to 2.2×10^{-7}, 6.8×10^{-6}, and 1.7×10^{-6} per liter, correspondingly. It means that to make water from natural sources drinkable, the concentration of microorganisms should be reduced by more than six orders of magnitude.

So, using water from natural sources for industrial purposes does not require its purification, but using it as potable water requires disinfection and in special cases removal of hazardous contaminants.

2.2. Wastewater

Contamination level of wastewater is much higher than that of water and the goal of wastewater purification, except for the problems of reuse [13], is to reduce contamination down to

Chemicals from industrial sources, human dwellings	**Chemicals from agricultural activities**	**Chemicals used in water treatment or materials in contact with drinking water**
Inorganic		
Cd, Hg, Cyanide	Nitrate/nitrite	Sb, Cu, Pb, Ni
Organic		
Benzene; Carbontetrachloride; Di(2-ethylhexyl)phthalate; 1,2-Dichlorobenzene; 1,4-Dichlorobenzene; 1,2-Dichloroethane; 1,1-Dichloroethene; 1,2-Dichloroethene; Dichloromethane; 1,4-Dioxane; Edetic acid; Ethylbenzene; Hexachlorobutadiene; Nitrilotriacetic acid; Pentachlorophenol; Styrene; Tetrachloroethene; Toluene; Trichloroethene; Xylenes	Alachlor; Aldicarb; Aldrin and dieldrin; Atrazine; Carbofuran; Chlordane; Chlorotoluron; Cyanazine; 1,2-Dibromo-3-chloropropane; 1,2-Dibromoethane; 1,2-Dichloropropane; 1,3-Dichloropropene; Dichlorprop; Dimethoate; Endrin; Fenoprop; Isoproturon; Lindane; MCPA; Mecoprop; Methoxychlor; Metolachlor; Molinate; Pendimethalin; Simazine; Terbuthylazine; Trifluralin	**Disinfectants:** Monochloramine; Chlorine **Disinfection byproducts:** Bromate; Bromodichloromethane; Bromoform; Chloral hydrate; Chlorate; Chlorite; Chloroform; Cyanogen chloride; Dibromoacetonitrile; Dibromochloromethane; Dichloroacetate; Dichloroacetonitrile; Formaldehyde; Monochloroacetate; Trichloroacetate; 2,4,6-Trichlorophenol; Trihalomethanes **Pesticides:** Chlorpyrifos; DDT (and metabolites); Pyriproxyfen **Organic contaminants from treatment chemicals:** Acrylamide; Epichlorohydrin **Organic contaminants from pipes and fittings:** Benzopyrene; Vinyl chloride

Table 1. Contaminants in water for which guideline values have been established (naturally occurring chemicals: As, Ba, B, Cr, F, Mn, Mo, Se, U).

level appropriate for discharge into environment. Usually, wastewater is divided into two main categories: industrial and municipal or domestic, in accordance with its specific composition. However, amenably to more strict definition adduced in [13]: "Wastewater is liquid waste discharged from homes and other residential premises, commercial and industrial premises and similar sources, to individual disposal systems or to municipal sewer pipes. It contains mainly human excreta and used water. Wastewater collected in municipal sewerage systems is called municipal wastewater or municipal sewage." A similar definition is contained in [17]: "Municipal wastewater originates from domestic, industrial, commercial and institutional sources within a given human settlement or community. Urban wastewater includes both municipal wastewater and urban runoff." It means that industrial wastewater may be regarded as a part of municipal one. Nevertheless, while considering wastewater composition, more useful is to break down wastewater by sources. **Table 3** lists the data on contamination of wastewater from different sources [17].

From the data of **Table 3**, it follows that the basic constituent of municipal and domestic wastewater is organic matter, including nutrients, which is substantially biodegradable. Special purification is required to remove pathogenic microorganisms and emerging pollutants. On the contrary, the composition of industrial wastewater differs markedly for different industries (see **Table 4**), the level of organic contamination is high, and organic matter is often almost non-biodegradable.

Pathogen or indicator group	Lakes and reservoirs	Impacted rivers and streams	Wilderness rivers and streams	Groundwater
Campylobacter	20–500	90–2500	0–1100	0–10
Salmonella	—	3–1000	1–4	—
E. coli (generic)	10,000–1,000,000	30,000–1,000,000	6000–30,000	0–1000
Viruses	1–10	30–60	0–3	0–2
Cryptosporidium	4–290	2–480	2–240	0–1
Giardia	2–30	1–470	1–2	0–1

Table 2. Examples of high detectable concentrations (per liter) of enteric pathogens and fecal indicators in different types of source waters.

Sources of wastewater	Typical components
Domestic wastewater	Human excreta (pathogenic microorganisms), nutrients, and organic matter. May also contain emerging pollutants (e.g., pharmaceuticals, drugs, and endocrine disruptors)
Municipal wastewater	Very wide range of contaminants, such as pathogenic microorganisms, nutrients and organic matter, heavy metals, and emerging pollutants
Industrial wastewater	Contaminants depend on the kind of industry

Table 3. Typical components of wastewater from different sources.

Industry type	Wastewater generation, m^3/ton	Typical content of effluent	COD, g/L
Alcohol refining	16–32	High level of BOD and COD	5–22
Beer and malt	5–9	BOD, COD, SS, nitrogen, phosphorus—variable by individual processes; pH variable due to acid and alkaline cleaning agents; high temperature	2–7
Coffee	No data	High levels of BOD and SS concentrations;	3–15
Dairy products	3–10	Dissolved sugars, proteins, fats, and additive residues; BOD, COD, SS, nitrogen, and phosphorus	1.5–5.2
Fish processing	8–18	High levels of BOD and SS concentrations; strong organics, antibiotics, growth hormones, pesticides, and insecticides	~2.5
Meat and poultry	8–18	High levels of BOD and SS concentrations; strong organics, antibiotics, growth hormones, pesticides, and insecticides	2–7
Organic chemicals	0–400	Pesticides, pharmaceuticals, paints and dyes, petro-chemicals, detergents, plastics, feed-stock materials, byproducts, product material in soluble or particulate form, washing and cleaning agents, solvents, and added-value products such as plasticizers	0.8–5
Petroleum refineries	0.3–1.2	Production of fossil fuels—contamination from oil and gas wells and fracking; hot cooling water	0.4–1.6
Plastic and resins	0.3–1.2		0.8–5
Pulp and paper	85–240	Chlorinated lignosulfonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbons—about 500 different chlorinated organic compounds identified; colored compounds and absorbable organic halogens (AOX); pollutants characterized by BOD, COD, suspended solids (SS), toxicity, and color	1–15
Starch production	10–1.5–42	High levels of BOD and SS concentrations;	
Sugar refining	4–18	High levels of BOD and SS concentrations;	1–6
Vegetable oils	1–5	High levels of BOD and SS concentrations; high particulates, some dissolved organics, surfactants;	0.5–1.2
Vegetables and fruits	7–35	High levels of BOD and SS concentrations; high particulates, some dissolved organics, surfactants;	2–10
Wine and vinegar	11–46	High levels of BOD and SS concentrations; high particulates, some dissolved organics, surfactants	0.7–3.0

Table 4. Wastewater characteristics in some industries (compiled from data of [17]).

The content of organic matter in wastewater from different sources varies, reaching on average up to several grams per liter. Thus, quoted in [18] the mean values for wastewater in France and USA are, respectively, the following: COD—300–1000 and 250–1000, BOD—100–400 and 110–400, suspended solids—150–500 and 100–350, total potash and nitrogen—30—100 and 20–85, and total phosphorus—1–25 and 4–15. More than twofold difference between COD and BOD shows that organic matter cannot be removed by biological treatment and additional treatment of wastewater is required.

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3. Principal ways of radiation-induced chemical processes promoting aqueous system purification

Impurities in water and wastewater are present, as a rule, at relatively very low concentration, except for some kinds of wastewater with very high content of organic compounds. Electron fraction of inorganic and organic substances in ground and surface water, as well as in industrial and municipal/domestic wastewater, usually does not exceed 1%. Since the absorption of ionizing radiation, both electromagnetic one and accelerated electrons in the range of energies 0.5–10 MeV, by a particular component of a mixture, is proportional to the electron fraction of the component, and almost all the radiations are absorbed by water resulting in primary processes of water radiolysis, the products of which (mainly—hydrated electrons e^{-}_{aq}, hydrogen atoms $^{\bullet}H$, and hydroxyl radicals $^{\bullet}OH$) do react with substances dissolved or dispersed in water. As a whole, the process of water purification with the use of ionizing radiation is presented in **Figure 1**.

In this section, the main processes induced by ionizing radiation, which can be applied to water purification technologies, are discussed together with a brief discussion on the formation and properties of the products of water radiolysis. Most principal reactions of reactive products of water radiolysis with a solute, concerning wastewater treatment by ionizing radiation, have been overviewed recently [5].

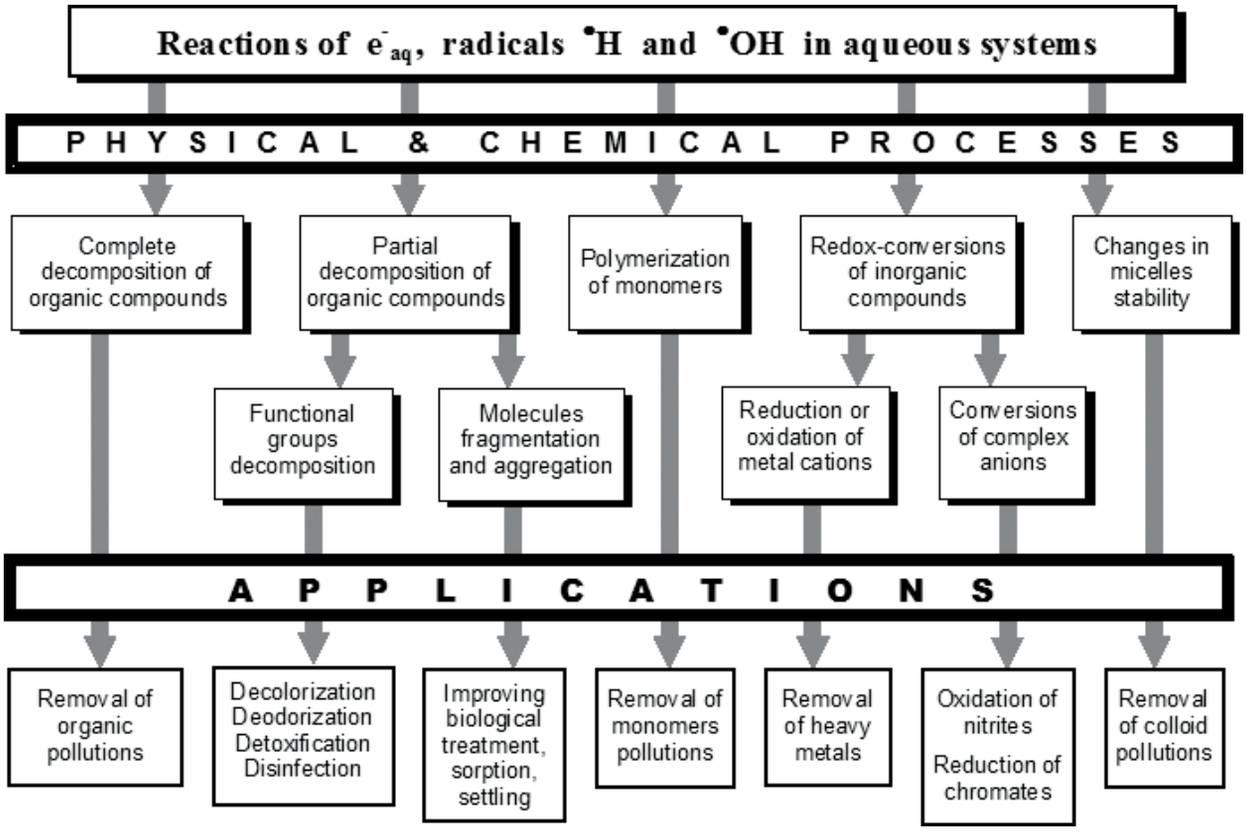


Figure 1. Main processes of radiation purification of aqueous systems.

3.1. Initial stages of ionizing radiation action on aqueous systems

As it has been mentioned earlier, reactive products of water radiolysis are the initiators of almost all the processes of dissolved or dispersed substance conversion in such aqueous systems as water and wastewater. The mechanism of primary processes in radiolysis of water including ionization and excitation of molecules by ionizing radiation, formation, and subsequent reactions of the products of radiolysis is well established both qualitatively and quantitatively [19–21]. Briefly, it can be described as the following:

3.1.1. Energy absorption

Ionizing radiation, such as electromagnetic one (gamma or X-rays) and accelerated electrons in the range of energies 0.5–10 MeV, is absorbed in the liquid medium by portions of near 30 eV in small volumes (referred to as "spurs") separated by about 100 nm. Because of high local concentration of reacting species formed in "spurs," their reactions with each other are weakly influenced by a solute.

3.1.2. Primary processes

Primary processes of ionizing radiation interaction with water molecules include

Excitation and ionization of water molecules, decay of singlet excited states, and primary particles formation ($\leq 10^{-14}$ s).

$$H_2O \longrightarrow H_2O^*$$

$$H_2O \longrightarrow e^- + H_2O^+$$

$$H_2O^* \longrightarrow {}^\bullet H + {}^\bullet OH$$

$$H_2O^* \longrightarrow H_2 + O$$

Formation of hydrated electrons e^-_{aq}, relaxation of ionized molecules of water ($\leq 10^{-12}$ s)

$$e^- \longrightarrow e^-_{therm} \longrightarrow e^-_{aq}$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + {}^\bullet OH$$

Main reactions of formed particles in "spurs" ($\leq 10^{-7}$ s)

$$e^-_{aq} + H_3O^+ \longrightarrow {}^\bullet H + H_2O$$

$${}^\bullet H + {}^\bullet H \longrightarrow H_2$$

$${}^\bullet H + {}^\bullet OH \longrightarrow H_2O$$

$${}^\bullet OH + {}^\bullet OH \longrightarrow H_2O_2$$

$$e^-_{aq} + {}^\bullet OH \longrightarrow OH^-$$

Product	Reactive			No reactive				
	e^-_{aq}	$^\bullet H$	$^\bullet OH$	O	H_2	H_2O_2	H_3O^+	OH^-
G, μmol/J	0.28	0.06	0.28	<0.01	0.04	0.07	0.33	0.05

Table 5. *G*-values of water radiolysis products at the end of "spur" processes.

3.1.3. "Initial" yields

After diffusive expansion of "spurs," when the distribution of formed particles becomes nearly uniform, further reactions proceed in the bulk of solution according to the so-called homogeneous kinetics, the concentrations of water radiolysis products being determined by their "initial" radiation-chemical yield—*G*-value, that is, number of moles of a product formed per 1 joule of absorbed energy of ionizing radiation (see **Table 5**).

3.1.4. Influence of oxygen

In the presence of dissolved oxygen, the following fast reactions take place:

$$e^-_{aq} + O_2 \longrightarrow {}^\bullet O_2^- \qquad k = 1.9 \times 10^{10}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

$$^\bullet H + O_2 \longrightarrow HO_2^\bullet \qquad k = \sim 2 \times 10^{10}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

the acid-base equilibriums being established:

$$^\bullet OH \rightleftarrows {}^\bullet O^- + H^+ \qquad pK_A = 11.9$$

$$HO_2^\bullet \rightleftarrows {}^\bullet O_2^- + H^+ \qquad pK_A = 4.7$$

$$H_2O_2 \rightleftarrows HO_2^- + H^+ \qquad pK_A = 11.6$$

$$\left(^\bullet H \rightleftarrows e^-_{aq} + H^+\right) \qquad pK_A = 4.4$$

3.1.5. Reactions in the bulk of solution

Mutual reactions of water radiolysis products go on in the bulk of solution as homogeneous ones (see **Table 6**), competing thereby with their reactions with a solute.

Properties of reactive free-radical products from water and their reactivity to some specific functional groups in organic compounds are listed in **Tables 7** and **8**.

3.1.6. Chemical properties of reactive radicals

Chemical properties of reactive radicals determining their reactions with a solute may be presented as the following:

Hydrated electron as a reducing particle is characterized by the following fast reactions of one-electron transfer from its hydrated state to a molecule/ion in

Reaction	k, L mol^{-1} s^{-1}	Reaction	k, L mol^{-1} s^{-1}
Hydrated electrons		Hydrogen atoms	
$e^-_{aq} + H_2O \rightarrow {}^\bullet H + OH^-$	19	${}^\bullet H + H_2O \rightarrow {}^\bullet OH + H_2$	10
$e^-_{aq} + H_3O+ \rightarrow {}^\bullet H + H_2O$	2.3×10^{10}	${}^\bullet H + H_2O_2 \rightarrow {}^\bullet OH + H_2O$	9×10^7
$e^-_{aq} + H_2O_2 \rightarrow {}^\bullet OH + OH^-$	1.1×10^{10}	${}^\bullet H + OH^- \rightarrow e^-_{aq} + H_2O$	2.2×10^7
$e^-_{aq} + HO_2^- \rightarrow {}^\bullet O^- + OH^-$	3.5×10^9	${}^\bullet H + {}^\bullet H \rightarrow H_2$	1.2×10^{10} ($2\,k$)
$e^-_{aq} + {}^\bullet H \rightarrow H_2 + OH^-$	2.5×10^{10}	${}^\bullet H + {}^\bullet OH \rightarrow H_2O$	7×10^9
$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2\,OH^-$	5×10^9 ($2\,k$)	${}^\bullet H + HO_2{}^\bullet \rightarrow H_2O_2$ ($2\,{}^\bullet OH$)	~1×10^{10}
$e^-_{aq} + {}^\bullet OH \rightarrow OH^-$	3.0×10^{10}	Oxide radical ions	
$e^-_{aq} + {}^\bullet O^- \rightarrow 2\,OH^-$	2.2×10^{10}	${}^\bullet O^- + H_2O \rightarrow {}^\bullet OH + OH^-$	1.8×10^6
$e^-_{aq} + HO_2{}^\bullet \rightarrow HO_2^-$	1.5×10^{10}	${}^\bullet O^- + H_2 \rightarrow {}^\bullet H + OH^-$	8×10^7
$e^-_{aq} + {}^\bullet O_2^- \rightarrow 2\,HO_2^-$	1.3×10^{10}	${}^\bullet O^- + H_2O_2 \rightarrow {}^\bullet O_2^- + H_2O$	~5×10^8
Hydroxyl radicals		${}^\bullet O^- + HO_2^- \rightarrow {}^\bullet O_2^- + OH^-$	4×10^8
${}^\bullet OH + H_2 \rightarrow {}^\bullet H + H_2O$	4.2×10^7	${}^\bullet O^- + O_2 \rightarrow O_3^-$	3.6×10^9
${}^\bullet OH + H_2O_2 \rightarrow HO_2{}^\bullet + H_2O$	2.7×10^7	${}^\bullet O^- + {}^\bullet O_2^- \rightarrow 2\,OH^- + O_2$	6×10^8
${}^\bullet OH + HO_2^- \rightarrow {}^\bullet O_2^- + H_2O$	7.5×10^9	Perhydroxyl/superoxide radical anions	
${}^\bullet OH + OH^- \rightarrow {}^\bullet O^- + H_2O$	1.3×10^{10}	$HO_2{}^\bullet + H_2O_2 \rightarrow {}^\bullet OH + H_2O + O_2$	~1
${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$	7×10^9 ($2\,k$)	(${}^\bullet O_2^- + H_2O_2 \rightarrow {}^\bullet OH + OH^- + O_2$)	~1
${}^\bullet OH + {}^\bullet O^- \rightarrow HO_2^-$	~2×10^{10}	$2\,HO_2{}^\bullet \rightarrow H_2O_2 + O_2$	7.6×10^5
${}^\bullet OH + HO_2{}^\bullet \rightarrow O_2 + H_2O$	6×10^9	$HO_2{}^\bullet + {}^\bullet O_2^- \rightarrow HO_2^- + O_2$	8.9×10^7
${}^\bullet OH + {}^\bullet O_2^- \rightarrow O_2 + OH^-$	8×10^9	$2\,{}^\bullet O_2^- \rightarrow HO_2^- + OH^- + O_2$	0.3

Table 6. Homogeneous reactions in the bulk of solution.

	e^-_{aq}	${}^\bullet H$	${}^\bullet OH$	${}^\bullet O^-$
Charge	−1	0	0	−1
Optical absorption band:				
λ_{max}, nm	720	<188	235	240
ε_{max}, m^2/mol	1850	<160	60	~30
$W_{1/2}$, eV	0.85	—	~1.5	1.5–2
Partial molar volume, m^3/mol	7×10^{-6}	4×10^{-6}	6×10^{-6}	8×10^{-6}
Diffusion coefficient D, m^2/s	5×10^{-9}	7×10^{-9}	2×10^{-9}	1×10^{-9}
Standard redox potential E^0, V	−2.87	−2.3	1.9	1.7

Table 7. Properties of radicals from water.

- *Inorganic compounds with*
  - all the metal cations, except for cations of alkaline and alkali-earth metals;
  - majority of oxygen-containing and other complex anions, like NO_2^-, NO_3^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, $Fe(CN)_6^{3-}$, and so on (low reactivity to SO_4^{2-}, ClO_4^-, CO_3^{2-}, and some others).

Functional group			e^-_{aq}	$^\bullet H$	$^\bullet OH$	Functional group		e^-_{aq}	$^\bullet H$	$^\bullet OH$
Saturated carbon		$>CH_2$	−−	+	++	Amine	$-NH_2$	−−	−−	++
Unsaturated carbon in:	Alkenes	>C=C<	−−	++	++	Nitro	$-NO_2$	++	+	− −
	Aromatics	>C=C<	−−	++	++	Hydroxy	>CHOH	−−	+	++
	Azines	>C=N–	++	+	++	Ether	–O–	−−	+	++
Nitrile		−C≡N	+	−−	+	Chloro	−Cl	+	−	−−
Carbonyl		>C=O	++	−−	+	Bromo	−Br	++	+	−−
Carboxylic acids		−C(OH) = O	+	−−	+	Iodo	−I	++	++	+
Ester		−C(OR) = O	+	−−	+	Thiol	−SH	++	+	++
Amide		$-C(NH_2) = O$	+	−−	+	Disulfide	−S−S−	++	+	++

Table 8. Reactivity of radicals from water to some specific functional groups in organic compounds (high ++, medium +, low –, and very low – –).

- *Organic compounds with*
  - benzene ring in aromatic compounds;
  - heteroatomic double or triple bonds (carbonyl, nitro, nitrile);
  - thiol, disulfide, halide, nitro functional groups in both saturated and unsaturated (including aromatic) hydrocarbons.

Hydrogen atom reacts with the solute in the following types of reactions:

- Reduction reactions (one-electron transfer $H^\bullet + M^{n+/-} \rightarrow H^+ + M^{(n-1)+/-}$) with
  - majority of metal cations (however, low reactivity to Cd^{2+}, Zn^{2+}, some rare-earth metal cations, etc.);
  - some strong oxidizing inorganic anions, like CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-;
  - disulfide, iodo, bromo, nitro functional groups, and benzene ring in organic compounds.
- Addition reactions to a double bond ($^\bullet H + > C=C< \rightarrow >CH–{}^\bullet C<$) in unsaturated hydrocarbons, aromatic compounds.
- Reactions of H-atom abstraction from saturated carbon ($^\bullet H + > CH– \rightarrow H_2 + > {}^\bullet C–$) in any organic compounds.

Reactions of the last type are formally the oxidizing ones. Also, H-atom can oxidize metal cations in acid solutions, for example, $H^\bullet + Fe^{2+}$ $(+H^+) \rightarrow H_2 + Fe^{3+}$.

Hydroxyl radical is a strong oxidizer and reacts with the solute in oxidizing reactions of the following types:

- Direct oxidation reactions (one-electron transfer), including those ones with
  - all transition metal cations in lower oxidation state, majority of inorganic anions;
  - benzene ring in aromatic compounds and some functional groups;

- Addition reactions to a double bond ($^{\bullet}OH + > C{=}C< \rightarrow >C(OH)-{}^{\bullet}C<$) in unsaturated hydrocarbons, aromatic compounds;
- Reactions of H-atom abstraction from saturated carbon ($^{\bullet}OH + > CH- \rightarrow H_2O + > {}^{\bullet}C-$) in any organic compounds.

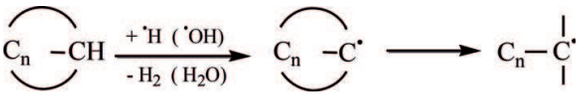
Kinds of the reactions of e^{-}_{aq}, $^{\bullet}H$, and $^{\bullet}OH$, listed in subdivision 3.1.6, determine the ways of conversions of compounds present in an aqueous system which are considered subsequently in this section.

3.2. Complete mineralization of organic compounds

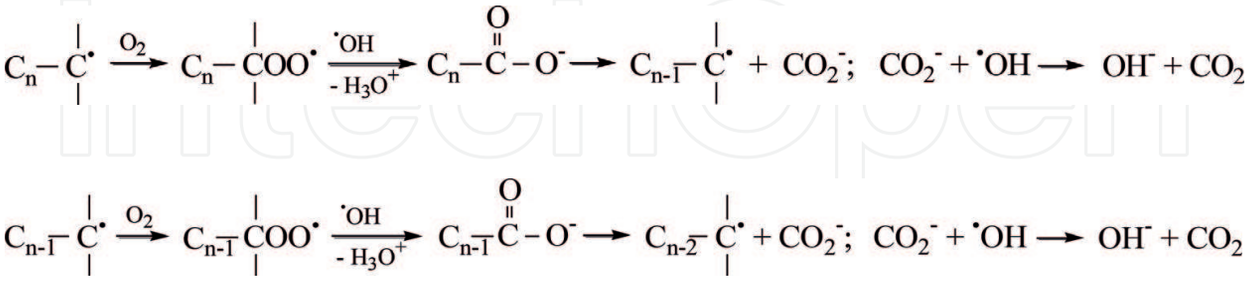
In principle, every organic compound in aqueous solution can be transformed into stable inorganic substances, such as CO_2 and H_2O, and, if other elements are present, also into ammonium, nitrogen and sulfur oxides, halogenides, and so on, under sufficient absorbed dose of ionizing radiation, the process being called "mineralization." Because of very high energy demand, this process is hardly applicable in practice to significantly reduce the amount of organic matter in a wastewater. However, it may be successfully used to remove hazardous pollutants from wastewater when their concentrations are relatively low.

Radiation-induced process of any organic compound destruction includes C–C bonds rupture reactions (it is necessary in the case of cyclic/aromatic compounds) and consecutive reactions of terminal carbon atom oxidation into carboxyl group followed by decarboxylation, that is, elimination of the atom in the form of CO_2. A simplified scheme of the process looks like this:

(a) *Rapture of* C–C *bond (opening the ring).*



(b) *Oxidation (by* O_2 *attachment) and decarboxylation.*



$$C_{n-2} \rightarrow C_{n-3} + CO_2, \text{ etc.}$$

In reality, the mechanism of mineralization is much more complicated, especially for aromatic and heteroatomic compounds, but anyway it is a multistage one, and the more composite is organic compound, the more energy it takes to mineralize it completely. Since the process of mineralization proceeds essentially via oxidation reactions, the presence of dissolved oxygen is

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important because of two main reasons: oxygen converts reducing radicals (e^-_{aq}, $^\bullet H$) into oxidizing ones ($^\bullet O_2^-$, $HO_2^\bullet$) and attaches itself to carbon-centered radicals, providing thereby the formation of carboxyl group. However, in the absence of dissolved oxygen complete decomposition of organic compounds also takes place while the yield of the process is much lower.

The degree of organic compounds mineralization in aqueous solutions upon the action of ionizing radiation can be easily controlled by TOC measurements. As TOC is a mass of all carbon atoms in organic matter, the yield of decarbonization (or mineralization) G_{miner}, expressed in moles of eliminated carbon atoms per 1 kGy of absorbed dose D, is $G_{miner} = (1/12) \times d\text{TOC}/dD$. It makes it possible to compare radiation-chemical yield of carbon elimination with that of initial organic compound degradation G_{degr}, as well as with the yields of radical products from water G_R, being initiators of degradation process. In the absence of radiation-induced chain processes, always the following inequation is right $G_R > G_{degr} > G_{miner}$. Numerous experimental data concerning various organic compounds destruction under irradiation confirm this relationship. Thus, from the data of recent researches it follows that the values of G_{degr} and G_{miner} for irradiation of some organic compounds solutions equals, respectively, for 2-naphthalenesulfonate [22]: 0.14 and 0.08, for monuron [23]: 0.15 and 0.08, for amphetamine [24]: 0.33 and 0.06, for phenol [25]: 0.25 and 0.05, for ibuprofen [26]: 0.25 and 0.05 μmol/J. Low yields of mineralization (0.05–0.08 μmol/J) compared to the yield of OH radicals (0.28 μmol/J) show that in different mechanisms of radiation-induced conversions of different compounds, the elimination of one carbon atom demands three to six radicals $^\bullet OH$, while the conversion of one molecule of initial compound occurs under the action of just one to two radicals. Maximal yields of mineralization, like quoted earlier, are reached at sufficient concentration of dissolved oxygen that requires some time aerating the solution during irradiation [27]. Also, it has been noted repeatedly (see, e.g., [24, 28–31]) that the presence of inorganic anions, such as Cl^-, HCO_3^-, HSO_4^-, reduces the yield of mineralization, mainly due to scavenging the $^\bullet OH$ radicals. A decrease in G_{miner} takes place when subjects of radiation treatment are real aqueous systems (water or wastewater), rather than model solutions prepared with purified water.

In spite of low values of G_{miner}, experimental data obtained (see, e.g., a review [32]) indicate that absorbed doses of several kilograys are sufficient to remove some hazardous pollutants, like pharmaceutical and personal care products, from contaminated water where the concentration of the pollutants is usually of the order of tens to hundreds μmol/L. It makes the process of radiation treatment of that kind promising for implementation.

3.3. Conversion of organic molecules and elimination of functional groups

Transformations in molecules of organic substance occurring under the action of active products of water radiolysis often play an important role in the purification of water and wastewater, even if TOC at that time changes slightly or does not change at all. It is of importance when the goal of "purification" is not to just remove organic compounds but to eliminate some unwanted properties of wastewater, like color, odor, toxicity, infection, or to increase the efficiency of further treatment in combined purification processes.

3.3.1. Disinfection

The process of polluted water/wastewater disinfection consists in the suppression of vital activity of microorganisms. Breaks occurred in the helix of DNA under direct or indirect (via

radicals from water) action of radiation, destroying the ability of the cell to reproduce itself and resulting in microbe inactivation. As interaction of ionizing particle or active radical with any DNA molecule is an accidental event, the dependence of a number of living cells N per unit volume on absorbed dose D during irradiation is exponential:

$$N = N_0 \cdot e^{-\lambda D};\ \ln(N_0/N) = \lambda D,$$

where N_0 is the initial number of living cells and λ—inactivation constant depending on the kind of microorganism and irradiation conditions. In practice, to assess the efficiency of radiation disinfection, instead of λ, the value D_{10} is used which means the dose demanded to reduce the initial concentration of living cells by a factor of 10 and relates to λ as: $D_{10} = \ln 10/\lambda \cong 2.3/\lambda$.

Database [33] contains more than 1000 values of D_{10} measured to date. Typical values of D_{10} for different types of microorganisms are in the range of 0.4–1.3 kGy. That is why radiation sterilization of medical equipment, cosmetics, and so on is widely used, becoming a developed branch of industry. The application of radiation treatment for the sterilization of water and wastewater is undoubtedly effective, rather easily realized and has no objections, but one: high costs of ionizing radiation sources, which restrain its implementation at present.

3.3.2. Detoxification

Toxicity of many organic compounds is attributable to any specific functional groups, for example, halogenide-, nitrate-, sulfide groups, and some other, attached to hydrocarbon moiety, elimination of which decreases the toxicity sharply. Among the most widespread toxic pollutions, there are chlorine derivatives, the major constituent of "red list substances" [17]. Also, nitro groups attached to aliphatic or aromatic compounds increase the toxicity of the compound. One of the most effective radiation-induced processes of such functional groups detachment is the so-called dissociative electron attachment with the participation of hydrated electron or hydrogen atom:

$$\text{R–Cl} + e^-_{aq} \longrightarrow R^\bullet + Cl^-, \text{ or R–Cl} + {}^\bullet H \longrightarrow R^\bullet + Cl^- + H^+$$

A clear example of such process is consecutive dechlorination of pentachlorobiphenyl [34] which occurs under reductive conditions, that is, in the absence of dissolved oxygen and other scavengers of e^-_{aq} and $^\bullet H$. The yield of the process is close to summarized yield of e^-_{aq} and $^\bullet H$, that is, rather high. A similar process takes place in organic sulfides and nitro compounds:

$$\text{R–SH} + e^-_{aq} \longrightarrow R^\bullet + SH^-, \text{ or R–SH} + {}^\bullet H \longrightarrow R^\bullet + SH^- + H^+$$

$$\text{R–NO}_2 + e^-_{aq} \longrightarrow R^\bullet + NO_2{}^-, \text{ or R–NO}_2 + {}^\bullet H \longrightarrow R^\bullet + NO_2{}^- + H^+$$

The yield of the latter is lower because of the longer life time of intermediate radical anions $R–NO_2{}^{\bullet -}$ which partially disproportionate. Lower yield is also characteristic of dechlorination by $^\bullet OH$ radicals which, nevertheless, does occur [35].

It is necessary to keep in mind, however, that besides elimination of toxic groups, conversion of composite organic compounds upon irradiation may be realized in the formation of some products, toxicity of which is higher than that of initial compound [36]. Thus, under the action

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of ionizing radiation on clofibric acid solutions the total toxicity of the solutions at the beginning of irradiation sharply increases with increasing the dose and then decreases together with a decrease in the total content of organic matter [35]. Possible occurrence of two opposite radiolytic processes: detoxification of initial compound and formation of new toxic compounds, requires, when using radiation detoxification, taking into account real composition of water/wastewater to be treated in every particular case.

3.3.3. Decolorization

Many kinds of wastewater, especially that of textile and dyeing industry, are colored due to contamination with organic dyes. Composite molecules of dyes include chromophore group, that is, system of conjugated double bonds, responsible for the ability of the molecule to absorb electromagnetic radiation in the visible region of spectrum, that is, light. It is enough to destroy just chromophore group, not a whole molecule, to make the molecule incapable of light absorption and, thereby, to decolorize the dye. Hydrated electrons, as well as radicals $^{\bullet}H$ and $^{\bullet}OH$, are easily attached to a double bond (see subdivision 3.1.6) destroying the conjugated bonds system

$$e^{-}_{aq} + >C=C< (+H^{+}) \longrightarrow >CH–{}^{\bullet}C<$$

$$^{\bullet}H + >C=C< \longrightarrow >CH–{}^{\bullet}C<$$

$$^{\bullet}OH + >C=C< \longrightarrow >C(OH)–{}^{\bullet}C<$$

The yield of decolorization, if only those reactions occurred, should be as high as 0.6 μmol/J corresponding to the total yield of all initial radicals from water. However, the occurrence of reduction-oxidation reactions of the latter resulted in the formation of two kinds of dye radicals: one in reaction of e^{-}_{aq} and $^{\bullet}H$, another in reaction of $^{\bullet}OH$, makes it possible, by electron and/or hydrogen transfer between two kinds of dye radicals, partial reparation of dye molecules. As a result, decolorization yields for aqueous solutions of soluble organic dyes, as a rule, are equal to 0.1–0.3 μmol/J, depending on the structure of dye (for disperse dyes, which are water-insoluble and form aqueous dispersions, the yield is lower because of impediments to radical penetration into dye particulates) [37, 38]. The yield of decolorization decreases with increasing absorbed dose, since the rate constants of radicals' reactions with original dye molecules and with the products of dye degradation are of the same order; so while the concentration of the latter increases during irradiation, the fraction of radicals being spent in reactions with those products also increases, reducing thereby the fraction of radicals required for "decolorization" of the original dye molecules.

In real wastewater, which contains, besides dye, rather high amounts of organic matter, decolorization yield is decreased due to competition of other organics for reactive radicals from water. Nevertheless, recently published results on radiation treatment of real wastewater from dyeing and textile industry [39] show that doses of several kilograys provide for sufficient decolorization of the wastewater.

3.3.4. Improvement of biological treatment

Biological treatment of wastewater with activated sludge is still the basic commercially applied method applied for the removal of great amount of organic matter from wastewater. However,

many organic compounds which wastewater often contains are not biodegradable, that is, are not "eatable" by microorganisms of sludge. Moreover, some compounds are toxic for those microorganisms, "killing" them and, thereby, reducing the activity of sludge in biodegradation process.

Radiation-induced elimination of functional groups, as well as other kinds of molecule fragmentation, makes non-biodegradable organic compounds biodegradable and increases biodegradability of poorly biodegradable compounds. Also, the decomposition of toxic for microorganism compounds under irradiation improves biological treatment. Recently published results [40, 41] demonstrated that upon irradiation an increase in biodegradability of organic matter was observed without a significant decrease in the Total Organic Carbon. However, it should be mentioned that radiation treatment may have insignificant effect on biodegradability of wastewater with high amount of biodegradable organic matters as it has been observed on real textile and dyeing wastewater [42]. In that case, radiation treatment was much more effective when applied after biological treatment.

3.3.5. Improvement of settling and sorption

A combination of organic radicals formed in organic compound reaction with any active radicals from water results in the formation of more complex molecules. Due to further increase in molecules' size, the formation of solid phase becomes possible, especially, it is characteristic of natural organic matter. The formation and aggregation of small particulates of organic matter facilitates subsequent processes of sedimentation, filtration, and sorption. Thus, it has been found [43] that electron-beam treatment of river water contaminated, mainly, with NOM, significantly decreases the color index and the amount of suspended solids and improves water quality. A dose of several kilograys was found to be sufficient for decreasing the color index to a maximum permissible value even in the most unfavorable seasons (spring and autumn). Moreover, irradiation accelerated the sedimentation of suspended solids by a factor of 50–100, as compared with non-irradiated water. The precipitate formed upon irradiation captures impurities present in water; this process along with the radiolytic decomposition of impurities resulted in water purification.

3.4. Radiation polymerization

Polymerization of monomers', or oligomers', molecules in aqueous solutions under the action of ionizing radiation is initiated by primary products of water radiolysis, both radicals and ions [44, 45]. Accordingly, the process of polymerization may correspond to either a free-radical or an ionic (cationic or anionic) mechanism. Since primary anion-radicals and cation-radicals, as well as carbanions and carbocations, are very unstable in aqueous media, free-radical mechanism of polymerization usually prevails. It includes stages of

chain initiation (reaction of primary radical with a monomer molecule M).

$$^{\bullet}R + M \rightarrow {}^{\bullet}M';$$

chain propagation (increase in chain length):

$$^{\bullet}M' + M \rightarrow {}^{\bullet}M'M; \ldots {}^{\bullet}M'M_n + M \rightarrow {}^{\bullet}M'M_{n+1}$$

chain termination (radicals disappearance by combination or disproportionation).

$$^{\bullet}M'M_n + {}^{\bullet}M'M_n\ (\text{or}\ ^{\bullet}R) \rightarrow \text{products};$$

the polymerization rate during irradiation being proportional to the square root of dose rate and average polymer chain length—inversely proportional to the square root of dose rate.

The conversion of soluble or slightly soluble molecules of monomers/oligomers into insoluble polymer upon irradiation makes it possible to apply the process of radiation polymerization to the removal of monomer impurities which are often present in wastewater of chemical and textile industries. However, because of a decrease in polymer length with increasing the dose rate using electron-beam irradiation of high intensity reduces the effectiveness of the process. Nevertheless, combined radiation-induced processes of decomposition and polymerization were shown to be quite effective in the purification of aqueous systems from such typical refractory organic pollutant as polyvinyl alcohol [46].

3.5. Oxidation-reduction processes in inorganic compound solutions

The application of radiation treatment to change mineral composition of water or wastewater is rarely considered to be an efficient one. Nevertheless, several radiation induces reductive-oxidative reaction of inorganic compounds may be used in the processes of inorganic toxic compounds removal.

Radicals $^{\bullet}OH$ possessing high oxidation potential oxidizes all transition metal cations in lower oxidation state and majority of inorganic anions (see subdivision 3.1.6.3". It may be applied to convert, for example, toxic nitrite anions present in water/wastewater into less toxic nitrate anions:

$$^{\bullet}OH + NO_2{}^- \rightarrow OH^- + NO_2{}^{\bullet};\ 2NO_2{}^{\bullet}\ (+H_2O) \rightarrow NO_3{}^- + NO_2{}^-\ (+2H^+)$$

Hydrated electrons and hydrogen atoms as strong reducing agents reduce majority of metal cations and oxygen-containing anions (see subdivisions 3.1.6.1 and 3.1.6.2). That process was tested in the conversion of highly toxic Cr(VI) ions into much less toxic Cr(III) ions [47] in reactions:

$$e^-{}_{aq}\ (^{\bullet}H) + Cr(VI) \rightarrow Cr(V)\ (+H^+);\ 2Cr(V) \rightarrow Cr(VI) + Cr(IV);\ 2\ Cr(IV) \rightarrow Cr(V) + Cr(III)$$

as well as in the removal of heavy metals, like cadmium [48] and lead [49] from aqueous system by reducing metal cations to metal atoms with subsequent sedimentation of solid phase and filtration or sorption:

$$e^-{}_{aq}\ (^{\bullet}H) + Cd(II) \rightarrow Cd(I)\ (+H^+);\ 2Cd(I) \rightarrow Cd(II) + Cd(0);\ nCd(0) \rightarrow Cd_n\downarrow$$

Since $^{\bullet}OH$ radicals oxidize reduced cations backward, the process becomes efficient in the presence of $^{\bullet}OH$ radicals scavengers, like formates, sulfides, sulfites, and so on. Combined radiation-flotation process based on radiation-induced reductive-oxidative reaction of Hg has been implemented to remove mercury from wastewater of hydrolysis works [50].

3.6. Processes of micelles recharging in aqueous dispersions

Aqueous dispersions are very sensitive to the action of ionizing radiation, which may either increase stability of such systems or initiate coagulation even at rather low-absorbed doses.

One of the main reasons for coagulation is recharging the micelles by interaction with short-lived products of water radiolysis. Thus, negatively charged micelles preferably interact with positively charged or uncharged intermediates, participating, for example, in reactions of protonation by H^+ ions or electron transfer to $^{\bullet}OH$ and $HO_2^{\bullet}$ radical:

$$Mic^{n-} + H^+ \rightarrow MicH^{(n-1)-}$$

$$Mic^{n-} + {}^{\bullet}OH \rightarrow Mic^{(n-1)-} + OH^-$$

$$Mic^{n-} + HO_2^{\bullet} \rightarrow Mic^{(n-1)-} + HO_2^-$$

Appearing misbalance in charges of nucleus and outer shell of micelle can promote consecutive combination with other micelles:

$$m\ Mic_m^{n-} + Mic^{(n-1)-} \rightarrow Mic_{m+1}^{(m+n-1)-}$$

and, finally, the formation of large aggregates settling down from the solution. A similar situation takes place with positively charged micelles, in which positive outer-shell charge is reduced by interaction with hydrated electrons and/or hydrogen atoms:

$$Mic^{n+} + e^-_{aq}\ ({}^{\bullet}H) \rightarrow MicH^{(n-1)+}\ (+H^+)$$

There exists, however, another source of influence on charged micelles, which is only characteristic of electron-beam irradiation unlike irradiation with gamma or X-rays. The most distinguishing feature of irradiation by electrons under condition of their complete absorption in irradiated medium consists in the accumulation of uncompensated charge due to incident electrons. These electrons after dissipation of their energy in the processes of ionization (thereby, equal quantities of oppositely charged particles arise) and excitation are finally thermalized and localized in aqueous medium giving rise to the formation of e^-_{aq}, which carry excess negative charge. Fraction of e^-_{aq} formed by deceleration of incident electrons is low relative to e^-_{aq} formed by ionization (for 0.7 MeV electrons it is about 0.05%), and their role in radiation-induced oxidation-reduction processes is negligible. However, while e^-_{aq} themselves have very short lifetime because of high reactivity, additional charge can be eliminated only by diffusion of anions to vial walls and discharging into environment, which courses relatively slow. Therefore, stationary concentration of uncompensated negative charge during irradiation may be sufficiently high to have an influence on coagulation process by stabilizing negative micelles. It was observed recently [51] in experiments concerning coagulation of humic acids and lignin in aqueous dispersions.

4. Ionizing radiation sources for radiation technologies of aqueous system treatment

Ionizing radiation includes electromagnetic radiation of wavelength shorter than 10^{-7} m and accelerated ions with kinetic energy higher than lowest ionization energy of molecules, that is, near 10 eV (neutron radiation is often referred to as ionizing one, but neutrons themselves do not interact with electron shells of molecules, ionization by neutrons being indirect). All the

sources of such radiation may be divided into two principal groups: radioactive isotopes (radionuclides) and accelerating techniques. With the help of the latter, both ion beams and electromagnetic radiation (X-rays) may be generated. All the ionizing radiation sources intended for commercial application must meet the following major requirements: be safe for environment, provide for sufficient depth of irradiation, and absorbed dose. Now, three kinds of sources are applied in radiation processing including radiation treatment of aqueous systems: radioisotope sources, X-ray generators, and electron accelerators.

4.1. Isotope sources

Radiation sources based on only two γ-emitting isotopes were used in radiation technologies. There are radioisotopes of cesium (Cs-137) and cobalt (Co-60).

Radioisotope Cs-137 is produced by separation from other fission products formed in nuclear reactors. It decays with a half-life of 30.17 years, emitting beta-rays with energy of 0.51 MeV and gamma-rays with energy of 0.667 MeV; the product of Cs-137 decay is stable isotope of barium (Ba-137). In radiation sources isotope Cs-137 is used in the form of cesium chloride salt encapsulated in a metal shell.

Radioisotope Co-60 is produced in nuclear reactors by bombardment of stable isotope Co-59 with neutrons. It decays with a half-life of 5.27 years, emitting beta-rays with energy of 0.32 MeV and gamma-rays with energies of 1.173 and 1.332 MeV (mean gamma-rays energy of 1.25 MeV); the product of Co-60 decay is a stable isotope of nickel (Ni-60). In radiation sources, radioisotope Co-60 is used in the form of metal slugs or pellets.

While penetrating a medium, gamma radiation is attenuated exponentially:

$$I = I_0 \cdot e^{-\mu l}; \lg(I_0/I) = \mu l; l_{1/2} = \lg 2/\mu \cong 0.7/\mu$$

where I is the intensity of gamma radiation (I_0—initial intensity), l—passed length ($l_{1/2}$—length of half-attenuation), and μ—linear coefficient of attenuation which depends on radiation quanta energy and on medium density. In aqueous systems, values of $l_{1/2}$ for cesium and cobalt gamma-radiations equal, respectively, 8 and 11 cm [19], differing due to difference in the energy of radiation.

Because of high penetration of gamma-rays gamma-emitting sources must be shielded from environment with a sufficient thick wall of dense material which is usually lead (in compact sources) or concrete (normally near 2 m in thickness, in industrial irradiation facilities). Major components of an industrial facility include irradiation room, shielded storage room (dry or wet) for the radiation source rack, source hoist mechanism, radiation shield surrounding the irradiation room, control console (room), feed system for a product to be irradiated, shielding maze, control and safety interlock system, and supporting service equipment [52].

When being used in the radiation treatment of aqueous systems, gamma sources, although, meet the requirement of irradiation depth, possess significant disadvantages:

- Radiation from the source is emitted spherically in all directions, so a part of it is wasted, reducing thereby power efficiency of the source.

- Radiation from the source is emitted continuously with constant intensity, so it is not easy to switch off and on irradiation promptly and to change the dose rate.
- Gamma sources have relatively low power; thus, the source of such high activity as 1 MCi (3.7×10^{16} Bq) has a power just near 10 kW. It makes gamma sources inapplicable for the treatment of aqueous systems at high flow rates.

Nowadays, Co-60 gamma sources are applied, as a rule, to reveal the mechanisms of processes in systems to be irradiated, to disinfect sewage sludge, and to develop technologies of some processes. Cs-137 gamma sources are presently not used for solving environmental problems including radiation treatment of water/wastewater.

4.2. X-ray sources

Both γ-rays and X-rays are electromagnetic radiation and differ by the principle of formation. While γ-rays are emitted in the process of energy transition from excited to ground state of a nucleus, X-rays are emitted by accelerated electrons when they pass near to atomic nuclei and are deflected by their electric fields, the effect being called bremsstrahlung. Contrary to γ-rays with defined energy, X-rays produced in this manner have a continuous spectrum of photon energies extending from about 30 keV up to a maximum energy equal to the kinetic energy of the incident electron. For example, with a 5-MeV electron, the most probable photon energy is about 300 keV, the average photon energy is near 1.0 MeV, while the maximum photon energy is 5.0 MeV. The X-ray intensity increases with the electron energy and beam current and with the atomic number of the target material [53].

Two kinds of X-ray sources are produced and used commercially: X-ray tubes (or Roentgen tubes) and X-ray generators, based on electron accelerators. The former have relatively low photons energy and low power. Because of this X-ray tubes are almost not applied in radiation processing, being widely applied in medicine, material and structure analysis, and for industrial inspection.

X-ray generators are powerful analog of gamma sources. A comparison of those two kinds of electromagnetic radiation sources has been made in [54]. A distinguishing characteristic of X-ray generators is ameliorating the parameters of generated electromagnetic radiation with increasing the energy of incident electrons. Thus, while at relatively low electron energies X-rays are emitted in all directions, with electron energies higher than 2.0 MeV the X-ray emission in the direction of the incident electron beam becomes prevailing. Further increase in electrons energy results in decreasing the angular dispersion of the X-ray beam: divergence measured at half of the maximum intensity (HMI) is reduced two times when increasing electrons energy from 5 to 10 MeV (see **Table 9**).

Electron energy (MeV)	Mean photon energy (MeV)	Emission efficiency (%)	Divergence at HMI (degrees)
5.0	1.19	8.2	20
7.5	1.38	13.3	15
10	1.56	16.2	10

Table 9. Parameters of generated electromagnetic radiation depending on electron beam energy (the data from [55]).

Also, both efficiency of electron beam conversion into X-ray beam and photon energy of X-rays are increased with increasing the energy of accelerated electrons. However, electron accelerators with energy higher than 7.5 MeV are forbidden to application in industry because of the danger of activating the matter under irradiation.

While being a prosperous competitor to radioisotope sources in many kinds of radiation processing (recent comparisons have shown that the capital costs and electric power costs for accelerators with electron energies of 5.0–7.0 MeV can be lower than the capital costs and source replenishment costs for cobalt-60 source loadings greater than 2.0 MCi [55]), X-ray generators, nevertheless, are not suitable for aqueous systems treatment. The reason is that in spite of capability to irradiate rather a thick layer of condensed media, the energy efficiency of X-ray generators is very low. At present, they are not proposed to be used in the field of environment conservation.

4.3. Electron accelerators

Among all accelerators of charged particles, only accelerators of electrons are suitable to application in radiation processing (excluding ion accelerators used in ion implantation industries). Chemical consequences of accelerated electrons action on many substances, including aqueous media, are almost the same as those of gamma and X-rays. The difference is in the depth of penetration. While the intensity of electromagnetic radiation (both gamma and X-rays) in a medium is attenuated exponentially with path length, accelerated electrons have limited penetration depth which depends on their energy. In **Table 10**, the penetration of gamma radiation is compared with that of accelerated electrons of different energies.

Principal characteristics of electron accelerators, important for industrial application, are energy of accelerated electrons E_e (or "accelerator energy") and beam power W_e, which is defined as E_e multiplied by electron beam current I_e: $W_e = E_e \cdot I_e$. While E_e determines the range of electrons in irradiated medium, that is, the depth of electron beam penetration, W_e determines the productivity of irradiation process. Market cost of accelerators is near proportional to their energy and to the square root of power. It is accepted in radiation processing to divide electron accelerators according to accelerator energy into three groups: 1—low-energy units ($E_e < 0.5$ MeV), 2—mid-energy units (0.5 MeV < E_e < 5.0 MeV), and 3—high-energy units (5.0 < E_e < 10 MeV), maximum energy of 10 MeV being set for industrial accelerators to avoid problems of induced radioactivity.

Two types of accelerator design have found industrial acceptance in the high-energy area (5.0–10 MeV): microwave linear accelerators (linacs) and the radiofrequency accelerator Rhodotron®. Now industrial linacs are produced by companies: Getinge Linac (formerly Linac Technologies), Budker Institute of Nuclear Physics, L-3 Communications Pulse

Gamma radiation		**Accelerated electrons**				
Cs-137	Co-60	0.5 MeV	1 MeV	2 MeV	5 MeV	10 MeV
8	11	0.2	0.4	0.8	2.3	4.7

Table 10. Depth of half attenuation for gamma radiation and penetration depth for accelerated electrons in cm (the data from [19]).

Sciences (formerly Titan Scan), Mevex, and EB-Tech Co Ltd. (in cooperation with the Budker Institute of Nuclear Physics); Rhodotron®—by Ion Beam Applications SA (formerly Radiation Dynamics Inc) [56].

While being rather widely used in other fields of radiation processing, industrial high-energy accelerators are not used in the radiation treatment of water and wastewater, mainly due to high cost (including the cost of accelerator itself and the necessity of strong biological shielding because of high-intensity level of induced X-ray radiation) and relatively low-energy efficiency of linacs (ratio of beam power to power consumption is about 30%).

Low-energy accelerators produced by companies: Energy Sciences Incorporated, Broadbeam Equipment, NHV Corporation, and Advanced Electron Beams, are used, mainly, for curing or crosslinking of inks, coatings, and adhesives that are based on liquid-reactive materials which do not contain solvents. Because of very thin layer of water which electrons generated by those accelerators can penetrate, they are not applicable in radiation treatment of aqueous systems but one case; irradiation of sprayed wastewater (see Section 5.1).

Mid-energy electron accelerators are the most suitable for aqueous systems treatment. Those accelerators produce scanned beams that range in energy from 400 to 5 MeV. The units that are suitable for industrial use are all characterized by the ability to produce high beam currents, many tens of milliamps, which provide high dose rates that are needed for the treatment of aqueous systems at high flow rates.

Five electrical design systems have been used to attain mid-energy and high beam current: 1—the Cockcroft-Walton and its enhancements by Nissin-High Voltage, 2—the Insulated Core Transformer, 3—the Dynamitron, 4—a magnetic-coupled dc system, and 5—high-current pulsed beams. The Dynamitron can attain very high beam currents (60 mA) at up to 5.0 MeV (300 kW). The ICT and ELV mid-energy accelerator designs are limited in electron energy to 2.5 MeV. Medium- and low-voltage direct current accelerators may have several accelerating tubes connected to one power supply by using cable connections or gas-insulated transmission lines, flexible cable connections being limited to 800 keV and gas transmission systems up to 2 MeV. The companies that have experience in providing industry with mid-energy, high-current electron accelerators are Ion Beam Applications SA (formerly Radiation Dynamics Inc), NHV Corporation, Budker Institute of Nuclear Physics, Efremov Scientific Research Institute of Electrophysical Apparatus (NIIEFA), Vivirad SA (formerly Vivirad-High Voltage Corporation), and Wasik Associates [56].

As mentioned earlier, the cost of accelerators of similar energy is near proportional to the square root of power. It means that the cost per unit power decreases with increasing the power of accelerator. The data cited in [57] show that typical prices of mid-energy accelerators with power of 20–400 kW increase from 0.5 to 2.5 $million, while the cost per 1 kW decreases from $25,000 to $5000.

5. Under-beam and other support equipment

Besides an accelerator, support equipment plays an important role in realizing radiation technology of water/wastewater treatment. The equipment includes radiation reactor, as a

main part, and other equipment necessary for normal functioning of radiation treatment facility.

5.1. Reactor types: systems of water feed

Radiation reactor is an installation where flow of water is irradiated. There exist three different methods to irradiate water flow. Conditionally, they may be called "natural flow method," "spray method," and "wide jet method," the reactors being called correspondingly.

5.1.1. Natural flow reactor

In this method, water/wastewater either flows over a surface and is irradiated from above by a vertical electron beam (**Figure 2a**), or falls as a wide waterfall and is irradiated by a horizontal electron beam (**Figure 2b**).

Water/wastewater treatment in this method may be carried out at high doses and dose rates. However, the velocity of natural flow is limited by about 1 m/s. Since the thickness of water layer is limited by accelerated electrons energy, the throughput of irradiation facility may be increased only by an increase in flow width, which results in increasing irradiation area and demand of additional accelerator (or additional accelerating tube).

The advantage of the method consists in a possibility of equipping the surface under flow with holes to input ozone or other necessary additions and/or to mix liquid under irradiation by gas bubbling. Reactors of that type were used in many pilot plans on radiation treatment of water, wastewater, and sludge, in USA, Brazil, European countries, Korea, Japan, and China.

5.1.2. Spray reactor

In this method, polluted water is sprayed under pressure into a chamber to be irradiated from above by a vertical electron beam (**Figure 3**).

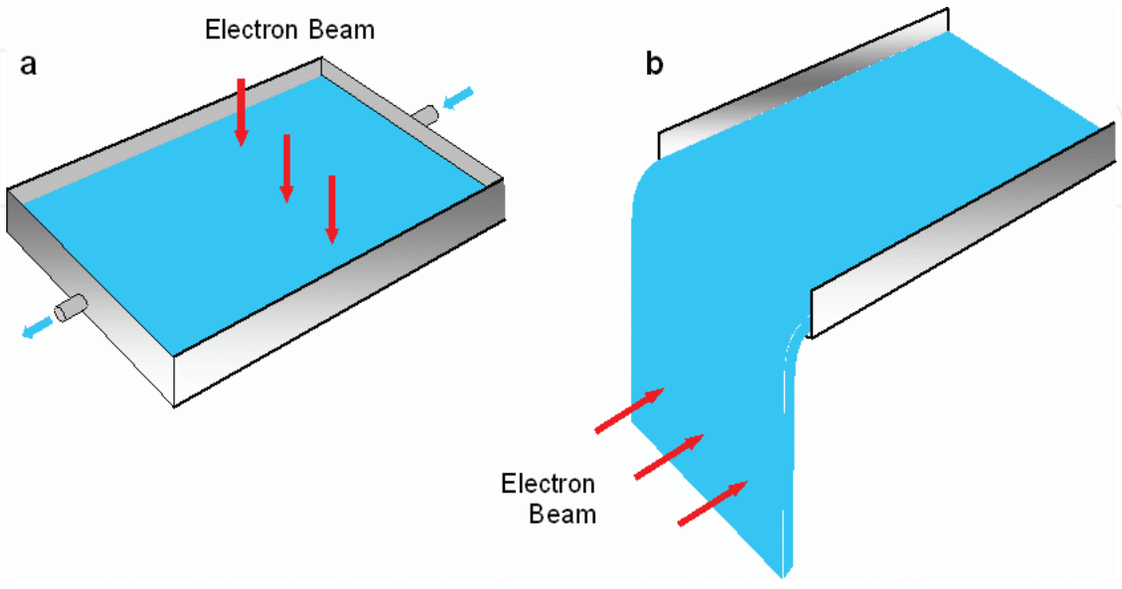


Figure 2. Natural flow reactor with vertical (a) and horizontal (b) direction of electron-beam irradiation.

While flow velocity is up to 3 m/s, the throughput of such irradiation facility is low. Also, the water before being input into reactor should be thoroughly purified from suspended particulates to prevent injector clogging and damaging.

An advantage of the method consists in the formation of large specific surface of sprayed liquid providing for efficient penetration of surrounding gas into liquid phase. If the gas is an air or oxygen, ozone being formed under irradiation and absorbed in solution takes part in radiation-chemical reactions which improve purification process; to create reductive conditions during irradiation, the chamber may be filled with inert gas.

5.1.3. Wide jet reactor

In this method, wastewater is fed under pressure to irradiation area in the form of wide jet and is irradiated from above by a vertical electron beam (**Figure 4**).

Since flow velocity in this method may be made several meters per second, this kind of reactors is the most promising to irradiate wastewater using powerful accelerators at high flow rates. It was employed in full-scale facility in Korea on radiation treatment of dyeing company wastewater with throughput of 10,000 m^3 a day [58].

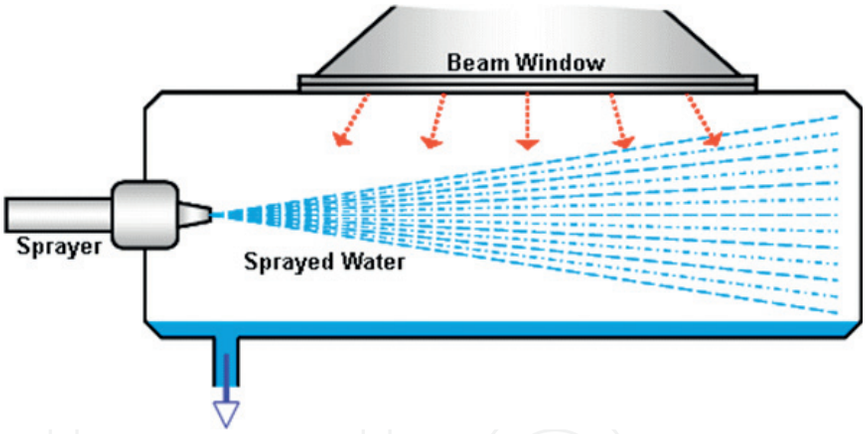


Figure 3. Spray reactor.

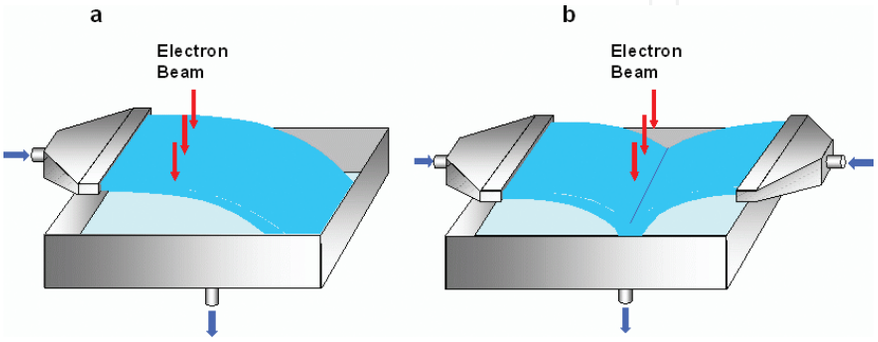


Figure 4. Wide jet reactor with one jet (a) and two opposite jets (b).

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5.2. Other equipment

In addition to an accelerator and a reactor, other equipment is necessary to provide functioning the facility on radiation treatment of water/wastewater. It includes

- Tubing for inlet and outlet water;
- Water pumps, some of which in the case of wide jet reactor should be of high pressure and capacity;
- Air fans (blowers) for cooling electron beam window of accelerator, discharge of ozone containing air from irradiation room, ventilation;
- Remote control to operate an accelerator;
- Chemical laboratory equipment to analyze inlet and outlet water;
- Measurement instrumentation, and so on. [58].

The cost of reactor and listed equipment may amount to one-third of accelerator cost.

Besides, the necessary part of the facility is biological shielding. Powerful accelerators must be situated in special irradiation room surrounded by walls made of dense concrete of 1.5–2.0 m thickness or more. The cost of the wall building amounts up to half of the accelerator cost. Thus, the capital cost of an industrial plant for wastewater treatment of middle productivity is near 4.0 $million, excluding costs of land, R&D, and approval from authorities [59]. The demand of such high investments is one of the main obstacles in developing and implementing radiation technologies of aqueous systems purification.

6. Conclusion

Radiation treatment of aqueous systems may be effectively used, without additional purification methods, for disinfection, detoxification, and decolorization of contaminated water at low concentration of organic matter. Purification of wastewater with high concentration of organic matter requires the application of combined radiation method, including biological treatment and/or filtration, sorption, and so on. Radiation technologies of aqueous systems treatment at present are being extensively developed. Electron accelerators are preferable radiation sources, especially at high flow rates. One of prerequisites for expansion of the technologies should be reducing the market prices for radiation equipment, namely electron accelerators.

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