

Remediation of polluted waters and wastewater by radiation processing*

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Abstract. Application of radiation processing for drinking water, wastewater, and groundwater treatment is a cost effective process which may insure adequate availability of that resource worldwide. This paper summarizes the results of a Coordinated Research Project (organized by the IAEA) with participants from 10 countries with the purpose of describing the degradation mechanism of organic impurities, and establishing optimal treatment conditions. Decoloration, disinfection, microbiological and toxicological experiments are also mentioned. These experiments led to pilot plants and also to a large scale industrial realization of radiation technology.

Key words: electron beam • wastewater treatment • pesticides • dyes • degradation • radiation technology

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* This paper summarizes the achievements of an IAEA Coordinated Research Project on Remediation of Polluted Waters and Wastewater by Radiation Processing with participants of 10 countries (Austria, Brazil, Ecuador, Hungary, Jordan, Korea, Poland, Portugal, Turkey, USA, and Italy participated as an observer) intended to focus on those areas where there appeared to be highest probability for the successful application of the process.

Introduction

Potable water is the cornerstone of development and essential for sustainable growth. The first consideration for drinking water is to produce water that has been disinfected. The most common process used throughout the world in the disinfection of drinking water is chlorine. However, it is now known that the use of chlorine leads to the formation of chemicals known as disinfection by-products (DBP's). Some of the DBP's may be carcinogenic or have other toxicological effects associated with consumption. Also, there are potential pathogens being found that are not easily inactivated using chlorine. Therefore, there is a major effort in water treatment industry worldwide to find alternatives to chlorine.

In addition to disinfection, there is an increasing problem with the presence of toxic chemicals in source waters (that is, waters used as sources of drinking water). These source waters may be surface waters or ground water. Surface waters often are influenced by the discharge of treated wastewater and the biological and chemical quality compromised. Ground waters used as a source of drinking water may also be contaminated. The contamination very often originates from agriculture (pesticides), or industry. The latter discharges into the environment large amounts of chlorinated hydrocarbons used as solvents, aromatic molecules e.g. from petrochemical or coal industry, dyes from textile industry, or wide variety of other compounds coming from pharmaceutical industry. The same contaminants (with highly different level of contamination and high variety) very often can be found in the drinking water, surface waters and in the municipal and industrial wastewaters.

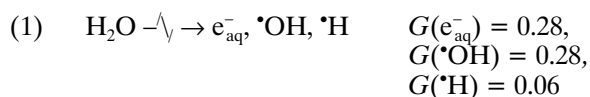
Composition of the municipal wastewater is badly defined and it is continuously changing. Industrial wastewater usually has fewer constituents. Its composition is subject to smaller changes and often contains harmful compounds of low biodegradability in high concentrations.

There is an increasing demand for reuse of municipal and industrial wastewater and of remediation of water resources contaminated by industry and agriculture. A major problem in wastewater treatment is that industrial wastewaters are usually mixed with municipal wastewaters.

Radiation chemical purification of drinking water, municipal and industrial wastewater is an emerging technology, several of the technologies are used on the pilot plant level, and there are also a few technologies established on full-scale level [22]. Radiation treatment is often combined with other techniques first of all with ozonation which greatly enhances the effectiveness of the pollutant degradation. In some experiments H_2O_2 or TiO_2 are used in combination with the irradiation treatment [21]. The present paper summarizes the newest results obtained in irradiation of aqueous solutions with different impurities.

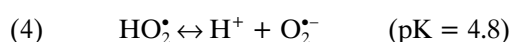
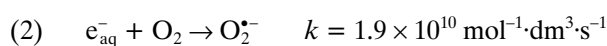
When water containing impurities in concentrations less than about $1 \text{ mol}\cdot\text{dm}^{-3}$ is irradiated it is generally accepted that the direct radiolysis of the solute is negligible and the chemical changes in the system take

place in the reaction of the reactive intermediates of water radiolysis:



G -values are yields of primary intermediates in $\mu\text{mol}\cdot\text{J}^{-1}$ units.

Since the wastewater usually contains about $10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ oxygen, e_{aq}^- and $\cdot\text{H}$ are mostly converted into peroxy radicals,



Therefore, even halogenated pollutants (which readily react with hydrated electrons) with lower concentrations have less chance to react with e_{aq}^- .

Halogenated organic compounds

As it was mentioned before, water often contains halogenated compounds (mostly halogenated hydrocarbons) but also halonitromethanes (HNMs). The latter form during disinfection of drinking water by chlorination, ozonation in the presence of nitrite ion [30]. Of the HNMs, trichloronitromethane (Cl_3CNO_2 , chloropicrin, TCNM) appears to be the most common. Many papers proved that haloalkanes can be effectively decomposed using ionizing radiation. Elegant mechanistic studies were performed using pulse radiolysis [7]. According to these investigations, the degradation mechanism is based on dehalogenation and uni- and bimolecular reaction of the peroxy radicals formed in oxygen scavenging (these reactions will be shown later on in the example of TCNM decomposition).

Many degradation efficiency studies were carried out both in laboratory experiments and under pilot plant conditions, e.g. with trihalomethanes [1, 7, 14, 30, 35]. The concentration of the impurities was followed by different analytical methods, such as gas chromatography, ion chromatography, etc. In laboratory scale experiments with a starting concentration of $100 \mu\text{g}\cdot\text{dm}^{-3}$ a dose of 1 kGy was sufficient to remove 98% of the THM [1]. Table 1 shows the results of pilot plant experiments on drinking water in a big industrial city [35]. This drinking water contains four THMs: CHCl_3 in $78.00 \mu\text{g}\cdot\text{dm}^{-3}$, CHBrCl_2 in $12.25 \mu\text{g}\cdot\text{dm}^{-3}$, and CHBr_2Cl in $168.32 \mu\text{g}\cdot\text{dm}^{-3}$ concentrations. With a flow rate of $1.3 \text{ m}^3\cdot\text{h}^{-1}$ a dose of 2 kGy was enough to remove approximately 87.4% of the chloroform, while the concentration of the other three THMs was decreased under the limit of detection. The increase of the dose until 6 kGy resulted in a near 92.5% removal efficiency for CHCl_3 . Other experiments were performed with high chloroform concentrations, varying from 145 to $780 \mu\text{g}\cdot\text{dm}^{-3}$ and the results showed reduction efficiency near to 95% at doses below 6 kGy [34].

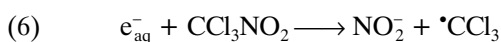
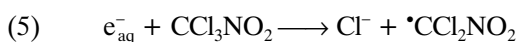
Table 1. Dose dependence of halomethane degradation [34]

Dose (kGy)	CHCl ₃ (μg·dm ⁻³)	CHBrCl ₂ (μg·dm ⁻³)	CHBr ₂ Cl (μg·dm ⁻³)	CHBr ₃ (μg·dm ⁻³)	pH
0	78.00	12.25	3.16	168.32	7.64
2	9.80	n.d.	n.d.	n.d.	5.81
3	7.11	n.d.	n.d.	n.d.	4.53
4	8.90	n.d.	n.d.	n.d.	4.20
5	6.78	n.d.	n.d.	n.d.	4.94
6	3.72	n.d.	n.d.	n.d.	4.22

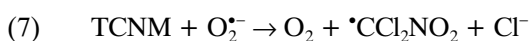
n.d. – not detected (below detection limits).

Much less results were published on the radiolytic degradation of HNMs in aqueous solution. The reaction taking place upon irradiation of dilute TCNM solution will be shown here [7, 30].

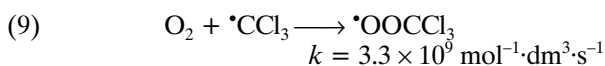
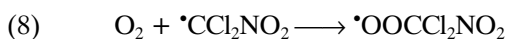
As a result of the radiolytic decomposition of TCNM, Cl⁻, NO₂⁻/NO₃⁻ final products were detected by ion chromatography. In the degradation, the hydrated electron (e_{aq}⁻) may play a decisive role, since pulse radiolysis experiments reveal a rate coefficient of $(2.13 \pm 0.03) \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ for the reactions (5) + (6), this rate coefficient is much higher than the rate coefficient of the [•]OH radical reaction with TCNM $((4.97 \pm 0.28) \times 10^7 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1})$.



Since under practical conditions oxygen is always present, reactions (5) and (6) are in competition with the e_{aq}⁻ scavenging reaction of O₂ (reaction (2)). The superoxide radical anion (O₂^{•-}) formed in the scavenging reaction is also suggested to induce reductive dehalogenation of TCNM (reaction (7)).



In aerated solutions, carbon-centered radicals react with O₂ to give peroxy radicals:

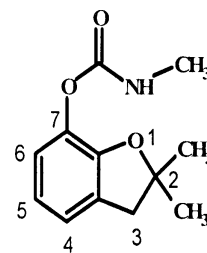


The peroxy radicals take part in complicated unimolecular and bimolecular reactions leading to the final products.

Using the rate coefficients determined and the reaction mechanism Mezyk *et al.* [30] developed a kinetic model describing the decomposition of chloropicrin and the formation of reaction by-products with high precision.

Pesticides

As a result of intensification of agriculture, surface and ground waters are more and more contaminated with

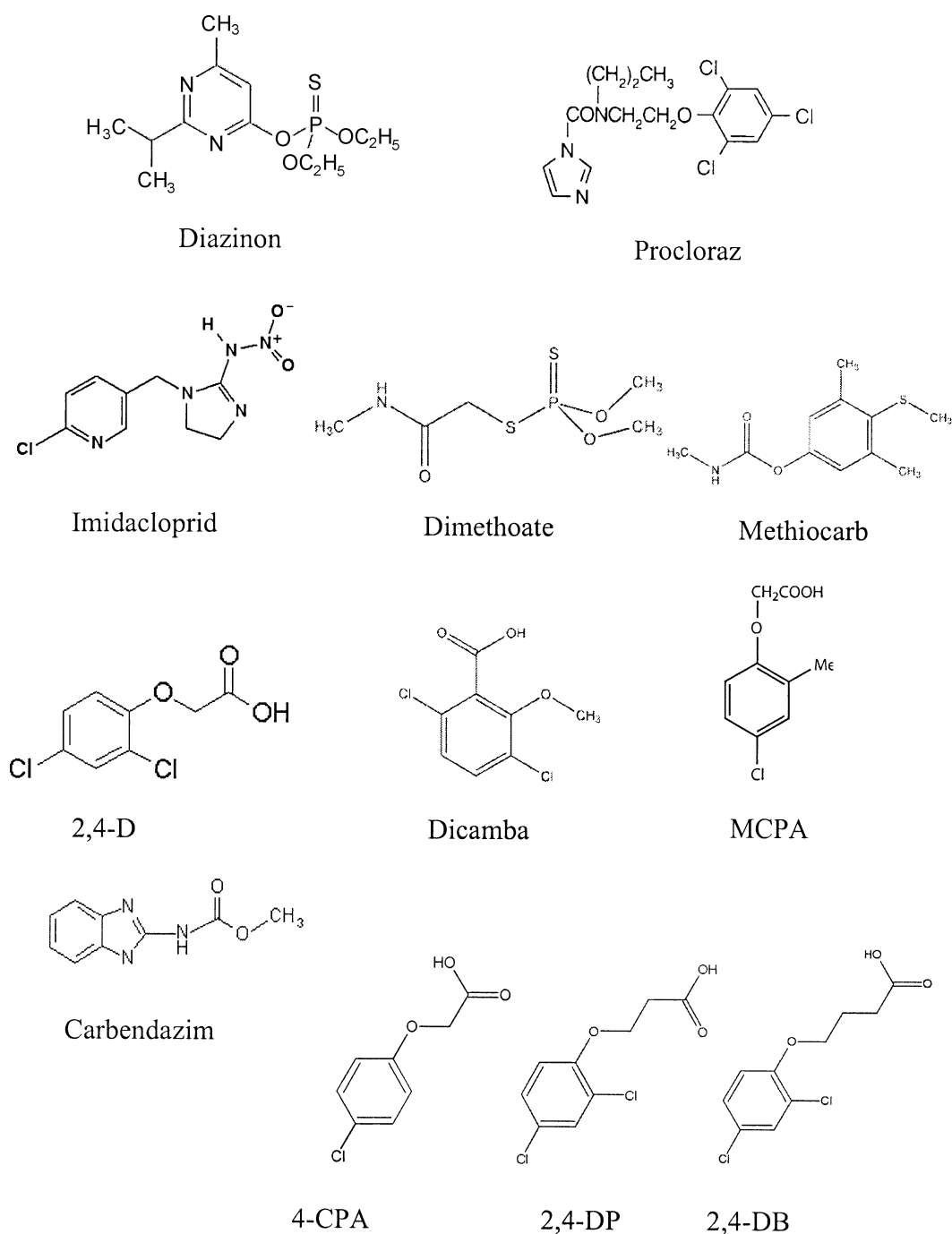
**Scheme 1.** Carbofuran.

pesticides [33]. These compounds are usually extremely stable and their degradation under natural conditions may need several years. Radiation treatment offers a good alternative to degrade pesticides and several papers were published on the degradation of these compounds. Relatively few mechanistic studies were performed; for that reason we discuss the mechanism in a bit more detailed way on the example of carbofuran (CF, its chemical structure is shown on Scheme 1). CF (a hydrogenated benzofuran ester of the carbamic acid) is used extensively as an insecticide and nematocide in North America and in some European countries, to preserve corn fields, beetroot, rice, potato, alfalfa, onion, garlic, etc. [2]. Its action directly inhibits the acetyl cholinesterase in parasite metabolism. It is toxic by contact, by ingestion and lethal at a level greater than of 5–14 mg/kg (LD₅₀, rats). CF may contaminate the ground water at areas far away from the application zone.

These types of compounds have high reactivity towards the [•]OH radicals, offering several places for the [•]OH radical attack: this attack mainly takes place on the benzene ring resulting in different cyclohexadienyl type radicals [15–17]. In the absence of oxygen these radicals recombine. Recombination is prevented when oxygen is present, as peroxy radicals are preferentially formed. It appears that O₂^{•-} takes part in the degradation process as well, by reacting with the secondary products. No reaction was seen between O₂^{•-} and CF. In both systems, without and with oxygen, the decomposition of CF was effective, as determined by the complete bleaching of the absorption spectrum of CF. The system containing oxygen required 17% of the dose needed in the N₂O saturated samples (reactive intermediate [•]OH radical), at similar concentrations. Measurements in heterogeneous phase containing 1% TiO₂ suggest that this catalyst may improve the efficiency by a further factor of 2.

There are detailed investigations on the efficiency of radiation induced removal of several pesticides shown below on Scheme 2 [3, 4, 10–13, 26, 36].

In Table 2, the results of a series of experiments are shown in which the degradability of six pesticides was compared in the pH range of 4.5–8 using doses of 2, 5 and 10 kGys. From the six compounds in the table, Prochloraz was found to be the most sensitive to irradiation, reaching a degradation percentage of 99% with a 50 ppm initial pesticide concentration and a 5 kGy dose. Methiocarb was the least sensitive pesticide with a degradation percentage of 67.7% under the same conditions. In this pH range the pH has relatively low effect on the degradability of the investigated pesticides [33].



Scheme 2. Chemical structure of different pesticides.

In another studies the radiation induced degradation of 2,4-dichlorophenoxyacetic acid (2,4-D), 3,6-dichloro-2-methoxy-benzoic acid (dicamba), 4-chloro-2-methylphenoxyacetic acid (MCPA), methyl-2-benzimidazole carbamate (carbendazim), (4-chloro phenoxyacetic acid (4-CPA), 2,4-dichloro phenoxyacetic propionic acid (2,4-DP), 2,4-dichloro phenoxyacetic butanoic acid (2,4-DB) was compared. The effect of some organic and inorganic compounds, commonly occurring in natural waters and wastewaters, together with the effect of combined treatment were investigated. Addition of ozone or hydrogen peroxide was found to improve the effectiveness of degradation of pesticides. Inorganic scavengers were found to affect the oxygen

consumption during irradiation. In the presence of nitrate and hydrogen carbonate oxygen is consumed at higher absorbed doses, than in pure solutions.

Sulfonated aromatic compounds

Due to their wide application in various chemical processes, sulfonated aromatic compounds have been produced in large quantities for a long time in many countries. Many of these compounds are poorly biodegradable. Naphthalene-1,5-disulfonate (1,5-NDSA) is the most persistent and regularly found in surface waters and bank filtrate [20, 27–29, 32]. Even

Table 2. Influence of pH and dose on pesticides degradation in aqueous solution [33]

Pesticide	Degradation (%)								
	pH 4.5			pH 5.5			pH 8		
	2 kGy	5 kGy	10 kGy	2 kGy	5 kGy	10 kGy	2 kGy	5 kGy	10 kGy
Diazinon	92.8	96.4	97.9	37.2	72.9	77.8	59.0	78.5	88.9
Prochloraz	53.9	92.1	96.5	62.8	99.6	99.8	58.3	99.2	99.7
Methiocarb	26.8	50.0	55.9	25.2	38.2	40.0	53.1	50.7	58.2
Dimethoate	75.5	87.2	98.7	42.4	82.8	86.5	84.8	92.0	98.6
Imidacloprid	52.3	94.5	99.3	39.2	78.8	95.2	83.7	94.9	99.8
Carbofuran	53.2	92.2	99.4	31.7	82.6	83.2	57.3	90.5	98.9

under the improved conditions of a membrane bio reactor 1,5-NDSA was not degraded and could not be removed from municipal wastewater.

In this study three different Advanced Oxidation Processes (ozonation at pH 7.5, electron beam irradiation and a combination of ozonation and electron beam irradiation) were applied to study decomposition of naphthalene sulfonic acids in aqueous solution with regard to mineralization and formation of biodegradable intermediates [20]. As Table 3 shows, electron beam irradiation treatment was the most efficient process for degradation of organic carbon contained in aqueous naphthalene sulfonic acid solutions. Applied to a real wastewater effluent from a mixed municipal/industrial wastewater, electron beam irradiation with a dose of 2 kGy was sufficient to reduce the concentrations of all naphthalene sulfonic acids and some of

the alkylphenol ethoxylates by about 2 orders of magnitude.

The first full scale application for the e-beam treatment of wastewater was established at the Voronezh synthetic rubber plant in the Russian Federation. The wastewater contained Nekal, a mixture of isomeric isobutyl-naphthalene sulfonates [22].

Microbiological contamination

Ionizing radiation is quite effective for inactivation of microorganisms which are always present in the treated wastewater (secondary effluents) [6]. Although there are only few studies dealing with this special subject it has been already demonstrated that both coli forms and coliphages could be effectively inactivated

Table 3. Electron beam irradiation treatment and ozonation, respectively, of an effluent from a wastewater treatment plant, for reduction of naphthalene monosulfonic acids (NSAs), disulfonic acids (NDSAs), benzothiazole sulfonic acid (BTSA) and some alkylphenol ethoxylates (APEOS) including metabolites [20]

Pollutants	Before treatment	Treatment processes		
		Electron beam irradiation		Ozonation
		2 kGy	5 kGy	22 mg O ₃ /dm ³
		Concentration (ng·dm ⁻³)		
2,6-NDSA	723	41	n.d.	317
1,5-NDSA	528	28	n.d.	256
2,7-NDSA	1743	58	n.d.	763
1,6-NDSA	3711	124	n.d.	1855
1,3-NDSA	520	7	n.d.	208
1,7-NDSA	3264	82	n.d.	1511
Σ NDSAs	10,488	340		4912
1-NSA	1620	27	2	317
2-NSA	2749	65	17	386
Σ NSAs	4369	92	19	703
BTSA	358	58	20	189
Σ (APEOs + metabolites)	273,630	13,693	2410	6102

n.d. – not detected (below detection limits).

in secondary effluents by means of ionizing radiation [5, 9, 19].

Inactivation of bacteria and bacterial spores by electron beam irradiation was found to be practically unaffected by the water matrix and suspended solids. These findings are also relevant to viruses of concern in water hygiene like e.g. poliovirus. The dependence of inactivation on dose usually follows the logarithmic rule: the logarithm of number of microorganisms in unit volume is linearly decreasing with the dose. In case of *E. coli*, 1 kGy dose is needed to bring about three orders of magnitude decrease in the number of microorganisms. Parallel with the microorganisms contamination the estrogens activity of the municipal wastewater, which is of major concern nowadays, is also reduced during irradiation treatment.

Han *et al.* [23] made laboratory experiments with effluent from a municipal wastewater treatment plant in a continuous flow irradiation system. Unchlorinated secondary effluent was irradiated at different doses between 0.2–1.0 kGy with a 1 MeV, 40 kW electron accelerator. Nearly 100% reduction in *E. coli* and total coliform bacteria was achieved with a dose of 0.8 kGy. Even with the dose of 0.2 kGy, the *E. coli* and total coliform bacteria were inactivated in sufficient degree. Based on the data obtained in the experiments, an industrial scale plant with 0.2 kGy dose irradiation with a flow rate of 100,000 m³ effluent per day was designed. The overall cost for plant construction is approximately 4.0 million US\$, and operational costs are estimated to be 1 million US\$ per year. This appears competitive when compared to other Advanced Oxidation Processes such as applying ozone alone, UV techniques etc.

Azo dyes

Azo dyes are produced in very large quantities and are used as reactive dyes by the cotton and paper industry. They are very stable and resistant to chemical and biochemical processes. Therefore, their removal from industrial effluents by conventional methods (mechanical screening, sedimentation, biological treatment, biofilters) alone is usually not very effective. This problem can be solved by combining the conventional techniques with high-energy irradiation. Detailed investigations were carried out on the radiation degradation of textile dyes in laboratory scale and on pilot plant and industrial scale [8, 18, 24, 25, 31, 37–42].

The kinetics and mechanism of dye destruction was studied on some azo dyes in dilute aqueous solution by pulse radiolysis with kinetic spectroscopic detection and also by gamma radiolysis. In the latter case UV-VIS spectroscopy was used to follow the dye decoloration. The dye degradation and the products formed were followed by HPLC with diode array detection. The dose dependence of color disappearance was found to be linear, when the reactive intermediates react with the color bearing part of the molecule. This causes destruction of the conjugation with nearly 100% efficiency. Such a linear dependence was observed when hydrated electrons or hydrogen atoms reacted with the dyes. However, in the case of hydroxyl radical reactions, some

Table 4. Gamma radiolysis of Apolofix Red dye [39]

	•OH		e _{aq} ⁻		•H	•O ₂ ⁻
pH	5.4	10.3	8.05	10.47	1.20	6.93
<i>G_d</i>	~2.5	2.2	2.6	2.3	2.2	~0.7
<i>f_i</i>	~0.3	0.25	0.89	0.75	0.67	~0.0

f_i – value calculated for the intermediate shown in the first line, these are the ratios of the number of dye molecules decomposed to the number of reacting species.

colored products form with absorption spectra very similar to those of the starting dye molecules. In this case there is a decline from the linearity on the decoloration-dose curves. The *G* values and efficiency factors of destructions of Apolofix Red induced by water radiolysis intermediates are collected in Table 4. An increase in the efficiency of decoloration was found by addition of hydrogen peroxide (1.2 mmol·dm⁻³).

As it is obvious from the previous paragraph by radiation treatment of dye stuff pollutants, the change of the color of bleaching, registered by absorption spectrometry, cannot be considered as an efficient degradation, because in such case the chromophore group of the dye is decomposed. The measured absorption spectra are superimposed: consisting of the degradation products and remainder of the original dye molecule.

A pilot plant for treating 1000 m³ of textile dying wastewater per day with electron beam irradiation was constructed and operated continuously in Daegu, Korea since October 1998 [25]. This plant was combined with biological treatment and has shown a high reduction of chemical additive consumption, and also a reduction in retention time, with an increase in removal efficiencies as detected by COD_{Cr} and BOD₅.

On the basis of data obtained from pilot plant operation, construction of an industrial scale plant was started in 2004, and finished December 2005 [24]. This plant is located on the area of existing wastewater treatment facility (Fig. 1) and its capacity is 10,000 m³ of wastewater per day using one 1 MeV, 400 kW accelerator combined with the existing bio-treatment facility. The continuous operation of this facility will provide additional data on reliability and for a detailed economic evaluation.

Conclusions

The results of these investigations can be summarized as follows:

- Large number of studies conducted has shown that the destruction of selected organic molecules, such as halogenated compounds, dyes and pesticides are efficiently solved by using irradiation techniques. Combination of ionizing radiation with oxidants, such as ozone or hydrogen peroxide, further improved the removal efficiency. It has also been shown that the addition of TiO₂ prior to irradiation, improved the destruction efficiency.
- Kinetic models describing the removal of organic compounds (with rate constants determined mostly

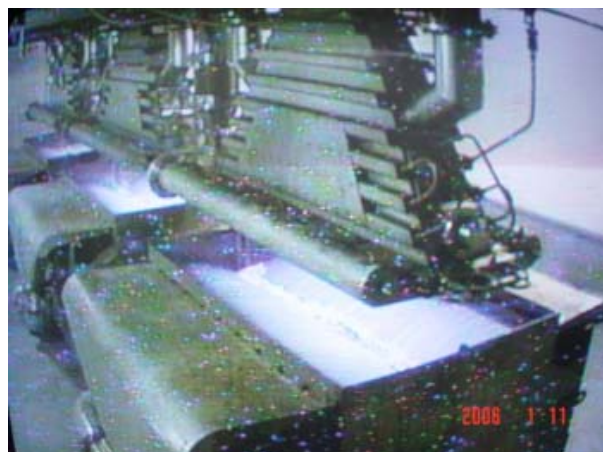


Fig. 1. Industrial e-beam plant for textile dying wastewater in Daegu, Korea.

- by pulse radiolysis techniques) including the formation and destruction of reaction by-products, have been formulated. These models appear to predict the formation of reaction by-products and could be used to guide analytical methodology and economic evaluation of the radiation processing.
- Radiation processing of secondary and tertiary effluents from municipal wastewater treatment plants has shown that destruction of organic compounds, elimination of estrogenic activity and efficient reduction in the number of microorganisms occurs simultaneously.
- The installation of the first full scale electron beam plant in Daegu, Korea, to treat $10,000 \text{ m}^3 \cdot \text{day}^{-1}$ textile wastewater has demonstrated the industrial applicability of the technique. The continuous operation of this facility will provide operational data on reliability and additional data for a detailed economic evaluation.

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