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RADIATION CHEMISTRY

Current Status of the Application of Ionizing Radiation to Environmental Protection: II. Wastewater and Other Liquid Wastes (A Review)*

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Abstract—Present-day applications of ionizing radiation to environmental protection are surveyed. This part of the review summarizes new data on the radiation-chemical purification of municipal, industrial, and agricultural wastewater; liquid radioactive wastes; oils; etc.

I. FEATURES OF WASTEWATER PURIFICATION**

In contrast to natural and drinking water, as a rule, wastewater is characterized by a wide variety and high concentrations of pollutants. In addition, the true composition of wastewater is unknown in many cases. The circumstance that this composition is often variable also makes wastewater treatment difficult. The wastewater composition depends on changes in the processing technique and reagents in use, storage time and conditions before treatment, climatic conditions, and other factors.

The pollution level is usually characterized by chemical oxygen demand (COD), biological (biochemical) oxygen demand (BOD), total organic carbon (TOC), and dissolved carbon content. All these characteristics are group parameters, which specify the chemical and biological oxidizability of wastewater pollutants, the total carbon content of these pollutants, and the carbon content of pollutants that occur in a dissolved state, respectively. Thus, COD (mg/l) is the amount of oxygen (or another oxidizing agent in terms of oxygen) required for the complete oxidation of organic matter in a test wastewater sample. BOD is the amount of oxygen consumed in the anaerobic biochemical decomposition of organic matter in the test wastewater for a specified period of time (5, 10, or 20 days, i.e., BOD_5, BOD_{10}, or BOD_{20}, respectively). Evidently, the greater the above group parameters, the higher the concentration of organic pollutants in wastewater.

In the majority of cases, doses required for wastewater purification are rather high (about several tens of kilograys or even higher), and this is not advantageous economically. Because of this, combined radiation-chemical methods are under development in recent years in order to decrease the required doses. These methods combine radiation treatment with a standard purification procedure (biological, flotation, coagulation, etc.). In these methods, radiation treatment (most frequently, electron-beam treatment) serves as an additional tool for purification. Synergistic effects are often observed with the use of combined methods.

By now, the following combined radiation-chemical methods for water and wastewater purification were described (see, for example, [2] and references wherein): radiation–flotation, radiation-biological, radiation–polymerization, thermoradiation, radiation–electrodialysis, radiation–adsorption, oxyradiation, and ozone–radiation treatments. Radiation-biological (electron-beam irradiation combined with biological treatment), radiation–coagulation (electron-beam treatment combined with the use of a coagulant), ozone–radiation (a combination of irradiation and ozonation), and radiation–adsorption (a combined use of radiation treatment and an adsorbent) treatment methods are in current use. Special features of the application of combine methods were considered in [2a].

Recently, two new combined radiation-chemical methods were developed. In one of them, wastewater was subjected to electron-beam treatment in an aerosol flow [3–6]. The other method consists in water irradiation with an electron beam in the presence of a substance that, for example, transforms an oxidizing product of water radiolysis into a reducing radical and thereby improves the purification efficiency [7].

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*Because of its large length, the review was divided into three parts. The first part devoted to the sources of ionizing radiation used for the purposes of environmental conservation and to the radiation-chemical purification of natural and drinking water was published in the first issue of *Khim. Vys. Energ.* (High Energy Chem.) [1]. The third part concerning new data on the radiation treatment of sewage sludge and on the radiation-chemical purification of gaseous and solid systems will be published in *Khim. Vys. Energ.* (High Energy Chem.), 2000, vol. 34, no. 3.

**See also the Introduction in the first part of the review [1].

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II. MUNICIPAL WASTEWATER

In recent years, as a rule, combined radiation-chemical methods were used for purifying municipal wastewater.

II.1. Application of a Combined Radiation-Biological Method

A combined radiation-biological method was most frequently used for purifying municipal wastewater [8, 9] (see also [2]). The treatment of wastewater with γ-radiation or electron beams after biological treatment results in disinfection, deodorization, noticeable decolorization, and a considerable decrease in pollutant concentrations. The required doses varied from 0.4–0.5 kGy to several kilograys.

The doses required for disinfection and for the decomposition of harmful impurities (detergents, organic sulfides, dyes, etc.) in the Tokyo municipal wastewaters after their biological treatment amounted to several kilograys (see [2]). It was recommended to use radiation-treated water for industrial purposes. It was found [9] that the disinfection of municipal wastewater of Sao Paulo was achieved at doses of 3–5 kGy. Some other characteristics of water were also improved. Similar data were also reported by American researchers, who pointed out that the required doses are higher for nonchlorinated than for chlorinated water (see [2]).

According to [10], comparatively low γ-radiation doses (up to 0.5 kGy) were sufficient for the disinfection of municipal wastewater and for the subsequent use of this water for industrial purposes if the wastewater was irradiated after biological treatment. However, pathogenic microorganisms repeatedly appeared 48 h after the radiation treatment. This did not occur in the event that a combined radiation-chemical and ozone treatment was used.

II.2. Electron-Beam Treatment of Water in an Aerosol Flow

As mentioned above, a new combined method for purifying municipal wastewater has been developed recently [3–6]. The purpose of this method was to apply relatively inexpensive low-energy electron accelerators to wastewater treatment. Wastewater was sprayed using injection nozzles and irradiated in an aerosol flow (in the absence or in the presence of ozone).

A pilot plant was designed for optimizing the process [3]. The plant was based on an Astra electron accelerator with the following characteristics: electron energy, 0.3 MeV; maximum beam power, 15 kW; beam cross section, 700 × 600 mm; and accelerator dimensions, 1200 × 800 × 170 mm [11]. Water was sprayed with the use of four injection nozzles. In this plant, irradiated air containing ozone circulated through the electron beam.

The performance characteristics of the plant were as follows: output, 500 m^3/day; power consumption, 58 kW; working area, 40 m^2; air flow rate, 288 l/s; wastewater flow velocity, 9.65 m/s; and irradiated water layer thickness, 9 cm [3].

The density of the aerosol formed by the injector nozzles is 0.02–0.05 g/cm^3. Thus, the electron range is 20–50 times as large as that in liquid wastewater. This fact allows the use of a low-energy electron beam. The energy of electrons is primarily absorbed by water droplets because the aerosol density is considerably higher than the density of air. For example, if the aerosol density is equal to 0.02 g/cm^3, water droplets absorb more than 90% electron energy. The droplet size depends on the diameter of the injection nozzle and on the feed rates of wastewater and air. The droplet diameters varied from 50 to 180 μm.

Experiments were performed with real wastewater from a village in the Vladimir oblast. Various characteristics of unirradiated and irradiated water were measured [3, 11]. It was found that the dose needed for purifying water was no higher than 4 to 5 kGy. This dose was somewhat lower when irradiated air containing ozone was blown through an electron beam.

Reactions of pollutants with the radiolysis products of water droplets and air (including singlet oxygen) were responsible for the purification. Pollutants were also removed as a result of trapping by a precipitate that was formed as a consequence of aggregation of dispersed particles upon electron-beam treatment. The precipitate formation also continued after irradiation (for 10–12 h). The postradiation effect was responsible for an additional decrease in COD by ~50%.

The fact that pollutants were trapped by a precipitate that appeared upon irradiation was confirmed by the analysis for pollutants in the initial and irradiated wastewater using chromatography–mass spectrometry [6, 12]. It was found that these substances passed from the liquid phase to the precipitate as a result of electron-beam treatment.

A preliminary economic evaluation demonstrated that the developed method is more economically profitable (by a factor of 2–2.5) as compared with the conventional treatment based on the use of biopondss, filtration, and chlorination. This method can be recommended for the disinfection and purification of municipal wastewater in villages and small towns.

II.3. Designs for Industrial Plants

In Russia, the designs of two large-scale facilities for purification of municipal wastewater were developed on the basis of the results of detailed studies [13]. One of these facilities was designed for the electron-beam treatment of the sewage of Peterhof (Leningrad oblast). This facility was designed to be equipped with four ELV electron accelerators (the total beam power is equal to ~0.5 MW). The planned output is 110 000 m^3/day. The other facility was planned to be built in Kirishi (Leningrad oblast) for treating a mixture of municipal and industrial wastewater. It was designed to be equipped with five ELV electron accelerators (the total beam power is higher than 0.5 MW) to attain an output of 78000 m^3/day including 30000 m^3/day for municipal wastewater. However, these projects were not implemented (the main reason consists in financial difficulties).

III. INDUSTRIAL WASTEWATER

Research and development works concerning the use of ionizing radiation for the treatment of industrial wastewater are performed in Russia, the United States, Canada, Italy, Brazil, the People's Republic of China, Republic of Korea, Austria, Japan, Indonesia, Egypt, Ghana, and Cuba. The investigations were concerned with wastewater from various sources such as integrated pulp-and-paper mills, dye manufacturing plants, dyeing complex of textile industry, integrated hydrolysis plants, and a synthetic rubber factory. Both real wastewater and aqueous solutions serving as model wastewater were examined. As a rule, the values of COD, BOD, TOC, dissolved carbon content, etc., were measured in these investigations. Combined treatment technologies have attracted considerable interest.

III.1. Hydrogen Peroxide Decomposition

Wastewater containing a considerable amount of hydrogen peroxide (up to 30 g/l) is generated in the manufacture of semiconductor devices. For water reuse, the amount of this substance in wastewater should be decreased to ~3 g/l. This decrease was achieved with the use of a combined electron-beam and adsorption treatment [14]. Initially, the major portion of hydrogen peroxide was adsorbed by activated carbon and decomposed in contact with the latter to form water and oxygen. Electron-beam irradiation was performed to complete the decomposition of the residual hydrogen peroxide and to improve the efficiency of purification. The final decomposition is based on the chain process initiated by water radiolysis products (see, for example, [15]).

III.2. Decolorization of Water Containing Dyes

Wastewater containing dyes is difficult to purify using standard methods. The use of radiation treatment can solve this problem. Many authors [16–26] found that the decolorization of water containing dyes can be accomplished at comparatively low doses. Figure 1 shows the optical absorption spectra of aqueous solutions of two commercial dyes manufactured in the Republic of Korea before and after irradiation [18]. It can be seen that the solutions were almost completely decolorized at doses lower than 10 kGy. Simultaneously, the values of COD and TOC significantly decreased.

Under particular conditions, the efficiency of purification was improved in the presence of ions such as Fe(II) and Cu(II) [22, 24]. According to the data [22], the addition of Cu(II) ions to azo dye solutions increased the degree of dye decomposition under simultaneous exposure to γ-radiation and ozone (this was examined by measuring TOC and BOD values); however, this additive played a negative role in the decolorization of solution. As follows from [24], the presence of Fe(II) ions is responsible for an increase in the degree of removal, and an optimum concentration of these ions is equal to 0.3–0.4 mmol/l. This effect was explained by the formation of a dye complex with Fe(II), which is slightly soluble in water and forms a precipitate. In the absence of Fe(II), the decolorization primarily resulted from dye reactions with $^{\bullet}$OH radicals.

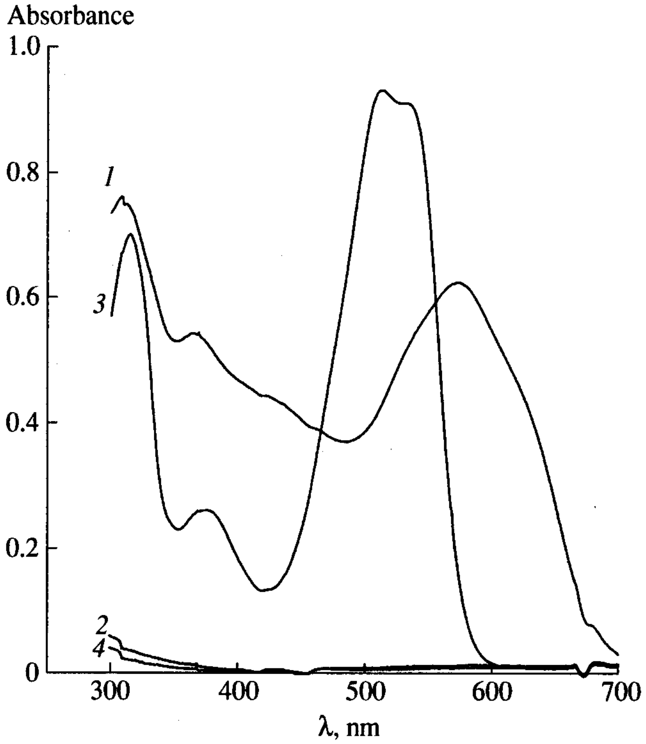

Fig. 1. Optical absorption spectra of aerated aqueous solutions (50 mg/l) of the dyes Acid Red 172: (*1*) unirradiated solution, (*2*) irradiated solution (dose of 9 kGy), and Reactive Red 21: (*3*) unirradiated solution, (*4*) irradiated solution (dose of 7 kGy).

The decolorization of water-soluble dyes primarily resulted from the reactions of these dyes with the $^{\bullet}$OH radicals produced by water radiolysis. This fact was supported by the finding [18] that the degree of removal in aerated solutions was higher than that in deaerated solutions. In the latter, hydrated electrons reacting with a dye form a semireduced species, which, in turn, can partially interact with the products of dye reactions with $^{\bullet}$OH radicals to regenerate the initial dye. In aerated solutions, e_{aq} reacts with oxygen; the resulting $HO_2^{\bullet}$ and O_2^- radicals are characterized by low reactivity (if any) toward dyes.

According to the data published in [21], the radiolytic decolorization of the azo dye Acid Orange 7 in an aqueous solution, as in the case of other dyes, was ini-

Table 1. Effect of the treatment technique on the averaged parameters of wastewater from a dye works (pH 6.5–7; parameters other than color index are expressed in mg/l)[a]

Treatment method	TOC	COD (Cr)	COD (Mn)	BOD_5	Concentration of suspended solids	Color index, deg
Initial wastewater	1000	2820	780	1620	50	290
Aeration[b]	710	2280	715	1060	120	195
Irradiation (dose of 0.6 kGy)	480	2180	530	1510	95	335
Irradiation (dose of 3 kGy)	500	–	600	1430	150	180
Irradiation (dose of 0.6 kGy) and aeration	560	1095	685	785	160	160
The same, but the dose was 3 kGy	530	–	740	670	155	695
Coagulation[c]	480	–	435	–	–	30
Irradiation (dose of 0.6 kGy), aeration, and coagulation	350	–	390	770	–	30
The same, the dose was 3 kGy	305	–	405	700	–	20

[a] A 1-MeV electron beam was used.

[b] The duration of bubbling air was 24 h in all cases.

[c] 1.5 mg/l $Fe_2(SO_4)_3$ was used in all cases.

tiated by $^{\cdot}OH$ radicals. This was supported by an increase in the process efficiency when the solution was saturated with nitrous oxide. It is well known [15] that this substance forms the $^{\cdot}OH$ radical by reacting with e_{aq}. In the given system, 4-hydroxybenzenesulfonic acid and 1,2-naphthoquinone are the major radiolysis products. The latter compound undergoes further oxidation, and its final yield is extremely low.

Kurucz *et al.* [24] examined combined radiation-chemical methods for the removal of dyes from water. They concluded that a combination of irradiation and adsorption at the final stage of treatment is promising for practical applications.

Data on the radiation-chemical decolorization of solutions of Levafix dyes, which are produced by German industry and used in the textile industry of Egypt, were published in [25]. It was found that the process efficiency increased with dose and decreased with concentration of the solution. The efficiency was found to depend on pH; it was maximum or minimum in acidic or alkaline media, respectively. It was found that decolorization followed the first-order rate law.

The radiolytic behavior considered above pertains to dyes soluble in water. If a dye is water-insoluble and forms a colloidal solution, irradiation is ineffective because the dye occurs in a solid phase and water radiolysis products have almost no effect on it. Thus, it was recommended [18] to use a combined electron-beam and coagulation treatment, if dyes occur in water simultaneously in dissolved and dispersed forms. Soluble dyes decompose upon electron-beam treatment, and the dyes present in a disperse state are precipitated by adding a coagulant (for example, $Fe_2(SO_4)_3$ [18]).

More recently, a similar technique was used in the study [26]. The decolorization of solutions of commercial dyes from Germany, which are employed in the textile industry of Ghana, was studied. Water-soluble dyes were decolorized under γ-irradiation, and disperse dyes underwent coagulation in the presence of Mohr's salt. It was also found in [26] that a hydrogen peroxide admixture improved the efficiency of decomposition of water-soluble dyes.

The decolorization and precipitation of disperse azo and anthraquinone dyes as a result of adding a coagulant ($Ca(OCl)_2$, $Al_2(SO_4)_3$, or $FeNH_4(SO_4)_2$) was also observed by Bagyo *et al.* [20]. Moreover, the cited authors also noted [20] that high doses were required for decomposing disperse azo dyes, whereas the doses were much lower in the case of anthraquinone dyes. It was found that the decolorization and precipitation of dyes of the both types was effected by the combination of irradiation and subsequent acidification of the solution to pH 1.

The electron-beam treatment of real wastewater from a dyeing complex in Taegu (Republic of Korea) was examined in detail in [27]. This water was polluted with dyes and organic substances (for example, terephthalic acid) and contained considerable amounts of ultrafine dispersed solid particles. Table 1 summarizes the characteristics of this wastewater. The currently available technology primarily includes coagulation, two steps of biological treatment, and sedimentation. The treatment capacity is close to a limiting value; thus, the output cannot be increased without a significant enlargement of the working area. For this reason, it was decided to examine a possibility to supplement the available technology with electron-beam treatment prior to coagulation.

Table 1 summarizes the data on the effect of various types of treatment on the properties of the wastewater under discussion (pH 6.5–7) [27]. It can be seen that irradiation combined with coagulation and aeration resulted in a considerable increase in the degree of removal, as compared with the available technology. Note that the concentration of suspended solids increased by a factor of 4 to 5. The concentration growth was accompanied by an increase in the particle size, the particles becoming looser, thus preventing, to a considerably extent, the caking (cementation) of the formed precipitate upon sedimentation. The measurements of terephthalic acid concentrations in wastewater demonstrated that as a result of treatment the concentration decreased by a factor of 4 to 5.

An appropriate pilot plant based on an ELV electron accelerator (electron energy of 1 MeV; electron-beam power of 40 kW) is in operation in Taegu since October, 1998 [28, 29]. Its output is 1000 m^3/day. Wastewater taken from different units of the available treatment facility is processed in the plant; this will provide an opportunity to find optimum conditions for the industrial-scale implementation of this combined method.

III.3. Wastewater from Integrated Pulp-and-Paper Mills

In recent years, the radiation treatment of wastewater from integrated pulp-and-paper mills was performed in the following two directions: (1) irradiation of wastewater from a paper mill and (2) irradiation of wastewater after bleaching pulp. The most important results obtained in these directions are given below.

III.3.1. Purification of wastewater from a paper mill. Data concerning the electron-beam treatment of real wastewater from a paper mill of the S-Paper Co. in Cheongwon (Republic of Korea) were presented in [27–29]. The mill primarily produces newsprint paper from recycled paper (91%) and pulp. The wastewater was polluted with organic substances (for example, printing ink residues) and suspended cellulose particles. The initial wastewater had the COD (Mn), BOD$_5$, and TOC values equal to 1100, 1000, and 800 mg/l, respectively. The currently available treatment technology includes coagulation, biological treatment, sedimentation, and filtration.

An important problem is to provide the recycling of purified wastewater in the production process. The above technology makes it possible to accomplish recycling by only 20–30%. In order to increase the degree of removal and hence the degree of recycling, in addition to the available technology, the use of electron-beam treatment after coagulation, biological treatment, and sedimentation was examined.

It was found [27–29] that electron-beam treatment even at a low dose (~1 kGy) noticeably increased the degree of removal. Table 2 summarizes the relevant data. It was estimated that the application of electron-beam treatment to the available treatment technology will increase the recycling of treated wastewater up to 70–80%. Based on this result, it was planned [29] to include four electron accelerators with the total beam power 320 kW in the available treatment facilities. This will provide a treatment capacity of 15000 m^3/day at a dose of ~1 kGy. Figure 2 shows the flowchart of the process.

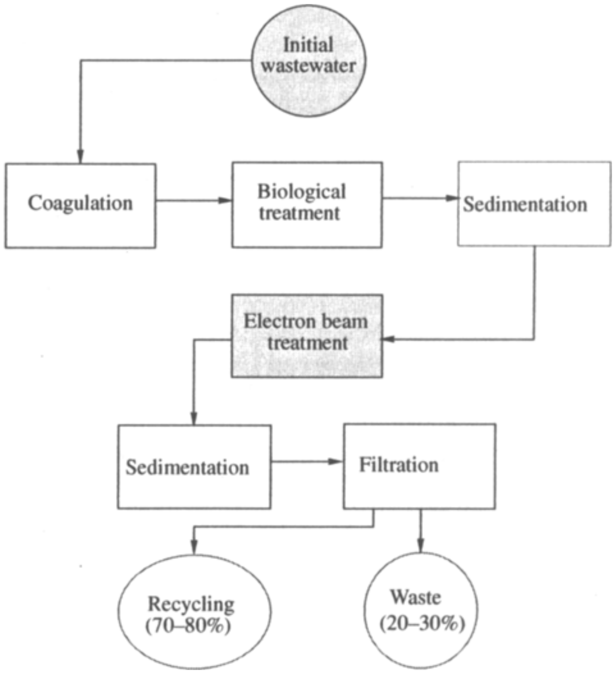

Fig. 2. Flowchart of the combined process including electron-beam treatment for wastewater from the paper mill.

III.3.2. Purification of wastewater after bleaching the paper pulp. The bleaching of the paper pulp with chlorine or chlorine dioxide results in the production of large amounts of wastewater containing chlorinated organic compounds in high concentrations. Among them are both low-molecular-weight and high-molecular-weight compounds. Low-molecular-weight chlorine-containing compounds number more than 200 [30]. These are, for example, chlorinated pyrocatechols and guaiacols and 2-chlorophenol. The nature of the high-molecular-weight compounds has not yet been clearly identified. Adsorbed (on activated carbon) organic halogen (AOH), which is commonly measured in mg/l, is an important parameter by which the degree

Table 2. Effect of electron-beam treatment on the properties of wastewater from a paper mill

Purification step	Parameter, mg/l	
	COD (Mn)	BOD$_5$
Initial wastewater	1100	800
After coagulation	150	100
After coagulation, biological treatment, and sedimentation	45	20
After coagulation, biological treatment, sedimentation, electron-beam treatment (dose of ~1 kGy), and filtration	20	5

of removal is frequently judged. This water is difficult to purify biologically; as a result of biological treatment, the AOH value decreased by less than 50% [30]. Thus, the possibility of applying radiation-chemical methods to solve this problem was examined [30–36].

The radiolytic dechlorination of chlorine-containing organic compounds both in real wastewater taken at different stages of standard treatment (after chlorination, extraction, and biological treatment) or in untreated wastewater and in model solutions containing individual chlorinated compounds that occur in wastewater was studied. It was found [30, 31, 33, 34, 37] that irradiation resulted in a decrease in the AOH values (Table 3). However, doses required for a noticeable decrease in AOH are comparatively high; this fact can restrict practical applications of the radiation-chemical purification of this wastewater. Note that reasonably low doses (below 10 kGy) are required for the dechlorination of the most toxic chlorinated low-molecular-weight organic compounds (for example, chlorinated pyrocatechols).

It follows from the data [32] that electron-beam treatment combined with ozonation caused a decrease in the COD and an increase in the BOD of the pulp after biological treatment. Thus, the COD value decreased from 1290 to 340 mg/l at a dose of 15 kGy and after ozonation for 5 h, whereas the BOD value increased from 17 to 140 mg/l under the same conditions.

The mechanism of dechlorination of chlorine-containing organic compounds in the wastewater under consideration is similar to the mechanism of this process in model solutions of individual compounds. Both hydrated electrons and $^{\bullet}$OH radicals initiated the dechlorination. In the case of solutions of individual compounds, the process efficiency was much higher than that in the case of wastewater [30]. This was explained by the presence of substances that are scavengers of $^{\bullet}$OH radicals and (or) e_{aq} in the wastewater. For example, the wastewater contained methanol (80–150 mg/l) [30], which rapidly reacts with $^{\bullet}$OH radicals.

Table 3. Effect of the absorbed dose on a decrease in AOH upon irradiation of wastewater for pulp decolorization

Purification step at which the sample was taken	Dose, kGy	Decrease in AOH, %	Reference
Untreated wastewater	8	76	[33]
"	10	40	[31]
"	10	70	[30]
"	50	70	[31]
"	60	95	[30]
Chlorination	20	42	[36]
"	60	60	[30]
Extraction	60	70	[30]
After biological treatment	10	60	[30]
"	60	90	[30]

III.4. Molasses Distillery Slops

Molasses distillery slops is dark brown wastewater formed in the hydrolytic processing of plant feedstock. Humic compounds and lignin derivatives constitute the major portion of pollutants. The color index of this water is as high as 10000–15000 degrees, and the COD amounts to 28700–35 900 mg/l. The pH of this wastewater is 4.1. Traditionally, the wastewater is biochemically treated; however, in this case, the degree of removal is no higher than 40–50%. For this reason, it was decided on applying combined electron-beam and coagulation treatment to purify the above wastewater [27]. The mixed complex wastewater made up of three parts molasses distillery slops and four parts municipal wastewater was also examined. Table 4 summarizes the characteristics of this wastewater.

The electron-beam treatment of molasses distillery slops resulted in a noticeable decrease in the optical absorption in the UV and visible regions of the spectrum [27]. At a dose of 20 kGy, this decrease in the UV region was 60–70%, and the absorbance in the visible region was decreased by a factor of 25–30. However, the color index remained to be high; it was equal to 300–500 degrees. Better results were obtained in the case of the mixed complex wastewater (Table 4). The data given in Table 4 correspond to the values acceptable to discharge the treated wastewater into a river under the condition that the river water discharge is higher than the wastewater discharge by a factor of two or more.

Thus, when the combined electron-beam and coagulation method is used, molasses distillery slops should be mixed with municipal wastewater prior to the treatment.

As follows from the data [32, 37–39], molasses wastewater from a factory in Austria retained its intense greyish-brown color and comparatively large amounts of pollutants even after biological treatment. It was found that the use of irradiation in combination with ozonation makes it possible to perform the advanced treatment of this wastewater to a level required for discharging the finished water into a river. It was planned to build a large-scale pilot plant based on an electron

Table 4. Characteristics of the initial complex wastewater and this wastewater treated by a combined method (dose of 5 kGy; bubbling air upon irradiation)

Characteristic	Wastewater	
	initial	treated
Color index, deg	900–2500	20–45
Suspended solids, mg/l	320–580	2–5
COD (Cr), mg/l	800–3500	30–60
BOD_{20}, mg/l	550–2420	8–20
pH	5.6–6.8	6.0–6.8

accelerator with the electron energy 0.5 MeV and the beam power 75 kW [37]. The output of the plant will be 50 m^3/h at a dose of 2.7 kGy and an ozone consumption of 37.3 kg/h.

The estimate of costs of molasses wastewater treatment by a standard technology (ozonation followed by biological treatment) and a combined electron-beam and ozonation method demonstrated that the treatment costs are almost equal (US $3.04 and $3.17 per cubic meter for the former and the latter methods, respectively) [37]. However, the combined electron-beam method comprises a single step without sewage sludge formation, whereas biological treatment results in the formation of sewage sludge, which should be subsequently removed.

III.5. Removal of Heavy Metals from Water

The following three radiation-chemical methods for removing heavy metals from water are known: (1) a radiation–flotation method [40], (2) combined electron-beam and chemical treatment [7], and (3) a combined electron-beam and adsorption method [41].

III.5.1. Radiation–flotation method. This method developed in the early 1980s [40] was proposed for the removal of mercury from industrial wastewater. It involves three steps: flotation (pH 12–13), γ-irradiation (dose of 1 kGy), and secondary flotation (pH 12–13). Irradiation is used for reducing dissolved bivalent mercury to insoluble pseudounivalent mercury and metallic mercury, because mercury that occurs in solution is not subjected to flotation. With the use of this method, mercury can be removed from wastewater to attain a maximum permissible concentration (5×10^{-3} mg/l). This methods was described in more detail in [42].

III.5.2. Combined electron-beam and chemical method. In this method, the electron-beam treatment of water containing heavy metal ions is performed in the presence of a scavenger of $^{\bullet}OH$ radicals or a reducing agent. Formate ions [7, 43–45], ethanol, isopropanol, or acetic acid [46–48] were used as $^{\bullet}OH$ radical scavengers. $Na_2S_2O_3$, Na_2SO_3, and Na_2S served as reducing agents in the presence of which solutions containing heavy metal ions were irradiated [49].

The electron-beam treatment of water containing heavy metal ions in the presence of formate ions is based on the radiolytic reduction of these ions to the metal state or to ions in lower oxidation states, which can be removed by filtration or centrifugation. In this case, two requirements should be fulfilled: oxygen should be absent from water and $^{\bullet}OH$ radicals, which can oxidize the reduced ions to the initial state, should be scavenged [7, 43–45]. This technique was used for the removal of Cd(II), Pb(II), and Cr(VI).

Upon electron-beam treatment, reduction proceeds in the reactions of ions with hydrated electrons and H atoms formed in water radiolysis. For example, in the case of Cd(II), the following reactions can be written [7]:

$$\mathrm{Cd(II)} + e_{aq} \longrightarrow \mathrm{Cd(I)}, \qquad (1)$$

$$\mathrm{Cd(II)} + \mathrm{H} \longrightarrow \mathrm{Cd(I)} + \mathrm{H}^+, \qquad (2)$$

$$\mathrm{Cd(I)} + \mathrm{Cd(I)} \longrightarrow \mathrm{Cd(0)} + \mathrm{Cd(II)}, \qquad (3)$$

$$n\mathrm{Cd(0)} \longrightarrow \mathrm{Cd(0)}_n. \qquad (4)$$

If water is saturated with air, oxygen reacts with e_{aq} and H and hence suppresses, either totally or partially, reactions (1) and (2). The resulting O_2^- and $HO_2^{\bullet}$ radicals slowly react with Cd(II) and Pb(II); they predominantly recombine to form hydrogen peroxide and oxidize the reduced ions back:

$$\mathrm{HO}_2^{\bullet} + \mathrm{O}_2^- + \mathrm{H}^+ \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2}, \qquad (5)$$

$$\mathrm{Cd(I)} + \mathrm{HO}_2^{\bullet} + \mathrm{H}^+ \longrightarrow \mathrm{Cd(II)} + \mathrm{H_2O_2}. \qquad (6)$$

Hydrogen peroxide can also oxidize these ions back:

$$\mathrm{Cd(I)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Cd(II)} + {}^{\bullet}\mathrm{OH} + \mathrm{OH}^-. \qquad (7)$$

Thus, the reduction takes place at relatively high doses after almost complete consumption of oxygen. Because of this, in order to decrease the dose required for the removal of the ions of interest from water, it is necessary to remove air from water prior to or in the course of irradiation.

The $^{\bullet}OH$ radicals formed by water radiolysis and in reaction (7) interact with the reduced ions:

$$\mathrm{Cd(I)} + {}^{\bullet}\mathrm{OH} \longrightarrow \mathrm{Cd(II)} + \mathrm{OH}^-. \qquad (8)$$

In the case of Pb(II), the following reactions can occur (see [15]):

$$\mathrm{Pb(II)} + {}^{\bullet}\mathrm{OH} \longrightarrow \mathrm{Pb(III)} + \mathrm{OH}^-, \qquad (9)$$

$$\mathrm{Pb(I)} + \mathrm{Pb(III)} \longrightarrow 2\mathrm{Pb(II)}. \qquad (10)$$

Because $G_{OH} + 2G_{H_2O_2} > G_{e_{aq}} + G_H$, the ultimate result is that heavy metal ions are not reduced upon irradiation.

In order to eliminate the negative effect of $^{\bullet}OH$ radicals, a scavenger that transforms these radicals into reducing species should be used. The formate ion is one of such scavengers. In reactions with $^{\bullet}OH$ radicals (and H atoms), it forms the $^{\bullet}COO^-$ radical ion, which can also reduce metal ions:

$$\mathrm{HCOO}^- + {}^{\bullet}\mathrm{OH\,(H)} \longrightarrow {}^{\bullet}\mathrm{COO}^- + \mathrm{H_2O\,(H_2)}, \qquad (11)$$

$$\mathrm{Cd(II)} + {}^{\bullet}\mathrm{COO}^- \longrightarrow \mathrm{Cd(I)} + \mathrm{CO_2}, \qquad (12)$$

$$\mathrm{Cd(I)} + {}^{\bullet}\mathrm{COO}^- \longrightarrow \mathrm{Cd(0)} + \mathrm{CO_2}. \qquad (13)$$

Carbon dioxide, which is formed in reactions (12) and (13) is a nontoxic substance. The $\mathrm{Cd(0)}_n$ and $\mathrm{Pb(0)}_n$ precipitates are removed from water by filtration or centrifugation.

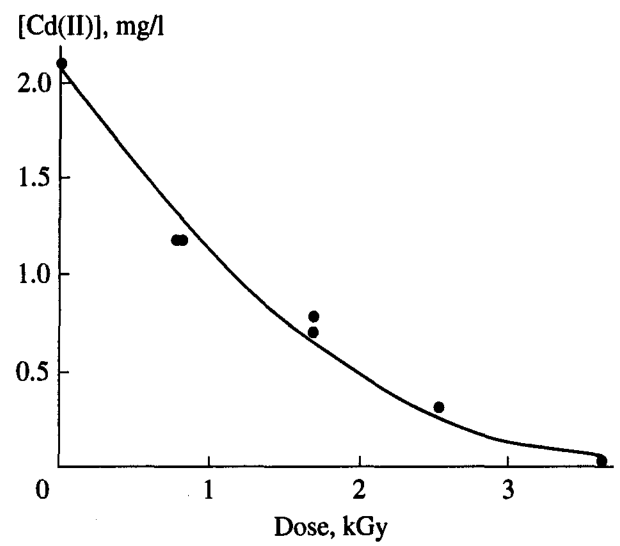

Fig. 3. Concentration of Cd(II) in a deaerated aqueous solution containing 5×10^{-3} mol/l formate as a function of the absorbed dose of electron radiation.

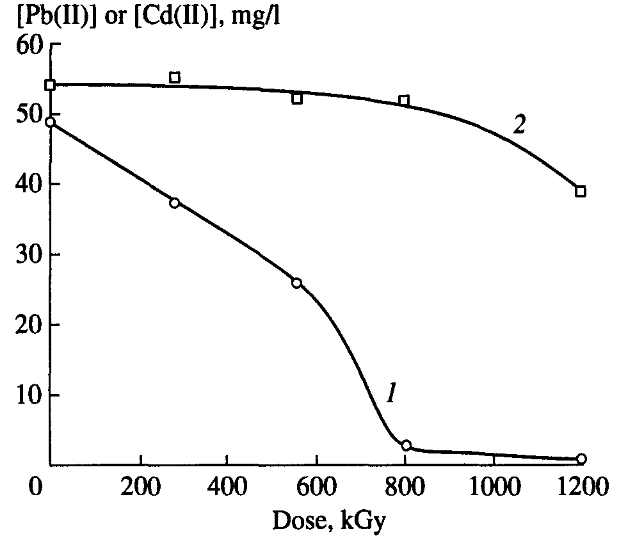

Fig. 4. Concentrations of (*1*) Pb(II) and (*2*) Cd(II) simultaneously present in an aerated aqueous solution containing 10^{-2} mol/l formate as functions of the absorbed dose of electron radiation.

Figure 3 shows the dose dependence of Cd(II) concentration in a deaerated solution containing formate upon electron irradiation. In the case of aerated solutions, an induction period is detected, which terminates after complete consumption of oxygen. For example, this was observed in a solution of Pb(II) ions [43]. Doses required for the removal of Cd(II) and Pb(II) to the maximum permissible concentrations in discharge wastewater (0.1 and 1 mg/l, respectively [50]) are 0.7–4 kGy (depending on metal ion concentrations).

If Cd(II) and Pb(II) ions were simultaneously present in water, the reduction of Cd(II) was observed only after reduction of the major portion of Pb(II) (Fig. 4) [43]. This fact can be explained as follows. The rate constants of Cd(II) and Pb(II) reactions with e_{aq} are similar [51], and e_{aq} reacts with both of the ions. However, the Cd(I) formed rapidly reduces Pb(II) ($k_{14} = 7.5 \times 10^7$ l mol^{-1} s^{-1} [52]):

$$\mathrm{Pb(II) + Cd(I) \longrightarrow Pb(I) + Cd(II)}. \quad (14)$$

Thus, the developed method makes it possible to consecutively remove heavy metals from water.

The addition of formate to water containing highly toxic Cr(VI) ions increased the efficiency of reduction of these ions to much less toxic Cr(III) ions [7, 53]. This follows, for example, from Fig. 5, which demonstrates the dose dependence of Cr(VI) concentration under different conditions of irradiation. The degree of reduction depends on the pH of the solution. The maximum reduction was attained at pH 3.5. At this pH, G[–Cr(VI)] upon γ-radiolysis was equal to 4.5 ion/100 eV. The Cr(III) formed can be removed from water as the hydroxide after alkalization of irradiated water to pH 10–11 and filtration or centrifugation.

Ethanol or isopropanol, which were used as $^{\bullet}$OH radical scavengers in [46–48], also form reducing species in the reactions with these radicals (and H atoms). For example:

$$\mathrm{C_2H_5OH + {}^{\bullet}OH\,(H) \longrightarrow {}^{\bullet}C_2H_4OH + H_2O\,(H_2)}. \quad (15)$$

The resulting alcohol radicals are capable of reducing various metal ions. This capability was used for the reduction and postreduction of Hg(II) and Pb(I), respectively [46–48]. For example:

$$\begin{aligned}&\mathrm{HgCl_2 + {}^{\bullet}C_2H_4OH \longrightarrow HgCl}\\&\quad\mathrm{+\,Cl^- + CH_3CHO + H^+}.\end{aligned} \quad (16)$$

The addition of acetic acid was used for the reduction of dichromate ions to Cr(III). In this case, Cr(VI) was reduced to Cr(V) by $^{\bullet}$CH$_2$COOH radicals [47] formed in the reaction

$$\begin{aligned}&\mathrm{CH_3COOH + {}^{\bullet}OH\,(H)}\\&\quad\mathrm{\longrightarrow {}^{\bullet}CH_2COOH + H_2O\,(H_2)}.\end{aligned} \quad (17)$$

The reduction of a Pb(II) complex with EDTA was also examined. It was found that irradiation was also responsible for the removal of lead from water in this case. According to the data [47], lead present in water as Pb(II) or $(\mathrm{PbEDTA})^{2-}$ (their concentrations were equal to 1×10^{-3} mol/l) was effectively removed at doses of 40 and 100 kGy, respectively. Doses of ~3 kGy were required for the removal of the same amounts of Hg(II) or $\mathrm{Cr_2O_7^{2-}}$. Note that toxic carbonyl compounds are formed in reactions of alcohol radicals with metal ions (for example, acetaldehyde, in reactions with the participation of α-ethanol radicals). In the case when acetic acid was added, the products of Cr(V) reactions with $^{\bullet}CH_2COOH$ were not identified.

The radiolytic reduction of Cr(VI) to Cr(III) in the presence of $Na_2S_2O_3$, Na_2SO_3, or Na_2S was studied in detail in [49]. In particular, it was found that in this case the reduction took place not only in an acidic medium, but also in neutral and alkaline solutions. Of the above three reducing agents, thiosulfate is most effective. It was noted that ions such as Cu(II), Ni(II), Cd(II), Zn(II), and Co(III) were also reduced in the presence of these reducing agents. Any explanation of the results obtained was not given in [49]. It may be suggested that $^{\bullet}OH$ radicals react with the reducing agents to form corresponding radical ions. For example, the $S_2O_3^-$ radical ion is formed in the case of the thiosulfate ion:

$$S_2O_3^{2-} + {}^{\bullet}OH \longrightarrow S_2O_3^{-\bullet} + OH^-. \qquad (18)$$

Thus, $^{\bullet}OH$ radicals are removed from the back oxidation of reduced ions. In other words, the effect of inorganic additives in these systems is similar to the effect of the organic additives described above.

III.5.3. Combined electron-beam and adsorption method. In this method, water containing heavy metal ions is subjected to electron-beam treatment in the presence of a sorbent. The following sorbents were used in this method: SiO_2 (in the presence of formate) [45, 54] and materials of plant origin (cellulose, carboxymethylcellulose, starch, wheat flour, and gluten) [41, 45]. The former sorbent was applied to the removal of Cd(II) from water. Materials of plant origin were used in the case of Cr(VI) and Hg(II). Upon the irradiation of these systems, heavy metal ions passed into precipitates, which were removed by filtration or centrifugation.

It was found [54] that the efficiency of Cd(II) removal from a deaerated solution containing formate dramatically increased in the presence of silica white (SiO_2) (Fig. 6). A major reason for this effect is the adsorption of cadmium ions on SiO_2. It is not inconceivable that the adsorption is intensified by the charging of SiO_2 particles as a result of irradiation.

Among the examined sorbents of plant origin, wheat flour and gluten were found to be most effective in the removal of Cr(VI) and Hg(II) from water. Two main reasons may be responsible for this effect. First, the additives, which are $^{\bullet}OH$ radical scavengers, suppress the back oxidation of reduced ions (Hg(I), Hg(0), Cr(III), etc.) by these radicals. Second, electron-beam treatment causes the aggregation of sorbent molecules, thus enhancing the capture of chromium and mercury ions by the sorbents. This is particularly typical of flour and gluten. The occurrence of aggregation was supported by the fact that coagulation and sedimentation of the above substances were considerably accelerated as a result of irradiation. The aggregation was caused by the dimerization of free radicals formed by the interaction of sorbents with $^{\bullet}OH$ radicals.

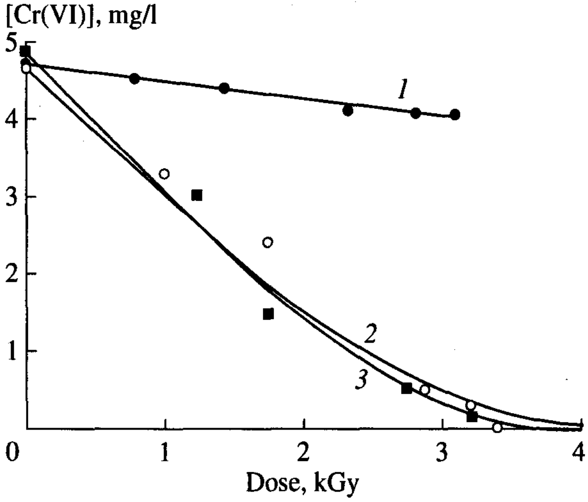

Fig. 5. Concentrations of Cr(VI) in an aerated neutral aqueous solution (*1*) in the absence of formate or (*2*) in the presence of 9.6×10^{-3} mol/l formate and (*3*) in a deaerated aqueous solution in the absence of formate as functions of the absorbed dose of electron radiation.

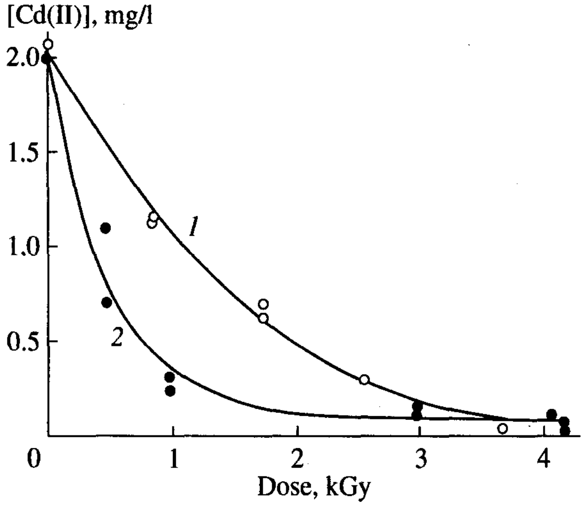

Fig. 6. Concentration of Cd(II) in a deaerated aqueous solution containing 5×10^{-3} mol/l formate (*1*) in the absence or (2) in the presence of 200 mg/l silica white SiO_2 as a function of the absorbed dose of electron radiation.

III.6. Removal of Petroleum Products from Water

The radiation-chemical removal of petroleum products (diesel fuel, motor oil and residual fuel oil), which were present in a dissolved state or in a heterogeneous system (in the dissolved state, as oil-in-water emulsions and as films on the water surface), was studied in [55, 56]. It was found that radiation treatment resulted in the removal of these pollutants from water. Thus, they were removed by 96 and 85% from a heterogeneous system and a solution at doses of 25 and 32 kGy, respectively. In this case, the behavior of petroleum product solutions is different from the behavior of the heterogeneous system. In the latter, the COD values decreased with increasing the dose, whereas these values in solution initially increased to reach a maximum and then decreased with increasing the dose (Fig. 7). Moreover, the irradiation of the heterogeneous system resulted in the formation of a precipitate.

The addition of CCl_4 or H_2O_2 to a solution of petroleum products was responsible for an increase in the removal efficiency [55, 56]. In the presence of 5×10^{-3} mol/l CCl_4, H_2O_2, or both of these substances, the degree of removal at a dose of 32 kGy was equal to 96, 92, or 98%, respectively. The above substances rapidly react with e_{aq}, and oxidizing radicals are produced in the corresponding reactions ($^{\bullet}OH$ and $^{\bullet}CCl_3$ in reactions (19) and (20), respectively)

$$H_2O_2 + e_{aq} \longrightarrow {}^{\bullet}OH + OH^- \qquad (19)$$

$$CCl_4 + e_{aq} \longrightarrow {}^{\bullet}CCl_3 + Cl^-. \qquad (20)$$

Thus, it may be concluded that the radiolytic decomposition of petroleum products was primarily initiated by their interaction with $^{\bullet}OH$ and $^{\bullet}CCl_3$ radicals. This conclusion was supported by the fact that hydrocarbons, which are highly reactive toward $^{\bullet}OH$ and, probably, $^{\bullet}CCl_3$ radicals, but almost do not react with e_{aq}, are the major constituents of these pollutants [51].

The formation of a precipitate in the heterogeneous system is associated with the dimerization and polymerization of hydrocarbons at high doses, when oxygen present in the system was completely consumed. Because of a low concentration of dissolved pollutants in solution, a stable colloid solution is formed. This is a prerequisite for the reactions of colloidal solid particles with water radiolysis products and, as a consequence, for the molecular fragmentation of these substances. Evidently, the fragmentation is responsible for an increase in the concentration of impurities. In turn, this causes an increase in the COD values at comparatively low doses and a decrease in these values at higher doses because of the subsequent radiolytic decomposition of fragments [55, 56].

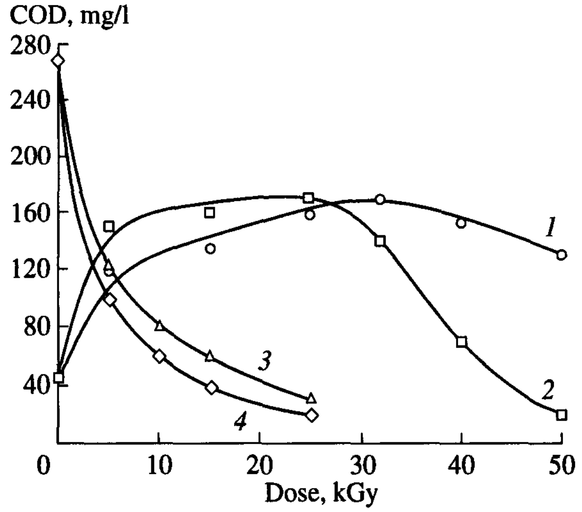

Fig. 7. COD values for (*1*) an aerated aqueous solution of petroleum products (10 mg/l) containing 5×10^{-3} mol/l CCl_4, (*2*) the above solution additionally containing 5×10^{-3} mol/l H_2O_2, (*3*) a heterogeneous system (150 mg/l), and (*4*) the above system containing 25 mg/l polyacrylamide as functions of the absorbed dose of γ-radiation.

Doses required for the removal of petroleum products from water are rather high; this is almost unacceptable for the practical implementation of this method. It is likely that lower doses can be practicable with the use of combined methods (for example, electron-beam treatment in combination with biological tertiary purification).

III.7. Removal of Isobutylnaphthalenesulfonates from Water

An isobutylnaphthalenesulfonate mixture known as Nekal was used as an emulsifier at the Voronezh synthetic rubber factory. Wastewater containing this substance was subjected to underground disposal. This resulted in the contamination of a groundwater reservoir with the total area 75 km^2 and gave rise to serious difficulties with the drinking water supply in a district of Voronezh [49]. Nekal (its concentration in water was as high as 150–200 mg/l) is a toxic substance; thus, it was impossible to use water from the polluted reservoir for public water supply. Moreover, this substance is nonbiodegradable. For the above reasons, a combined electron-beam and biological treatment method was developed [57]. In this method, the electron-beam treatment resulted in partial decomposition of Nekal, that enabling the final biological treatment of water.

It was found [57, 58] that in order to remove Nekal from wastewater this substance need not be decomposed completely (evidently, the complete decomposition requires high doses). The elimination of the alkyl group and the sulfonate group or both from the molecule was found to be sufficient for the subsequent biological treatment. As was demonstrated using pulse radiolysis [59], the interaction of isobutylnaphthalenesulfonates with $^{\bullet}OH$ radicals plays a crucial role in the above processes. The radiolysis of Nekal solutions was considered in more detail in [60, 61].

The obtained data formed the basis for constructing a plant with an ELV-3 electron accelerator in 1984. In 1988, this plant was equipped with an additional ELV-4 accelerator [49]. The performance characteristics of this plant were given in the first part of the review ([1], Table 1).

The wastewater was irradiated as a foam produced by intensely bubbling air; the foam density was 0.02–0.1 g/cm^3. The dose required for the purification was 2–3 kGy at a Nekal concentration of ~100–150 mg/l. The average output of the plant was equal to

12000 m^3/day [60, 61], and the maximum output was 30000 m^3/day [49]. These values are given for water irradiated as a foam. If the calculation was performed for initial (unfoamed) water (density of 1 g/cm^3), the resulting output was much lower. If water was saturated with irradiated air, which contains ozone, the output was somewhat higher. After electron-beam treatment, water was admitted to final biological treatment.

With the use of this technique, the degree of water purification was as high as 99.5%. By now, the purification of groundwater from the polluted reservoir was almost completed.

III.8. Radiation Treatment of Mixed Radioactive Wastes

As a rule, liquid radioactive wastes formed at radiochemical plants and nuclear facilities contain not only radionuclides, but also toxic and nontoxic organic substances (aromatic compounds, acetic acid, complexons, extractants, decontaminating agents, etc.). In the foreign literature, these wastes are commonly referred to as mixed radioactive wastes.

III.8.1. General problems. Organic substances present in radioactive wastes make the waste management upon storage and disposal much more difficult. They may be responsible for a chemical explosion similar to that happened in Kyshtym (Russia) in 1957; as a result of this accident, a large area in the south Ural Mountains was radioactively contaminated. The accident originated from the overheat of mixed radioactive waste stored in a special tank. Moreover, organic substances increase the yield of gases (among them are explosive hydrogen and methane) upon radiolysis by radiation from radionuclides present in the waste. It is obvious that organic substances should be removed for the safe management of mixed radioactive wastes.

Relevant studies are performed in a number of countries (predominantly, in Russia and the United States where these wastes were accumulated in large amounts [62–64]). These studies are primarily oriented to examine gas evolution from waste and decomposition of organic substances. Experiments are mainly performed with model systems in the absence of radionuclides.

III.8.2. Radiolytic gas evolution. Radiolytic gas evolution from aqueous nitrate–acetate solutions, which simulate radioactive wastes from Russian radiochemical industry, was studied in [65–68]. The yields of hydrogen, oxygen, methane, nitrogen, carbon dioxide, and N_2O upon γ-radiolysis were measured depending on the composition of solutions (Table 5).

Three features of the gas evolution were found. First, the nature of gases depends on the composition of solutions. The gases evolved from an acetic acid solution are H_2, CO_2, and CH_4. In alkaline solutions of sodium acetate, H_2 and CH_4 escaped to the gas phase, whereas CO_2 formed carbonate by reacting with the alkali. The radiolysis of $NaNO_3$ or $NaNO_3 + HNO_3$ solutions resulted in the formation of H_2, O_2, N_2, and N_2O; however, the yields of the two last-named gases were extremely low. The addition of acetate ions to acidic solutions was responsible for a considerable increase in $G(N_2O)$; however, this effect was almost absent in neutral and alkaline nitrate–acetate systems. Note that the effects of organic additives and of the acidity on the $G(N_2O)$ value were also described in [69].

Second, the dose dependence curves for the amount of evolved gas exhibit an initial "slowed" portion due to the saturation of the solution with gases.

Third, the amount of evolved gases in nitrate–acetate solutions was greater than that in solutions containing nitrate ions alone. An increase in the concentration of nitrate affected the gas evolution only slightly, whereas a twofold increase in the yields was observed in the presence of acetic acid.

The radiolytic gas evolution from nitrate–acetate solutions is characterized by the occurrence of three major sources [65, 66]. The first is the formation of hydrogen in spurs. The second source consists in the reactions of solutes with primary products of water radiolysis. For example, the reaction of acetate ions with H atoms is one of the most important sources of H_2 in solutions containing acetate ions. The appearance of nitrogen-containing gases is associated with the transformations of $NO_3^{2-\bullet}$ and $NO_2^{\bullet}$ formed in the reactions of nitrate ions with e_{aq} and H, respectively. The third source is the direct action of ionizing radiation on the solute. This effect results from the fact that the test systems are concentrated solutions. Evidently, the direct action of radiation on acetate ions is responsible for the appearance of CH_4 and CO_2 (in part):

$$CH_3COO^- \rightsquigarrow CH_3COO^{\bullet} + e, \qquad (21)$$

$$CH_3COO^{\bullet} \longrightarrow {}^{\bullet}CH_3 + CO_2, \qquad (22)$$

$${}^{\bullet}CH_3 + CH_3COO^- \longrightarrow CH_4 + {}^{\bullet}CH_2COO^-. \qquad (23)$$

Stel'makh *et al.* [68] examined the temperature effect on the gas yields upon γ-radiolysis of nitrate–acetate solutions. It was found that upon γ-radiolysis of nitrate–acetate solutions at 60°C the yields of CH_4 and CO_2 were noticeably higher than those at room temperature. This fact was explained by a decrease in the thermal stability of the $CH_3COO^{\bullet}$ radical, produced by reaction (21), with increasing temperature. The yields of other gases remained almost unaffected upon varying the temperature within the above limits.

III.8.3. Radiolytic decomposition of organic substances. Radiolytic degradation of the following organic compounds in aqueous solutions that simulated mixed liquid radioactive wastes was studied: acetic acid [70]; benzene and its derivatives [71]; EDTA [72,

Table 5. G values (molecule/100 eV) for gases from nitrate--acetate solutions (concentrations of substances in mol/l are given in parentheses)

Solution composition	H_2	O_2	N_2	N_2O	CH_4	CO_2
NaOH (0.25)	0.04	–	–	–	–	–
$NaNO_3$ (2.35)	0.042	0.027	0.008	0.007	–	–
CH_3COOH (0.08)	0.63	–	–	–	0.05	0.16
$NaNO_3$ (2.35) + HNO_3 (0.32)	0.037	0.017	0.023	0.007	–	–
NaOH (0.25) + CH_3COONa (1.0)	0.13	–	–	–	NA	NA
NaOH (0.75) + CH_3COONa (1.0)	0.19	–	–	–	0.5	–
HNO_3 (0.32) + CH_3COOH (1.0)	0.067	–	0.05	0.26	0.025	0.44
$NaNO_3$ (1.2) + CH_3COONa (0.3)	0.04	–	NA[a]	NA[a]	0.01	0.06
$NaNO_3$ (1.2) + CH_3COONa (1.7)	0.05	–	NA[b]	NA[b]	0.08	0.07
$NaNO_3$ (2.35) + CH_3COONa (1.7)	0.02	–	NA[c]	NA[c]	0.07	0.07
NaOH (0.5) + $NaNO_3$ (1.5) + CH_3COONa (1.0)	0.02	–	NA[d]	NA[d]	0.10	–
Na_2CO_3 (0.062) + $NaNO_3$ (0.75) + CH_3COONa (0.72)	0.11	–	NA	NA	0.06	~0.01
$NaNO_3$ (1.17) + HNO_3 (0.32) + CH_3COOH (0.17)	0.025	–	–	0.283	0.001	0.302
$NaNO_3$ (1.17) + HNO_3 (0.32) + CH_3COOH (0.67)	0.036	–	–	0.344	0.004	0.406
$NaNO_3$ (2.35) + HNO_3 (0.32) + CH_3COOH (0.17)	0.025	–	–	0.286	0.002	0.315
$NaNO_3$ (2.35) + HNO_3 (0.32) + CH_3COOH (0.67)	0.04	–	–	0.352	0.026	0.453
$NaNO_3$ (1.76) + HNO_3 (1.5) + CH_3COOH (0.67)	0.08	–	NA	NA	0.11	NA

[a] NA denotes not analyzed. In this system, the total yield of nitrogen-containing gases ≤ 0.005 molecule/100 eV.

[b–d] The total yields of nitrogen-containing gases in these solutions were equal to ≤ 0.005, 0.03, and 0.06 molecule/100 eV, respectively.

73, 73a, 74, 75, 75a, 75b], nitrilotriacetic acid, and other complexons [73–75].

The decomposition of acetic acid was examined in aqueous acidic nitrate–acetate solutions as models of the most widespread radioactive wastes in Russia. It was found that the acidity of these systems decreased upon irradiation; in this case, $G(-H^+) = 2.84$ molecule/100 eV, and $G(-CH_3COOH) = 1.109$ molecule/100 eV.

The radiolytic decomposition of benzene and its derivatives was examined in aqueous solutions that simulated mixed liquid radioactive wastes from the atomic center in Savannah River (USA) [71]. The above substances were added to a solution containing $NaNO_3$, Na_2SO_4, KH_2PO_4, $FeCl_2$, and the detergent Alconox. The benzene concentration was equal to 100 mg/l. The solution volume irradiated with an electron beam was from 26.1 to 11 400 l. It was found that a dose of 50 kGy was required for decreasing the benzene concentration from the above value to 1 μg/l (US drinking-water quality standard). In this case, not only benzene, but also products of its radiolytic transformations (such as nitrophenols) were decomposed.

The radiolytic decomposition of EDTA in aqueous solutions in the absence and in the presence of TiO_2 was studied as applied to radioactive wastes from the atomic center in Hanford (USA) [72]. It was found that, upon γ-radiolysis of aerated solutions in the presence of TiO_2, the EDTA yield of decomposition increased by approximately 30%, as compared with solutions containing no TiO_2. Thus, in the absence of TiO_2, G(–EDTA) was equal to 2.5 molecule/100 eV, whereas the yield was 3.7 molecule/100 eV in the presence of this dioxide (0.1 g/l). Su *et al.* [72] concluded that $^{\bullet}OH$ radicals were primarily responsible for the initiation of EDTA decomposition.

The last conclusion is confirmed by the fact that G(–EDTA) in EDTA solutions saturated with nitrous oxide is equal to 5.4 molecule/100 eV, i.e., it is close to $G_{OH} + G_H + G_{e_{aq}}$ [75c]. The mechanism of this process was studied in [75c] by pulse radiolysis method.

The detailed study of radiolytic conversions of EDTA in aqueous solutions modeling radioactive wastes of atomic center in Hanford was conducted in [73a]. It was shown that degradation of EDTA (11.45 mmol/l) upon γ-radiolysis of aqueous solutions modeling these wastes at 90–95°C reaches 89.1% at dose ~70 kGy. Seven fragments of the complexon (the main of them are *N*-hydroxy-*N*-methyliminoacetic and *N*-(ethil)ethylenediamine-*N'*,*N'*-carboxyacetic acids) and three dicarboxylic acids were obtained among the radiolysis products.

The study of radiolysis of EDTA aqueous solutions under various conditions was performed in [75d]. It was found that the degradation yields considerably increase in the presence of ozone and especially in the presence of ozone and TiO_2. In the case, G(–EDTA) = 13.5 molecule/100 eV.

The results of studies concerning radiolytic transformations of nitrilotriacetic acid and other complexing agents, which are contained in mixed liquid radioactive wastes of the atomic center in Hanford were considered in [73, 73a, 74, 75, 75a, 75b]. It was found that nitrilotriacetic acid (12 mmol/l) was almost completely decomposed at a dose of ~70 kGy upon γ-radiolysis at 90–95°C of aqueous solutions modeling these wastes. Among the radiolysis products, four fragments of the complexone and two carboxylic acids were detected. It was noted that the decomposition of the complexone proceeded more effectively when it was present individually in the solution, as compared with solutions also containing other complexing agents. Other substances present in the wastes also underwent decomposition. Thus, *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid was completely decomposed under the specified conditions, whereas citric acid was decomposed only by 50%. In this case, the TOC after irradiation under these conditions was 27% of the initial value. It was found [75b] that the main products of radiolytic conversions of citric acid are oxalic and malonic acids. In order to achieve the complete decomposition of organic substances, it was recommended to use γ-irradiation in combination with other treatment methods.

III.9. Water Containing Other Organic Substances

Data on the radiolytic decomposition of other contaminants in water are available in the literature. Among these compounds are *tert*-butanol [75], formic acid [77], substances simulating toxic chemical agents [78–80], ethylene glycol (used against icing of airplanes) [81], aryl halides [82], phenolic compounds [83, 84], etc.

III.9.1. Decomposition of *tert*-butanol. It was found [76] that *tert*-butanol in an aqueous solution underwent decomposition under exposure to ^{60}Co γ-radiation. The products of this process are acetone, lactic acid, pyruvic acid, acetic acid, and formic acid. The decomposition of this alcohol was more effective in the presence of ozone. In this case, 79, 82, and 92% of the TOC value were transformed into radiolysis products at doses of 2.0, 2.7, and 4.1 kGy, respectively. The values of G(–*tert*-butanol) at a dose of 2.7 kGy were measured to be 1.7 and 6.0 molecule/100 eV in the absence and in the presence of ozone, respectively. It was concluded that the radiolytic decomposition of *tert*-butanol in the absence of ozone was initiated by $^{\bullet}$OH radicals. This follows from the fact that G(–*tert*-butanol) is close to $G_{\mathrm{OH}^{\bullet}}$. In the presence of ozone, e_{aq} and H were converted into $^{\bullet}$OH radicals by reactions with ozone, and the yield of decomposition approached the sum of the yields of e_{aq}, H, and $^{\bullet}$OH. The addition of trace amounts of Cu(II) ions accelerated the decrease in TOC; this was explained by more effective decomposition of lactic and pyruvic acids in the presence of these ions.

III.9.2. Decomposition of formic acid. Deep radiolytic decomposition of formic acid was studied in [77]. This study was impelled by the presence of that acid as the major component of wastewater from some power plants. It was found that electron-beam treatment of an aqueous solution resulted in decomposition of the acid, which was accompanied by an increase in pH and a decrease in TOC. Upon irradiation, the optical absorption of the solution initially decreased and then increased. This was explained by the formation of products of radiolytic transformations of HCOOH (for example, oxalic acid). The decomposition proceeded more effectively in solutions containing oxygen than in deaerated solutions. The data obtained made it possible to perform computer simulation of the radiolysis of this system based on a process mechanism that involved 39 reactions.

III.9.3. Decomposition of organophosphorus compounds. The radiolysis of aqueous solutions of a number of organophosphorus compounds that model some toxic chemical agents and pesticides was studied in [78–80]. Data on the radiolytic transformations of dimethyl methylphosphonate in aqueous solutions under exposure to ^{60}Co γ-radiation or an electron beam were published in [80]. A model solution of volume 4000 l was used for the electron-beam treatment. It was found that the yield of decomposition depends on concentration and pH of the solution and on the absorbed dose. For example, the yield of decomposition by electron beam irradiation (concentration of 172–175 mg/l; dose of 5 kGy) was equal to 0.81 or 0.31 molecule/100 eV at pH 4 or 9, respectively. It was noted [80] that phosphate ions, methyl methylphosphonate, methylphosphonic acid, formic acid, and formaldehyde are the products of radiolytic transformations of this substance. At low concentrations of the substance and at low doses, the quality of water used for preparing solutions affected the decomposition. Thus, the process proceeded more effectively in distilled water than in ordinary drinking water. The computer simulation performed took into account 64 possible reactions.

O'Shea *et al.* [78] performed a comparative study of the decomposition of dimethyl and diethyl methylphosphonates by γ-radiolysis and TiO_2 photocatalytic treatment. They concluded that the mechanisms of the processes were similar in both cases, and the same products were formed. It was noted that $^{\bullet}$OH radicals played a main role in the decomposition by both γ-radiolysis and photocatalytic treatment.

The mechanism of radiolytic transformations of diethyl benzylphosphonate in aqueous solutions was studied in detail using pulse radiolysis [79]. The main conclusion drawn from this study consists in that, as in the case of the above model substances, the reactions with $^{\bullet}$OH radicals are primarily responsible for the decomposition of diethyl benzylphosphonate. The rate of decomposition resulting from radiolytic reduction in the reaction with e_{aq} is lower by two orders of magnitude than the rate of oxidation with $^{\bullet}$OH radicals.

III.9.4. Decomposition of ethylene glycol. Ethylene glycol is a substance used against icing of airplanes; it may be responsible for water and soil pollution with rainfall. It was found in [81] that this substance was decomposed to CO_2 upon irradiation. However, doses required for removing ethylene glycol are comparatively high. For example, 85.8% of the compound was decomposed at a dose of 1 MGy and at an initial solution concentration of 100 mg/l. The efficiency of decomposition considerably increased on the addition of hydrogen peroxide. Thus, at a dose of 2 MGy and at an initial solution concentration of 1300 mg/l, the addition of 450 mol/l H_2O_2 resulted in 93.6% decomposition of ethylene glycol. Because hydrogen peroxide added to the solution was incompletely decomposed upon irradiation, the toxicity of the irradiated solution was somewhat higher than that of unirradiated solution. It was recommended to add a small amount of Fe(III) ions to the solution in order to prevent an increase in the toxicity. The ethylene glycol decomposition was initiated by $^{\bullet}OH$ radicals. In the presence of H_2O_2, reaction (19) occurs, which produces an additional amount of $^{\bullet}OH$ radicals. Moreover, hydrogen peroxide can react with secondary radicals, and these reactions may intensify the decomposition. The radiolysis mechanism of this system was studied in detail previously [15].

III.9.5. Decomposition of aryl halides. Data on the radiolytic transformations of aryl halides in aqueous solutions were given in [82]. Deaerated water–ethanol, water–acetonitrile, and aqueous solutions (in the presence of a detergent) of chloro and bromo derivatives of naphthalene and anthracene (for example, 1-chloronaphthalene, 1-chloroanthracene, 9,10-dichloroanthracene, and 1-bromonaphthalene) were examined. Some stable radiolysis products were identified; the kinetics of a number of radiation-chemical reactions was measured; and the efficiency of dehalogenation of these compounds was determined. For example, almost complete decomposition of 1-chloronaphthalene in a deaerated 1.1×10^{-3} mol/l water–ethanol solution was attained at a dose of 3.3 kGy. In aqueous solutions containing detergents, the degree of decomposition increased in the case of cationic micelles and decreased in the case of anionic micelles, as compared with homogeneous solutions. The mechanism of radiolysis involves the formation of radical anions in the reactions of aryl halides with solvated electrons followed by elimination of halide ions and the appearance of aryl radicals, recombination of aryl radicals, their interaction with organic solvents, etc.

III.9.6. Decomposition of *tert*-butyl methyl ether. The mechanism of radiolytic transformations of *tert*-butyl methyl ether in aqueous solutions was studied by pulse radiolysis [85]. Transient products of these transformations were determined, and the rate constants of many reactions occurring in this system were measured. A kinetic simulation (based on 81 reactions) of the ether decomposition in solutions at different pH was performed. It was found that the model adequately described the results of electron-beam treatment of this system at pH < 5. The decomposition was examined at a solution flow rate through the electron beam equal to 0.45 m^3/min.

III.9.7. Decomposition of phenolic compounds. Data on the radiation-chemical decomposition of phenolic compounds are available in the literature. As follows from [83], the values of $G[-C_6H_5OH]$ are equal to 0.5, 3.1, and 12.5 molecule/100 eV for 10^{-5}, 10^{-4}, and 10^{-3} mol/l solutions, respectively. Data on the radiolytic decomposition of resorcinol, *o*-cresol, and *m*-cresol in aqueous solutions (pollutant concentrations were equal to 50–60 mg/l) were published in [84]. It was found that these substances were removed at a dose of 6 kGy (at pH 9); in this case, oxalic acid was the major product of radiolysis.

III.9.8. Decomposition of thioanisole. The radiation-chemical removal of thioanisole from water was examined in [85]. It was found that $\sim 8 \times 10^{-5}$ mol/l of this substance was almost completely decomposed at doses of ~1 kGy (pH 5) and 3 kGy (pH 9). The mechanism of radiolytic transformations of thioanisole was studied by pulse radiolysis. The optical absorption spectra of transient products of these transformations and the rate constants of radiation-chemical reactions were measured. Based on these data, a kinetic simulation of thioanisole decomposition was performed.

III.9.9. Decomposition of chlorinated benzaldehydes. Recently, a detailed study of the radiolytic decomposition of 2-, 3-, and 4-chlorobenzaldehydes in neutral aqueous solutions saturated with oxygen was performed [85a]. It was found that chloride ions, formaldehyde, and a mixture of acids are the main radiolysis products. In this case, the radiation-chemical yields of the above products depend on the position of chlorine atoms on the benzene rings. The initial yields of decomposition and of formation of chloride ions and formaldehyde were highest in the case of 4-chlorobenzaldehyde, whereas the initial yields of a mixture of acids were lowest in a solution of this aldehyde.

III.9.10. Purification of industrial wastewater in Sao Paulo. Sampa and coworkers [8, 86–88] performed a series of studies concerning the electron-beam treatment of mixed industrial wastewater in Sao Paulo. Chemical and textile industries are the primary sources of wastewater. Water was sampled at the inlet and outlet of the purification facilities of this city. Irradiation was performed on a pilot plant [8, 87]; the performance characteristics of this plant were given in the first part of the review ([1], Table 1). It was found that a dose of 3 kGy exerted almost no effect on the COD value in the case of influent wastewater; however, the COD decreased by 45% upon irradiation of effluent water to the specified dose. Organic pollutants present in the effluent water (chlorinated aliphatic compounds in amounts of 1000 mg/l or higher, benzene in an amount of 10 mg/l, toluene in an amount of 8 mg/l, xylene in an amount of 10 mg/l, and phenol in an amount of 3 mg/l) were found to decompose by more than 90% at a dose of 2 kGy when the water was irradiated in the presence of air. In the case of aerated water, the degree of decomposition was somewhat lower (80% at a dose of 2 kGy). At the specified dose, phenol underwent no detectable changes in the presence of air. However, the degree of phenol decomposition in deaerated water was 50%. The absence of changes in the influent wastewater at the above doses resulted from high pollutant contents of this wastewater. Preliminary estimates given in [86] demonstrate that the electron-beam treatment costs are equal to US $1.0 and $10 per cubic meter at doses of 2 and 20 kGy, respectively.

III.9.11. Landfill leachate. Landfill leachates containing large amounts of organic and inorganic pollutants are formed near large cities (as a result of leaching by rain, thermal processes, etc.). The presence of pollutants is responsible for high COD and BOD values (up to several grams per liter). Moreover, landfill leachates are characterized by considerable turbidity due to the presence of suspended solids. The currently available methods for the purification and disinfection of landfill leachates involve biological treatment, coagulation, and chlorination. However, these methods often cannot provide a required level of purification. Because of this, the applicability of radiation treatment combined with coagulation [89] or ozonation [38] was examined.

Leachates from landfills near Seoul and Taejon (Republic of Korea) [89], Vienna [38], and Halle (Germany) [90] were examined. It was found that the landfill leachates from the two first-mentioned cities became more transparent as a result of electron-beam irradiation (doses up to 11 kGy). This was particularly pronounced in the case of leachates subjected to biological treatment. Moreover, irradiation followed by coagulation resulted in a decrease in the COD values, the effect depending on the pH of the medium. For example, these values for the initial leachate from a landfill near Seoul decreased as a result of irradiation (dose of 3.4 kGy) from ~1500 to 850 mg/l at pH 8.5 or from ~1500 to 480 mg/l at pH 3. A decrease in COD was greater in aerated water than in deaerated water. Leachate samples from landfills near Seoul and Taejon, which were taken after biological treatment, were more sensitive to the electron beam treatment and to coagulation than samples of the initial leachates. Thus, it was recommended to treat the landfill leachates using a combined electron-beam and coagulation treatment after biological purification.

According to the data [38], the COD value of the leachate from a landfill near Vienna subjected to biological treatment remained unaffected as a result of γ-irradiation to a dose of 10 kGy. However, the combined action of γ-irradiation and ozonation decreased this value from 2400 to 900 mg/l. Ozonation was responsible for an increase in the BOD value by a factor of about 3. The BOD value was almost retained at the initial level after γ-irradiation combined with ozonation. It was concluded that this combined method, as well as in many other cases, was effective for the purification of the landfill leachate examined. Nevertheless, the treatment costs are rather high because of a large consumption of ozone (6 to 7 mg of O_3 per milligram COD).

A mobile pilot plant equipped with an electron accelerator was used for the purification of leachates from a landfill near Halle [90]. It was found that the irradiation to a dose of 90 kGy resulted in a decrease in COD from 670 to 375 mg/l. Pollutants present in this leachate (benzene, toluene, chlorobenzene, and chlorinated aliphatic hydrocarbons) were almost completely decomposed at doses of 30–50 kGy.

III.9.12. Decomposition of nitrate esters. Electron-beam treatment of wastewater polluted with nitroglycerol and propylene glycol dinitrate was studied in [90a]. It was found that the radiolysis products of deaerated solutions of these organic nitrates are glycerol, nitrate and hydrogen ions. The dose required for decomposition of 240 mg/l of nitroglycerol to 1 mg/l is equal to 200 kGy. The dose required for removal of propylene glycol dinitrate is much higher. The evaluation conducted has shown that the cost of purification of wastewater from nitroglycerol is equal to 23 US $/m^3 that is about 3 times cheaper than the purification by conventional method (with activated coal). However, electron-beam treatment is unprofitable in comparison with the conventional method in the case of propylene glycol dinitrate.

IV. AGRICULTURAL WASTEWATER

Presently, radiation-chemical techniques are not so widely used for the treatment of agricultural wastewater as in the case of water and industrial liquid wastes. Only two lines of corresponding investigation can be mentioned.

First of all, the problem of the disinfection and purification of manure waste in connection with the building and operation of large-scale hog-raising farms should be considered. Many specialists (see [2] and references wherein) have shown that this problem can be solved in principle by using radiation-chemical methods. Four pilot plants (three with electron accelerators and one with a ^{60}Co γ-radiation source) were constructed for the development of a large-scale technology for the disinfection and purification of manure waste in a number of regions in the former Soviet Union (Minsk, Moscow, and Omsk oblasts) and operated for a long time. However, the process was never implemented on the industrial scale. One of the reasons is that it was necessary for the transportation of liquid waste under an electron beam to dilute it with water; this dilution considerably increased the volume of waste. Naturally, this made the subsequent disposal of treated waste difficult. The research and development work in this area of radiation technology is not being performed now.

Hilmy *et al.* (Indonesia) [91] found that a γ-radiation dose of 2 kGy considerably decreased the amount of microorganisms in chicken manure. It was recommended to use this manure as a fertilizer in agriculture. However, fowl manure may contain heavy metals [92], thus being able to substantially restrict its applications.

Recently, the use of γ-irradiation for the purification of wastewater formed in the production of coffee was described [93]. Large volumes of water are frequently used in this process. This results in the appearance of considerable amounts of wastewater containing various pollutants (acetic acid, propionic acid, valeric acid, caffeine, phenol, etc.); the COD values of this wastewater are 10–16 g/l. It was found [93] that γ-irradiation caused decomposition of these substances. The highest efficiency of the process was observed in a combination of γ-irradiation with continuous bubbling of air followed by coagulation. At a dose of 25 kGy, the COD value decreased by approximately 85% under particular experimental conditions.

V. OTHER LIQUID WASTES

Studies on the applicability of radiation-chemical methods to the purification of transformer and hydraulic oils contaminated with toxic polychlorinated biphenyls (PCBs) receive considerable attention in a number of laboratories. The radiolytic transformations of these substances dissolved in alcohols and hydrocarbons are also under study because PCBs were extracted from oils with these solvents in order to improve the efficiency of radiation-chemical degradation. Moreover, these solvents are used for the extraction of PCBs from contaminated soil. The results obtained in these studies were published in [46, 78, 94–99a, 99b, 99c]. Early publications concerning this area can be found in [95, 98, 99b] and review [99d].

The radiolytic decomposition of PCBs was examined in the following solvents: transformer and hydraulic oils, isopropanol, *tert*-butanol, isooctane, a mixture of water and methanol, and an aqueous surfactant solution. It was found that in many of these solvents the decomposition of PCBs proceeds as a pseudo-first-order reaction (with respect to dose) with the rate constant d expressed in terms of $\mathrm{kGy^{-1}}$. This constant is the slope of the straight line that describes the natural logarithm of PCB concentration as a function of the absorbed dose. For example, the values of d for 3,3',4,4'-tetrachlorobiphenyl are equal to 0.019 and 0.021 $\mathrm{kGy^{-1}}$ in isopropanol and transformer oil, respectively [78]. In isooctane, the d constant depends on the concentration of PCBs [95].

The primary process of PCB decomposition is stepwise dechlorination as a result of reactions with solvated electrons, for example:

$$\mathrm{PCB{-}Cl}_x + \mathrm{e_s} \longrightarrow {}^{\bullet}\mathrm{PCB{-}Cl}_{x-1} + \mathrm{Cl^-}. \qquad (24)$$

The occurrence of this reaction was supported by a decrease in the efficiency of decomposition in the presence of electron scavengers (such as SF_6 or nitrobenzene) [95]. Another support is the formation of nitroxyl radicals of dechlorinated PCBs in irradiated benzene solutions containing PCBs and *N-tert*-butyl-α-phenylnitrone [100]. In isopropanol, the dechlorination was also effected by the alcohol radicals $(CH_3)_2\dot{C}OH$ [95]. In a water–methanol solution of 2,6-dichlorodiphenyl, the radiation-chemical yield of elimination of the second chlorine atom is lower than the yield of elimination of the first chlorine atom by a factor of 20 [46]. Biphenyl is the end product of the dechlorination. It exhibits extremely high radiation stability and almost does not decompose upon irradiation.

Note that the products of reductive dechlorination are much less toxic than the initial substances. High doses are required for the decomposition of PCBs in oils. Thus, the concentration of octachlorobiphenyl in transformer oil decreased from 46 to 3 mg/l at a γ-radiation dose of ~120 kGy [96]. According to Ref. [99b], the total decomposition of 2,2',6,6'-tetrachlorobiphenyl (0.27 mg/g) in transformer oil is achieved at a dose of 200 kGy. A dose of 1.1 MGy was needed to decompose Arochlor 1260 (trademark of a mixture of PCBs) in hydraulic oil from 98 to 2 mg/kg [96]. Dechlorination proceeds more effectively in alcohols and isooctane. In alkaline isopropanol, the decomposition resulted from a chain reaction [101].

VI. CONCLUSION

The general conclusions given below can be drawn from the consideration of the current status of applications of ionizing radiation to the purification of wastewater and other liquid wastes.

As in the case of natural and drinking water treatment [1], the research and development work in the radiation-chemical purification of wastewater (both municipal and industrial) is expanded and performed on a higher scientific and technical level than in the past years. First of all, computer simulation of processes that occur in the radiation-chemical decomposition of pollutants should be noted. An important special feature of the current status of the development in this area of technology is the treatment of real municipal and industrial wastewater. It should be emphasized that, at present, combined purification methods that combine electron-beam treatment with ordinary treatment (biological one, coagulation, adsorption, ozonation, etc.) are being increasingly studied.

New advances should be expected when powerful high-energy accelerators (like IMPELA or Rhodotron) will be applied to the purification of water and wastewater.

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