IAEA-TECDOC-1407

Status of industrial scale radiation treatment of wastewater and its future

Proceedings of a consultants meeting held in Daejon, 13–16 October 2003

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International Atomic Energy Agency

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STATUS OF INDUSTRIAL SCALE RADIATION TREATMENT OF WASTEWATER AND ITS FUTURE

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FOREWORD

Providing access to clean water resources is one of the most important objectives of the UN's Millennium Project. Contamination of surface water is a big problem for many, mostly developing countries. The main sources of liquid polluted effluents are municipalities and industry. Effective, mostly biological wastewater technologies for wastewater purification are available nowadays. However, they cannot be applied to solve all existing problems. Destruction of non-biodegradable organic compounds is one problem and biological contamination (caused by viruses, bacteria, parasites, etc.) of sludge is another. Methods of their purification are sought. Ionizing radiation (gamma or X rays, electron beams) is a very effective form of energy, which can destroy organic or biological contaminants.

The IAEA promotes and supports research on radiation treatment of liquid effluents. The Co-ordinated Research Project (CRP) on Remediation of Polluted Waters and Wastewater by Radiation Processing aims to establish optimal treatment methodologies to disinfect and decontaminate actual samples of drinking water and wastewater by using ionizing radiation. Quite a few technical co-operation (TC) projects concerning radiation treatment of wastewater and sludge are under development. In the frame of one of such TC projects pilot plant for electron beam treatment of textile dyeing complex wastewater was constructed in the Republic of Korea.

To discuss developments achieved under these projects and results of the pilot plant operation, the IAEA organized a consultants meeting in Daejon, Republic of Korea, 13–16 October 2003.

These proceedings will be of value to research groups working in the field of radiation technology development. Developing Member States with radiation technology programmes will benefit from research in this area.

The IAEA wishes to thank all the participants in the consultants meeting for their valuable contributions. The IAEA officer responsible for this publication was A.G. Chmielewski of the Division of Physical and Chemical Sciences.

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SUMMARY

1. BACKGROUND

Contamination of surface water and groundwater from industrial waste and anthropogenic activities is a serious problem in many countries. With population growths and declining fresh water supplies the need for clean water is one of the critical challenges for the 21st century. Because of the increasing levels and complexity of polluted effluents from municipalities and industry, current wastewater treatment technologies are often not successful for the remediation of polluted waters and disinfection. The development and implementation of alternative technologies for the clean up of industrial wastewater, municipal water, groundwater and drinking water is critical to the sustainability of many countries. Among the possible water treatment alternatives radiation processing, a very effective form of energy use, can degrade toxic organic compounds and biological contaminants.

Radiation processing is currently used in a number of industrial processes including use for sterilization, cross linking of polymers, food irradiation, rubber vulcanization in the manufacturing of tires, contaminated medical waste, etc. These are examples of well-established economical applications of radiation processes employing gamma and electron beam sources.

One of the key missions of the International Atomic Energy Agency (IAEA) is to promote the peaceful use of nuclear and radiation technologies through technical co-operation programmes, co-ordinated research projects, consultants and technical meetings, conferences, etc. These programmes and collaborations have lead to the development and transfer of important new technologies to member states during the past ten years. As examples, IAEA activities have lead to applications of radiation technologies for flue gas and sludge treatment. The installation and operation of electron accelerators exceeding a power of 1 MW at an industrial plant for the treatment of SOX and NOX represent a further break through in EB technological applications. A pilot plant using electron beam at a relatively low dose in combination with biological treatment for wastewater has been successfully demonstrated in the Republic of Korea.

At the beginning of the 21st century, new science and technology development programmes are being elaborated and implemented including UN resolutions concerning sustainable development, the Johannesburg protocol, 6th EU Thematic Framework and others. All of which are addressing issues concerning water and air pollution and have been incorporated in the resolution adopted by the recent General Conference of the IAEA. Therefore, the IAEA organized a consultants meeting in Daejon, Republic of Korea, 13–16 October 2003, to review the present situation and possible developments of radiation wastewater and sludge treatment. The advantages over conventional technologies and constraints from point of view of industrial scale implementation were discussed.

2. TRENDS IN RESEARCH AND DEVELOPMENT

The IAEA has organized numerous meetings and co-ordinated research projects in which trends and new developments concerning environmental applications of radiation processing were discussed. Representatives of industry, universities and research institutes discussed recent developments in this field during the International Meeting on Radiation Processing (IMRP), held in Chicago, USA in September 2003. A variety of aspects of the process were reported during the symposium on radiation technologies in emerging industrial applications organized by the IAEA in Beijing, China in 2000, following a major symposium on radiation technology for conservation of the environment in Zakopane, Poland in 1997.

The main research and implementation developments concentrated on three areas: electron beam flue gas treatment, wastewater purification and sludge hygenization. Since separation and enrichment technologies play an important role in the products recovery and pollution control, the possibility of radiation synthesis of stimuli-responsive membranes, hydrogels and adsorbents is being

investigated as well. Finally, applied technologies for flue gas treatment and further research efforts are underway for the treatment of organic contaminants in the gaseous and condensed phases.

The development of radiation sources to be applied in environmental radiation technologies is focused on high power beam machines because of their higher effectiveness and more economical operation compared to lower powered electron beam machines.

3. PURPOSE AND DISCUSSION TOPICS

The fundamental studies of the radiation process for wastewater treatment, its analogues and differences to other AOPs, combined processes were discussed during the meeting. Possible fields of application, technical solutions and economical factors concerning engineering and other applications were addressed as presented below. Developments concerning accelerator design engineering, and construction as well as other features of radiation sources were also discussed. Further discussion included design of under-beam systems. Such progress and developments are critical for further applications. A reduction in cost and improvement of technical reliability are expected, especially high power is needed for environmental applications. Such applications should be carefully revised in accordance to the existing regulations and state of the art knowledge. The results of these discussions as presented below will serve as basis for the preparation of guidelines and feasibility studies for full-scale process implementation. Public awareness and technology acceptance are additional factors to be considered for further dissemination.

The programme included technical tours and visits to bench-scale gamma wastewater treatment system in KAERI, E-Beam wastewater treatment system in EB-Tech, wastewater and sludge analytical laboratories at Chungnam National University in Daejon, E-beam pilot plant for textile dyeing wastewater treatment in Daegu. The pilot plant in operation since 1998 equipped with 1.0 MeV 40 kW, ELV type electron accelerator, has the capacity of treating 1,000 m^3/day in combination with a biological system with good removal efficiencies.

4. CONCLUSIONS AND RECOMMENDATIONS

Industrial developments: Radiation processing for wastewater treatment will become a reality very soon. The first full-scale plant for treating 10,000 m^3/day of wastewater from textile industries will be constructed in textile dyeing industrial complex in Daegu, Republic of Korea. It will employ a 1 MeV 400kW electron accelerator which is available in the market.

In competition with existing technologies, radiation treatment of textile dye wastewater was more economical by improving the efficiency of the removal process. In this application the radiation treatment reduced the cost of chemicals and the amount of sludge compared to the conventional process.

General assessment for industrial wastewater: Due to the tremendous variety of wastewaters generated by different industries, universal treatment protocol is not currently possible. The main focus of radiation processing should be towards the treatment of non-biodegradable contaminants. The goal is to convert recalcitrant pollutants into biodegradable substances. Removal of biodegradable substrates present in the original wastewater may be considered prior to radiation treatment. Significance on the quantities of wastewater and the use of high power electron accelerators are usually required to make radiation treatment for industrial wastewaters cost effective.

General assessment for municipal wastewater: At present there is no full-scale radiation treatment plant in operation. Research activities in different countries have demonstrated that

inactivation of fecal coli-forms in secondary effluents from municipal sewage plant can be obtained with doses less than 1 kGy. While conventional disinfectants are adversely affected by the water matrix, radiation processing for bacteria inactivation is generally unaffected by the matrix. Therefore radiation processing has a clear advantage over the existing methods for municipal wastewater disinfection. Application of such low doses also leads to the degradation of synthetic and natural estrogens usually present in trace amounts in municipal wastewaters. Regulations currently exist for E-coli concentrations in secondary effluents in some countries. It is likely that such regulations will be adopted by a significant number of countries in the near future and hence radiation processing is a highly attractive technology for meeting such standard regulation, especially given the advantages compared to conventional technologies.

General assessment for municipal sludge: Radiation disinfection of sludge has been successfully demonstrated in a number of countries. For future application both gamma and electron accelerator may be employed. Experiments have demonstrated electron accelerators can be used to improve the dewatering of sludge.

Requirements for electron accelerators for wastewater treatment: It is imperative the electron accelerator is reliable under continuous operation and computer controlled. The cost of the accelerator must be on a level which allows competitive treatment relative to other processes. Mobile systems may be used for small wastewater streams and specific treatment objectives.

Public awareness: There remains a critical need for greater public awareness of the environmental and societal benefits of radiation processing. Successful projects involving the use of radiation processing have been demonstrated for the clean up of flue gases by removing undesirable emissions, to enhance the safety of the food supply and now for the detoxification of wastewater. The resources of the IAEA should be used to make the public at large more aware of these commercial successes. In addition the use of radiation processing for water and wastewater treatment warrants greater public support.

REPORTS OF THE PARTICIPANTS

ADVANCES IN RADIATION PROCESSING OF WASTEWATER — BASICS OF THE PROCESS

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Abstract

High energy electrons effectively inactivate indicator bacteria in effluents from municipal wastewater treatment plants and eliminate simultaneously any estrogenic activity originating from natural and synthetic hormones also contained in the wastewater effluents. Inactivation of bacteria and bacterial spores by electron beam irradiation was found to be practically unaffected by the water matrix and suspended solids. There is a strong indication from literature data that these findings are also relevant to viruses of concern in water hygiene like e.g. poliovirus. Consequently electron beam irradiation for effluent reclamation represents a true alternative to chemical and UV treatment. As compared to chemical disinfection it proved to be a clean technology without formation of hazardous by-products; as compared to UV irradiation electron beam irradiation is technically much more simple, almost insensitive to color, suspended solids or gas bubbles in the effluent stream, and, moreover, to effluent composition and fouling characteristics, respectively.

1. INTRODUCTION

Although wastewater is usually characterized by rather high solute concentrations as compared to ground or drinking water with regard to the effect of ionizing radiation wastewater has also to be classified as dilute aqueous solution. When dilute aqueous solutions are irradiated practically all the energy absorbed is deposited in water molecules and the observed chemical changes are brought about *indirectly* via the free radical species formed in water by so-called water radiolysis (Figure 1). *Direct* action due to energy deposited directly in the solute is generally unimportant in dilute solutions.

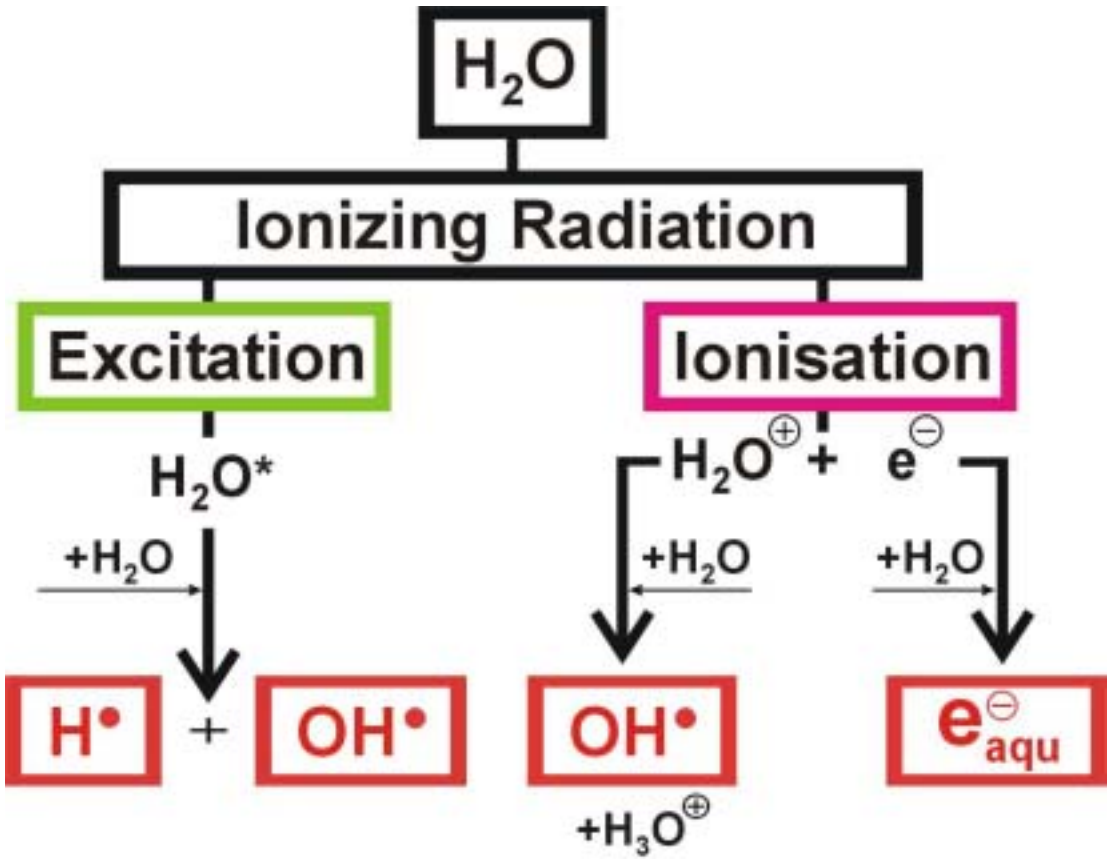


FIG. 1. Water Radiolysis: Formation of free radical species in water by means of ionizing radiation.

Figure 1 illustrates the effect of ionizing radiation on water, which is known to result in the formation of molecular species (not shown) and free radicals, as well as some ions. For pollutant decomposition and microorganism inactivation, respectively just the free radical species are of interest. Pollutants and microorganisms are quite different targets for the attack of the free radical species. In spite of some similarities the differences between them are more dominating, a discussion concerning the effect of free radicals must be performed separately. In the following just pollutant decomposition will be discussed. Inactivation of microorganisms will be addressed later.

The free radicals formed during water radiolysis are highly reactive, the OH radicals are the most powerful oxidant known to occur in water, the same is valid for the hydrated electron e_{aq}^- as reductant. In consequence these radicals do not only react with target pollutant(s) but also with many other solutes contained in the water, even with some inorganic ions like e.g. bicarbonate and nitrate, respectively. In consequence a competition for the free radical species between the target pollutants and other solutes in the aqueous system occurs which determine the efficiency of the radiation process for pollutant decomposition. However, a discussion of this basic issue is possible just in a well-defined system, i.e. in a well-known water matrix. This is not the case with wastewater, but with ground or drinking water. Wastewater is too complex and therefore not apt for such considerations although the basic situation is the same.

2. COMPETITION KINETICS

Figure 2 shows the decomposition rate of two solutes A and B when reacting with OH free radicals. In the present case which is quite common with radiation processing the reaction rate depends on three factors: (1) a constant k which is specific for the respective substance for reaction with OH radicals, (2) the concentration of the substance reacting with the OH free radicals and (3) the concentration of the OH free radical concentration itself. The product of these three factors determines the position of the respective substance in the competition with another or with others and makes it possible to calculate the amount of a specific radicals available scavenged by the respective substance. See the calculation of the probabilities P_{A+OH} and P_{B+OH} in Figure 2.

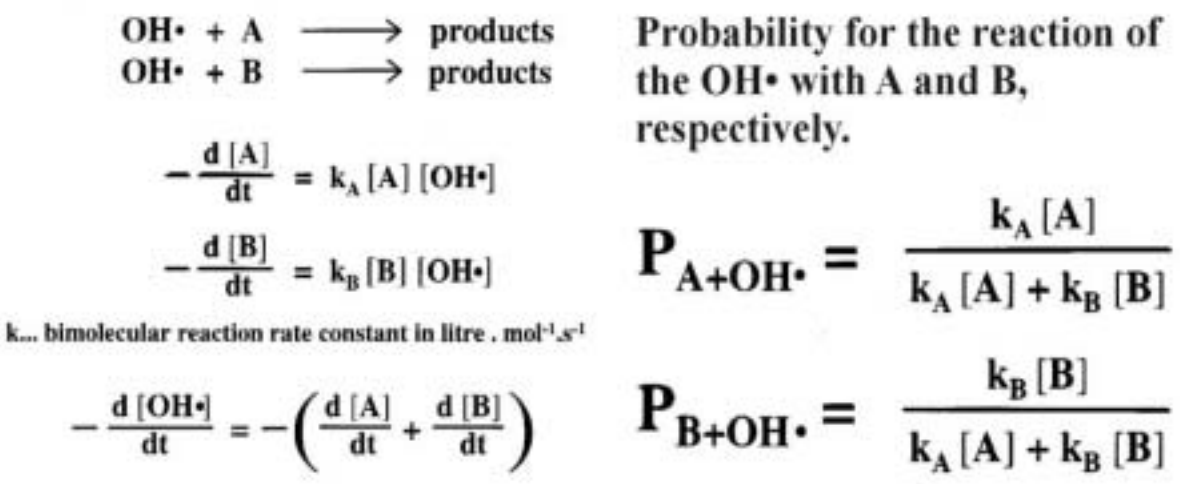


FIG. 2. Fundamentals of Competition Kinetics

For the most frequently occurring pollutants in ground and drinking water the constant k, called bimolecular reaction rate constant, is known and can be found in the literature. Table 1 gives the rate constants for some chlorinated substances well known from groundwater contamination. Moreover, the k-values for some of the inorganic solutes usually contained in ground and drinking water are also given.

TABLE I. BIMOLECULAR REACTION RATE CONSTANTS OF LOW-MOLECULAR CHLORINATED COMPOUNDS AND OF SOME INORGANIC SOLUTES USUALLY CONTAINED IN GROUNDWATER.

Compound	Rate constant for $OH^{\bullet}$ $dm^3 . mol^{-1} . s^{-1}$	Rate constant for e^-_{aqu} $dm^3 . mol^{-1} . s^{-1}$
Perchloroethylene	1.7×10^9	1.3×10^{10}
Trichloroethylene	2.6×10^9	1.9×10^{10}
Dichloroethylenes	$\sim 7 \times 10^9$	$\sim 7.5 \times 10^9$
Vinylchloride	1.2×10^{10}	2.5×10^8
1,1,1-Trichloroethane	$\sim 4 \times 10^7$	not known
Chloroform	$\sim 5 \times 10^6$	3×10^{10}
Bikarbonate	8.5×10^6	-
Nitrate	-	9.7×10^9
Oxygen	-	1.9×10^{10}

Perchloroethylene (PCE) and Trichloroethylene (TCE) are most prominent groundwater contaminants. The reaction of PCE and TCE with both OH radical and hydrated electrons have very low activation energies so that most, if not all, of the collisions between the reactants lead to reaction, and the rate of reaction is governed by the rate at which the reactants diffuse together. Such "diffusion controlled" reactions have rate constants of the order of 10^{10} $dm^3 . mol^{-1} . s^{-1}$ and represent the fastest possible reactions.

PCE and TCE contamination of groundwater is usually just on a ppb-level. From natural solutes only bicarbonate has to be considered as competitor when OH radical reaction are discussed. The reaction rate constant of bicarbonate ions with OH radicals is about two orders of magnitude lower as compared to PCE and TCE but the bicarbonate concentration is usually two orders of magnitude higher as the PCE and TCE concentrations. Consequently the competition for the OH radicals is rather balanced. The reaction rate constants of PCE and TCE with hydrated electrons are one order of magnitude higher as compared to the reaction with OH radicals. The analogous reaction rate constants of the both competitors nitrate ions and oxygen are of same order of magnitude, their concentrations, however, usually at least one order of magnitude higher. Under such circumstances hydrated electrons would not contribute to PCE or TCE decomposition. The situation is even more complicated what is shown in Figure 3.

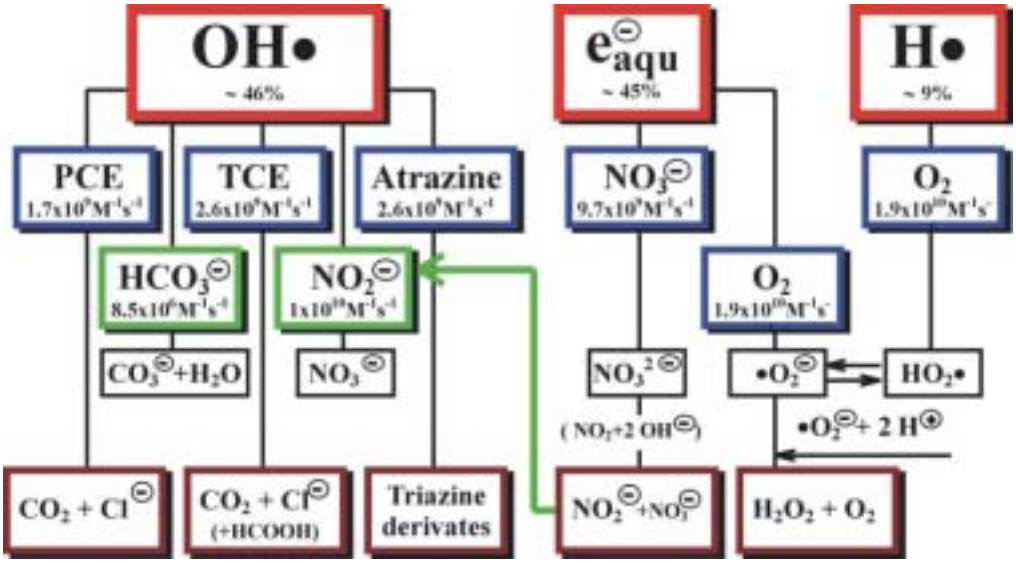


FIG. 3. A simplified model of the competition for the free radical species in a natural groundwater. Numerical data given with some components are the bimolecular rate constants with the corresponding free radical species. Natural organic matter is not considered here.

Among the organic pollutants known to occur frequently in groundwater PCE, TCE and atrazine are the most common. Since these contaminants are usually contained in groundwater in trace amounts only (< 1mg/L) the simplified model shown in Figure 3 can be used to describe the competition of the pollutants and the natural solutes for the free radical species formed during water radiolysis. Low level contamination means that the reductive detoxification becomes insignificant although the reaction rate constants for the reaction of TCE and PCE with hydrated electrons are higher as compared to the reaction with OH radicals (see Table 1). The reasons have been already discussed just before.

The higher oxygen concentration together with the high reaction rate constant for oxygen causes that most of the hydrated electrons are scavenged by oxygen forming superoxide radical anion O_2^-. Moreover, oxygen also scavenges almost all H atoms. The resulting hydroperoxylradical HO_2 is in an acid-base equilibrium with O_2^- (pK = 4.7). At the usual pH-values of groundwater the equilibrium is shifted toward O_2^-, i.e. most of the reducing species is converted into O_2^-, which is a rather inert radical. It certainly does not react with PCE and TCE and not with atrazine either. Its probable fate is disproportionate into H_2O_2 and O_2. Roughly speaking only OH radicals remain as active species for pollutant decomposition under the conditions given. In other words: more than 50% of the radiation energy is lost for pollutant decomposition.

Under the conditions given and as long as nitrate concentration is low only bicarbonate ions are serious competitors for OH according to their usually high concentration in groundwater. However, for usual nitrate concentrations in groundwater (> 5 mg/L) scavenging of solvated of hydrated electrons and subsequent formation of nitrite ions cannot be longer ignored. Nitrite ions scavenge OH radicals very effectively and, therefore, considerably worsen the conditions for pollutant decomposition. Since nitrite itself belongs to toxic substances and its concentration in drinking water is limited to < 100 ppb by regulation radiation processing for groundwater remediation cannot be applied to produce drinking water when nitrate concentration is above about 5 mg/L.

This situation may be overcome by addition of ozone before or during irradiation. On the one hand, ozone is known to oxidize nitrite to nitrate very fast; on the other hand, ozone reacts with

hydrogen peroxide. Therefore, a residual ozone concentration present after the irradiation process eliminates residual hydrogen peroxide to a large extent and nitrite as well. Moreover, most importantly ozone acts as an additional OH radical source.

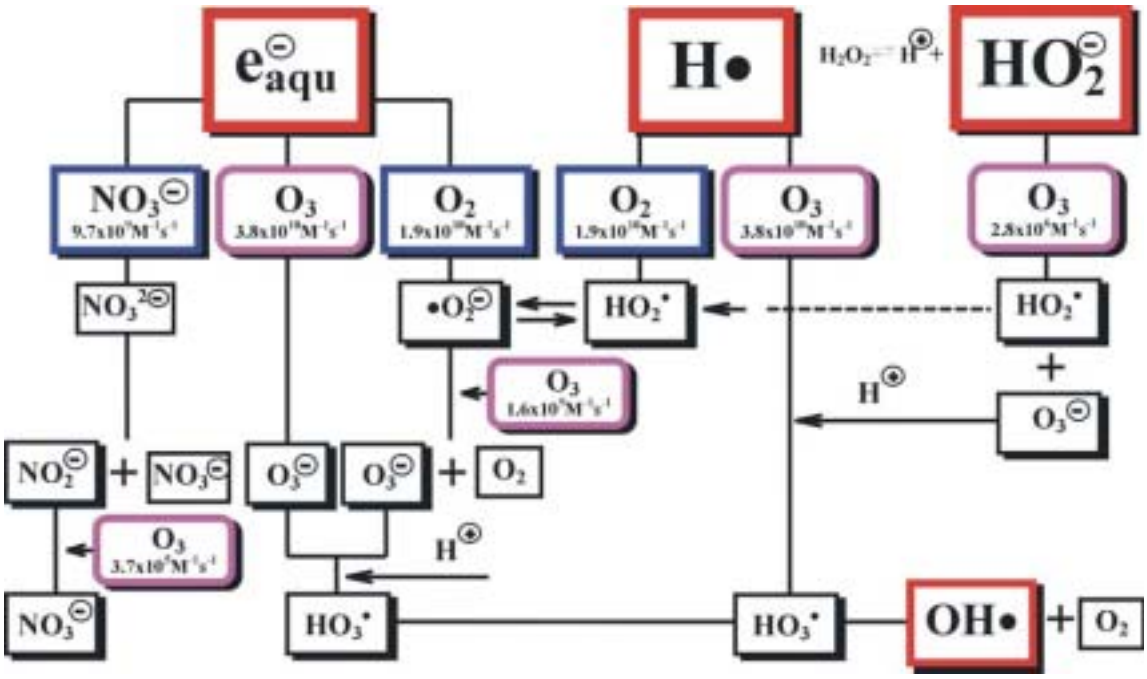


FIG. 4. Main reaction pathways of the hydrated electrons e^-_{aqu} the H atom and hydrogen peroxide in ozone containing groundwater. Natural organic matter not considered.

Figure 4 illustrates how the ozone converts both the reducing species and the hydrogen peroxide into OH radicals. This is due to the very fast reaction of ozone with the reducing species but is mainly attributed to the fast reaction of the O2- with ozone (see the reaction rate constants given in Figure 4). Moreover, under the conditions given O2- formation is considerably enhanced because the ozone transfer into the water simultaneously increases the oxygen concentration in the water. The enhanced oxygen concentration does also influence the competition between oxygen and nitrate for the hydrated electrons which results in less nitrite formation. Moreover, hydrogen peroxide formation is also abated since the O2- now reacts preferably with ozone.

In consequence water radiolysis which originally is a „hybrid“ process due to formation of equal amounts of oxidizing and reducing species is converted into a pure Advanced Oxidation Process (AOP) what has two important aspects:

- almost the whole radiation energy is used now for OH radical generation
- the combination ozone /electron beam irradiation represents an unique AOP because there are two OH radical generation processes involved at the same time.

In consequence higher OH radical concentration results as compared to other AOPs because all others with a potential for technical application have just one source for OH radical production. This is demonstrated in Figure 5 in which the main features of the technically most interesting AOPs are compared. This figure illustrates, moreover, that the both AOPs ozone/UV irradiation and ozone/hydrogen peroxide are one and the same with respect to OH radical generation: in the former, one is merely forming hydrogen peroxide in situ, rather than adding it from external source.

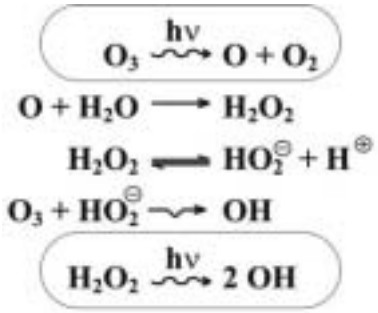
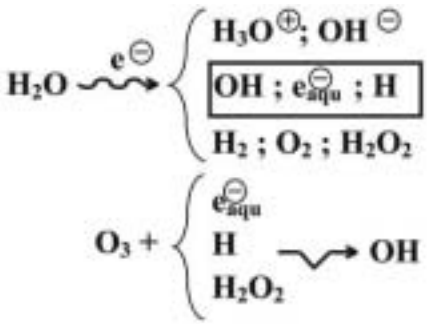
UV-irradiation	Electron beam irradiation
of aqueous solutions	
	
Radiation is absorbed by solutes not by water ! Always just **one** source for OH (O_3 and H_2O_2, resp.)	Radiation is absorbed by the water not by solutes ! Two sources for OH (water radiolysis and O3 decomposition)

FIG. 5. The fundamental reactions for OH radical generation in different Advanced Oxidation Processes.

According to the equation given for pollutant decomposition rate in Figure 2 higher OH radical concentration accelerates decomposition rate what is equivalent to a more effective pollutant decomposition. This is demonstrated by the results given in Figure 6 for two aromatics.

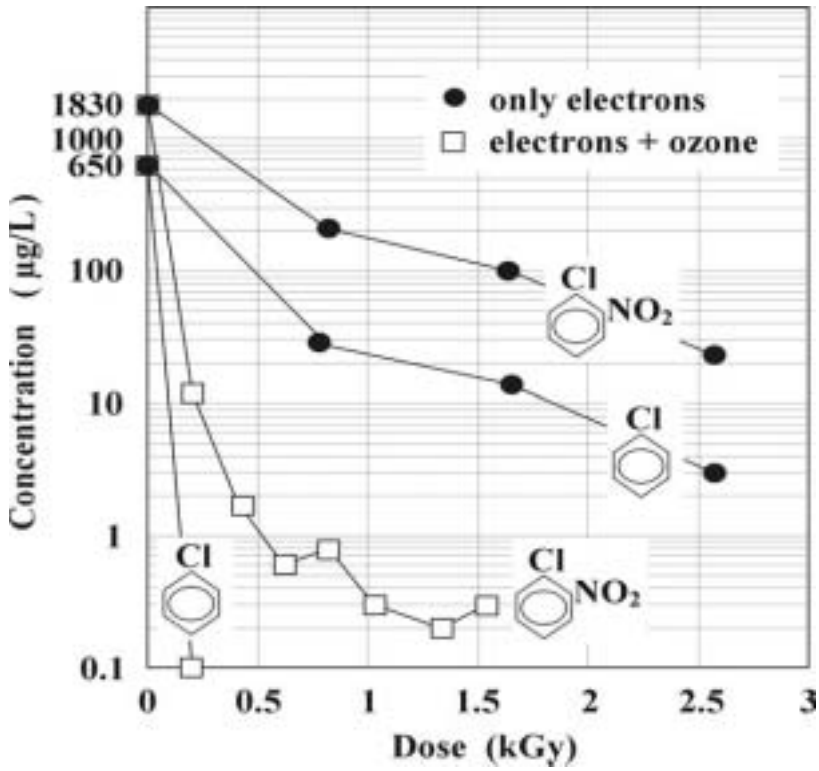


FIG. 6. Decomposition of o-chloronitrobenzene and chlorobenzene,respectively in groundwater by electron beam irradiation with and without addition of ozone.

It is evident that decomposition of both aromatic pollutants proceeds much more effective by addition of ozone as compared to electron beam irradiation alone what can be seen by the considerable reduction of the dose requirement for a certain residual pollutant concentration. With regard to economy this reduction in radiation dose for a certain pollutant decomposition by addition of ozone may sometimes overcompensate the cost for the ozone needed.

However, due to the equation also given in Figure 2 for the probability a given substance will react with OH radicals in competition with another (or others) it is obvious that OH radical concentration does not affect at all the competition situation. Competition is just determined by the product of the reaction rate constant and the concentration of the respective substance.

Figure 7 shows the decomposition of three different chlorinated compounds with different reaction rate constants (see Table 1) in groundwater by electron beam irradiation. Since analogous initial concentrations have been used with all three compounds the effect of the difference in the reaction rate constants becomes clearly visible.

Figure 8 shows the effect of pollutant concentration with regard to scavenging of the free radical species formed during water radiolysis. PCE has to compete with bicarbonate ions for the OH radicals, and with nitrate ions and oxygen for the hydrated electrons. It is obvious that with increasing PCE concentration the amount of radicals scavenged by PCE increases for both species. In the competition with bicarbonate ions PCE clearly dominates at higher PCE concentrations due to the much higher reaction rate constant. However, in the competition for the hydrated electrons PCE could even at the highest concentration (PCE saturated solution) just scavenge about 44% of the hydrated electrons. The reason is obvious: the three competitors PCE, nitrate ions and oxygen are all present in mg/L concentrations, their reaction rate constants for the reaction with hydrated electrons are quite similar (see Table 1). Therefore, none of them could really dominate this competition.

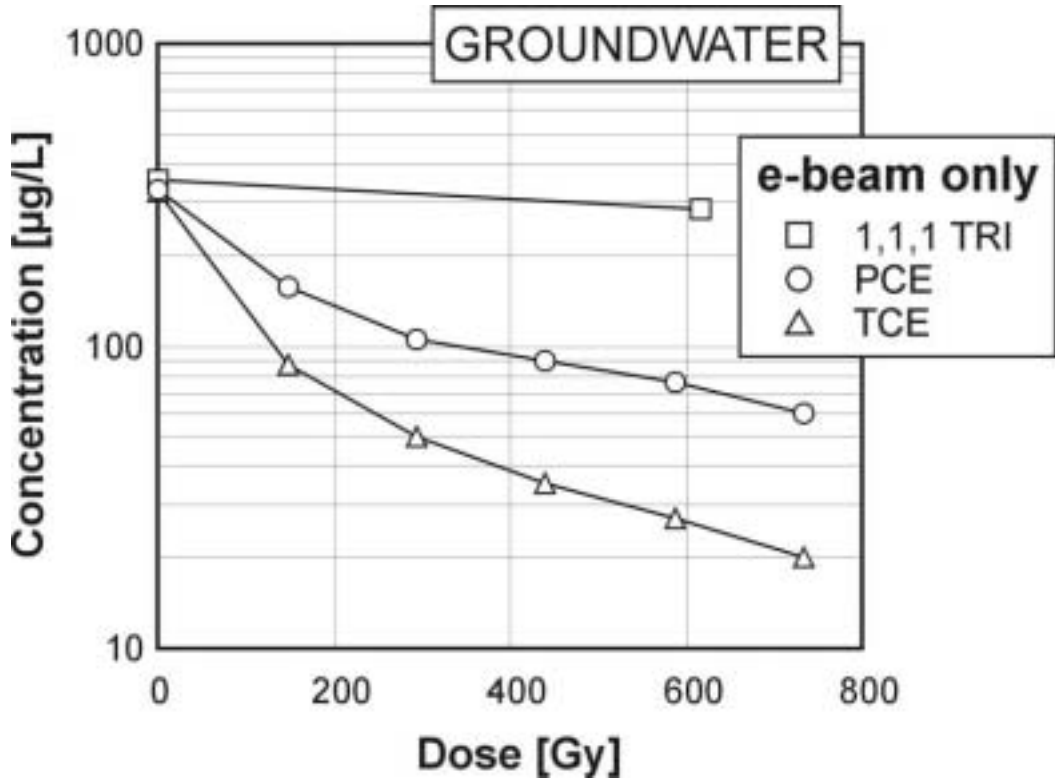


FIG. 7. Radiation induced decomposition of 1,1,1-trichloroethane, TCE and PCE in groundwater by means of electron beam irradiation.

In groundwater competition of the different components present could be at least roughly assessed, in wastewater such an assessment is totally impossible. Wastewater can be characterized just by sum parameters which say nothing about the individual substances involved and, of course, nothing about their reaction rate constants. Consequently no general kinetic law can be given for wastewater.

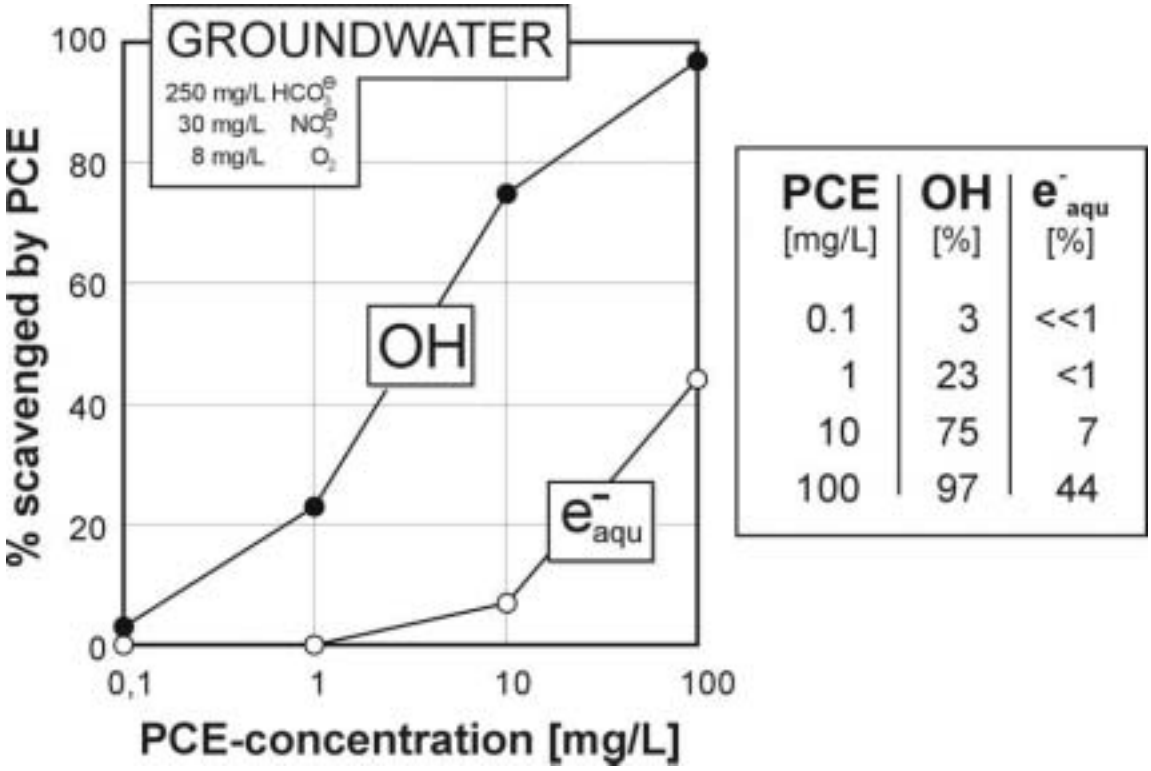


FIG. 8. The influence of pollutant concentration to the scavenging of free radical species generated in groundwater by irradiation

Discussion of basic mechanisms related to radiation processing of aqueous systems can never be performed with wastewater but only with water representing a well-defined water matrix like e.g. groundwater or tap water. Generally speaking, groundwater contamination is usually related to low pollutant concentrations while wastewater usually may be attributed with high pollutant concentrations. Ozone addition may be applied for both cases. However, with wastewater the effect of both irradiation and ozone addition can never be assessed without performing experiments.

3. ADVANCES IN RADIATION PROCESSING OF WASTEWATER

The biggest advance in radiation processing of wastewater certainly is the construction of the first wastewater treatment plant for a capacity of 10 000 m^3/day which is close at hand in Korea. With such a demonstration plant it might be expected that further implementation of radiation processing of wastewater will be strongly accelerated. For more details of this plant see J.-S. Choi „Electron Beam Treatment of Textile Dying Wastewater“ contained in this Meeting Report.

Moreover, one of the main water pollution problems at present concerns a large group of substances both of anthropogenic and natural origin which may disrupt the hormone system of living beings. This phenomenon is known as „endocrine disruption“ and the appropriate definitions are given in Table 1. Table 2 summarizes the most important information about endocrine disrupters and illustrates with that the extremely worrying dimensions of the problem.

TABLE II. DEFINITION OF ENDOCRINE DISRUPTION AND POTENTIAL ENDOCRINE DISRUPTER.

ENDOCRINE DISRUPTION

has become a significant focus of environmental toxicology and medicine.

Definitions:
It is agreed that an endocrine disrupter could be adequately defined only in terms of effects on intact animals, although identification of *potential* disrupters is possible *in vitro*.

"An endocrine disrupter is an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function."

(Adverse hormonal effects may relate to disturbances in any of the major endocrine systems, including the reproductive, thyroid end adrenal systems).

"A *potential* endocrine disrupter is a substance that possesses properties that might be expected to lead to endocrine disruption in an intact organism."

As regards wastewater treatment a lot of endocrine disrupting chemicals are not biodegradable and contained, therefore, in secondary and also tertiary effluents from wastewater treatment plants. At present especially nonylphenol and its derivates (see Table 4) which were used all over the world as surfactant and are now ubiquitous in the aquatic environment and estrogens (natural and synthetic ones) are of major concern.

TABLE III. MAIN CHARACTERISTICS OF ENDOCRINE DISRUPTERS

ENDOCRINE DISRUPTERS

- anthropogenic and natural occurring chemicals disrupting the normal operation of the endocrine (hormonal) system
- may potentially cause adverse effects on human health
- more than 70 000 synthetic chemicals are potential endocrine disrupters with between 500 and 1000 new chemicals being added to the list each year
- over 700 different organic compounds, particularly pesticides and their breakdown products, surfactants a.s.o. may be found in drinking water
- effective also at very low concentrations (ppt-level)
- do often not follow a typical toxicological dose-response curve
- synergism definitely exists
- DBP are suspected to be endocrine disrupters

NONYLPHENOL AND ITS DERIVATES

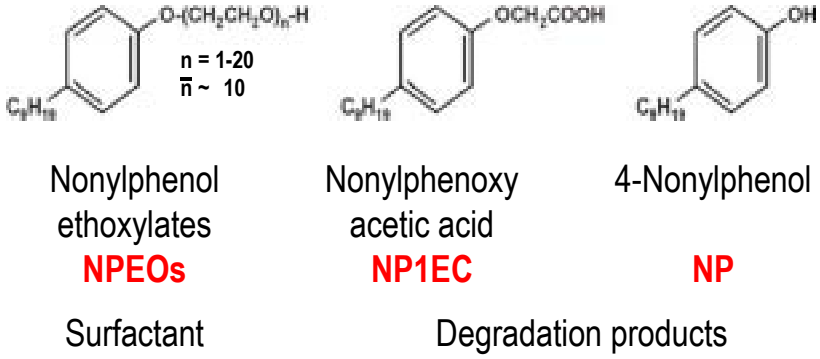


FIG. 9. Nonylphenol and its derivates

Preliminary experiments performed with a NPEO mixture dissolved in groundwater have demonstrated that these chemicals can be effectively decomposed by electron beam irradiation at reasonable doses (see Figure 9). However, NPEOs represents a minor problem because they are biodegradable to a high extent and, therefore, contained in the effluents from wastewater treatment plants just in rather low concentrations. The more serious problem is NP and NP1EC originating from the biodegradation of the NPEOs. Both are much more efficient endocrine disrupters as compared to the starting material. Figure 10 shows that electron beam irradiation is also able to efficiently decompose these substances with doses of about 1 kGy.

DECOMPOSITION OF AN NPEO-MIXTURE IN GROUNDWATER BY ELECTRON BEAM IRRADIATION

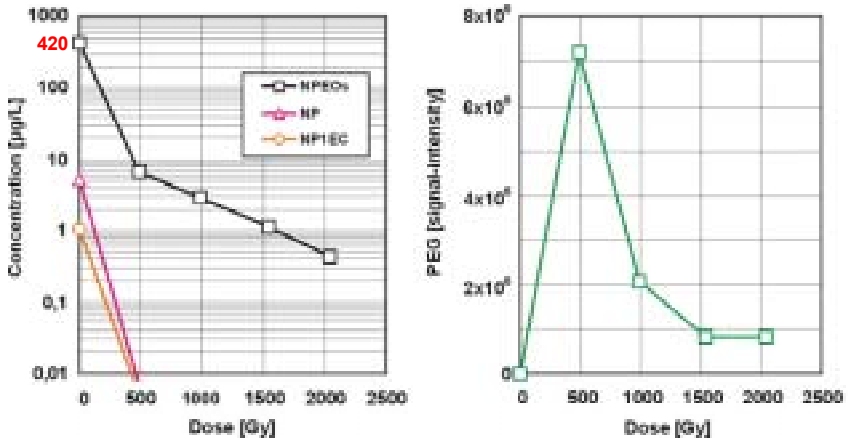


FIG. 10. Decomposition of NPEOs by EB irradiation

DECOMPOSITION OF NP1EC AND NP IN GROUNDWATER BY ELECTRON BEAM IRRADIATION

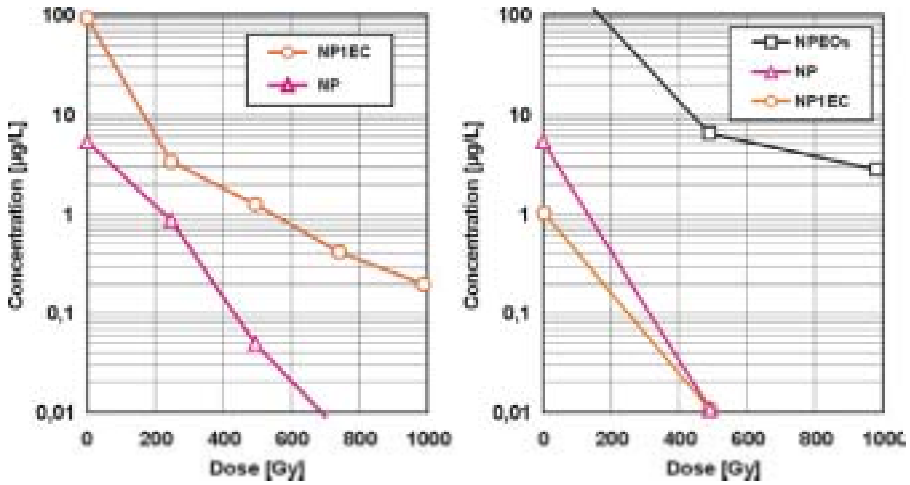


FIG. 11. Decomposition of NP by EB irradiation

Additional experiments performed with secondary effluents from a wastewater treatment plant for inactivation of indicator bacteria and for removal of some estrogens also contained in the effluent indicated that it is possible to effectively reduce the amount of bacteria by three orders of magnitude by means of electron beam irradiation and a dose requirement of about 1 kGy. Such a dose was, moreover, sufficient to significantly reduce natural estrogens to a level where the recombinant yeast estrogen screen, a biological test, confirmed that no more estrogenic activity exists in the irradiated effluent.

To sum up high energy electrons effectively inactivate indicator bacteria in effluents from municipal wastewater treatment plants and eliminate simultaneously any estrogenic activity originating from natural and synthetic hormones also contained in the wastewater effluents. Inactivation of bacteria and bacterial spores by electron beam irradiation was found to be practically unaffected by the water matrix and suspended solids. There is a strong indication from literature data that these findings are also relevant to viruses of concern in water hygiene like e.g. poliovirus. Consequently electron beam irradiation for effluent reclamation represents a true alternative to chemical and UV treatment. As compared to chemical disinfection it proved to be a clean technology without formation of hazardous by-products; as compared to UV irradiation electron beam irradiation is technically much more simple, almost insensitive to color, suspended solids or gas bubbles in the effluent stream, and, moreover, to effluent composition and fouling characteristics, respectively. It needs considerably less maintenance and is very easy to control. There is certainly a high potential for radiation processing of wastewater to successfully compete with the state-of-the-art processes. With the new generation of powerful and cost-effective electron beam accelerator which starts implementation with the full scale plant in Korea position of radiation processing in the competition with existing technologies will be further improved.

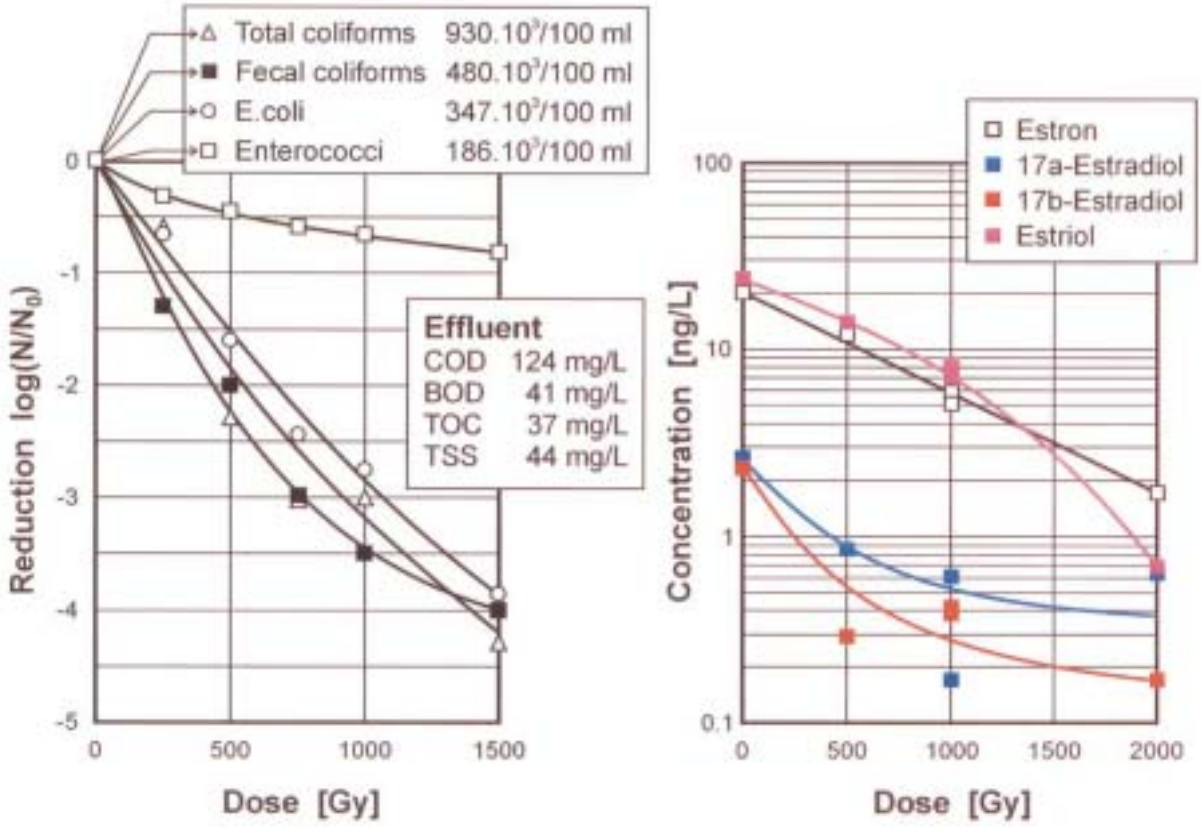


FIG. 12. Radiation induced inactivation of some indicator bacteria as well as decomposition of some natural estrogens by means of electron beam irradiation in a secondary effluent as function of the radiation dose.

TECHNICAL AND ECONOMICAL ASPECTS OF RADIATION TECHNOLOGY FOR WASTEWATER TREATMENT APPLICATIONS IN INDUSTRIAL SCALE

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Abstract

Technical and economical aspects of radiation technology for wastewater treatment applications in industrial scale are discussed based on different experiences and case studies.

1. INTRODUCTION

Groundwater and drinking water represent well-defined systems, i.e. the different solutes contained and their concentrations are known. In case of contamination also contaminant(s) and their concentration(s) are usually known. In such cases competition kinetics could be applied and a sound assessment regarding the amount of free radicals available for pollutant decomposition could be performed. Wastewater, on the other hand is not well-defined but just defined very poorly by means of sum parameters.

General characteristics of wastewater are as follows:

- Mixture of individual substances with various reactivity
- Characterized by group parameters only
- No general kinetic laws possible.

However, also in wastewater pollutant decomposition will proceed via free radicals formed during water radiolysis, i.e. there is no direct effect of the high energy radiation on any solute, pollutant decomposition will occur exclusively by indirect action of the radiation. In consequence radiation processing of wastewater is based on the same effect of radiation as radiation processing of ground and drinking water, respectively but with wastewater no kinetic laws can be applied as it is possible with ground or drinking water. It is, therefore, obvious that in search for possible solutions of a wastewater problem experiments are the only key to deal with such problems seriously. However, some general considerations can be performed which should be generally applicable to radiation processing of wastewater.

If biodegradable substances are contained in the wastewater they should be removed before irradiation because biodegradation is usually more cost-effective than radiation processing.

General considerations regarding radiation processing of wastewater are:

- Biology before
- Toxicity test afterwards
- Economy competition with:
  - Ozone + biology
  - Other AOPs

Radiation processing should be applied just for decomposition of recalcitrant pollutants. After irradiation of wastewater a toxicity test should be performed to establish that toxicity of the treated wastewater has not been increased. Such tests have been performed e.g. by Thompson and Blatchley III, 1999. If pollutant decomposition proceeds mainly via oxidation competition with ozonation in combination with a subsequent biology has to be always considered with regard to economy.

In the following results of bench scale experiments are presented to elucidate more in detail the problems often associated with wastewater and, moreover, to corroborate the impossibility to make

any prediction about the effect of high energy radiation on wastewater without performing some experimental studies.

2. RESULTS FROM BENCH SCALE EXPERIMENTS WITH SELECTED INDUSTRIAL PROCESS WATER

Figure 1 shows the results from experiments performed with a native chlorination effluent from a pulp bleaching process. Three different processes have been applied: ozonation alone, irradiation alone and a combined ozone/irradiation treatment.

Due to the BOD value of 490 mg/L given for the untreated effluent it is clear that this wastewater still contained a considerable amount of biodegradable substances. Irradiation did not result in a noticeable COD reduction even at a dose of 15 kGy and also the change in BOD was negligible over the dose range applied. Irradiation alone certainly is no option for a wastewater treatment in the present case. Ozonation alone reduced steadily COD with increasing ozone dosage.

Most interestingly COD reduction after 95 minutes was not accompanied by an appropriate BOD reduction, that means that obviously non-biodegradable substances have been attacked and decomposed. The combined ozone/irradiation treatment did not result in an efficient COD reduction. There was some reduction with a radiation dose of 5 kGy but a further dose increase to 10 and even 15 kGy did not reduce COD in an equivalent amount. BOD was increased by the combined treatment but the amount of the BOD increase was not sufficient to justify a subsequent biological treatment. In the present case radiation processing with or without ozone combination certainly is no option at all.

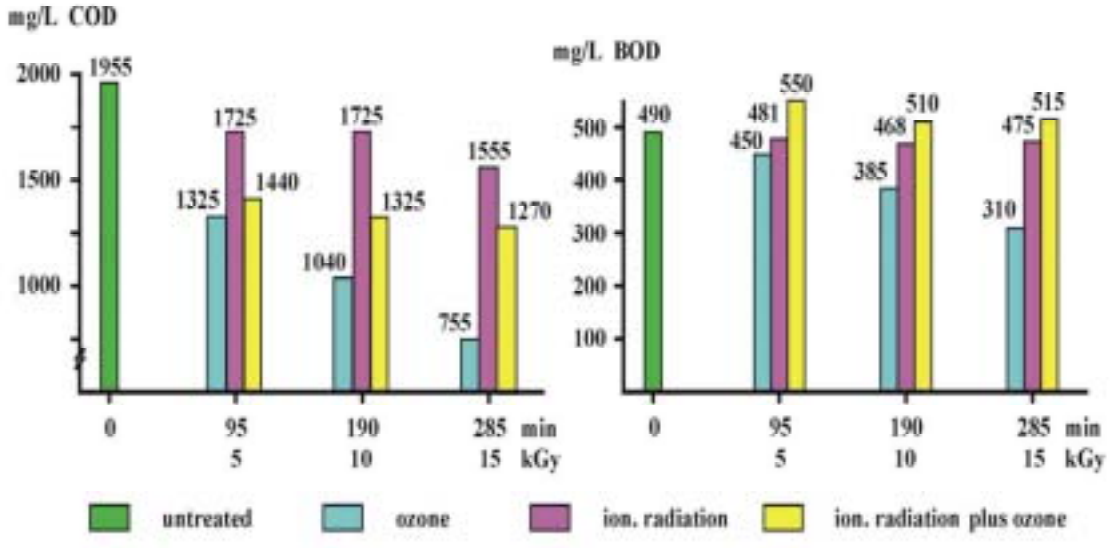

FIG. 1. Application of different treatment processes on a native chlorination stage effluent from a pulp-bleaching process.(The time given in the figure is the time of ozone action and is valid for both ozonation alone as well as ozone/γ-irradiation)

Figure 2 shows the effect of the three processes described above to the same effluent but after a biological treatment indicated by a BOD of just 17 mg/L. Irradiation alone again was not very effective, results have not been included, therefore. Now the combined ozone/irradiation process is clearly more effective as compared to ozonation alone, i.e. biological pretreatment changed the efficacy of the both processes under discussion to the opposite.

However, the effect of the combined process is more pronounced in the beginning but decreases with increasing dose. Most likely with such results a cost-effective wastewater treatment is hardly

conceivable. However, the problem has been solved in another way. The technology of pulp bleaching has been totally changed resulting in production of a process water which could be much easier handled and is considerably less toxic.

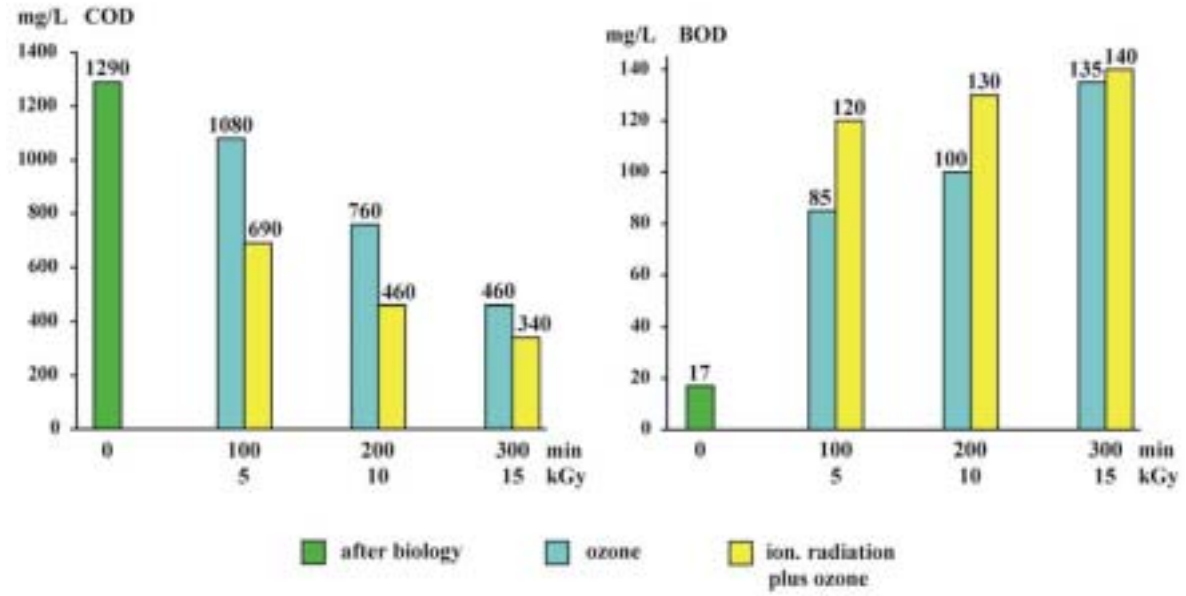

FIG. 2. Oxidative treatment of an effluent from a pulp-bleaching process after previous biological treatment. (Regarding time scale see Figure 1).

Figure 3 shows the effect of the three treatment processes under discussion on a wastewater stream from molasses processing. Even after multiplex biological treatment this effluent is still deeply colored and loaded with recalcitrant organics.

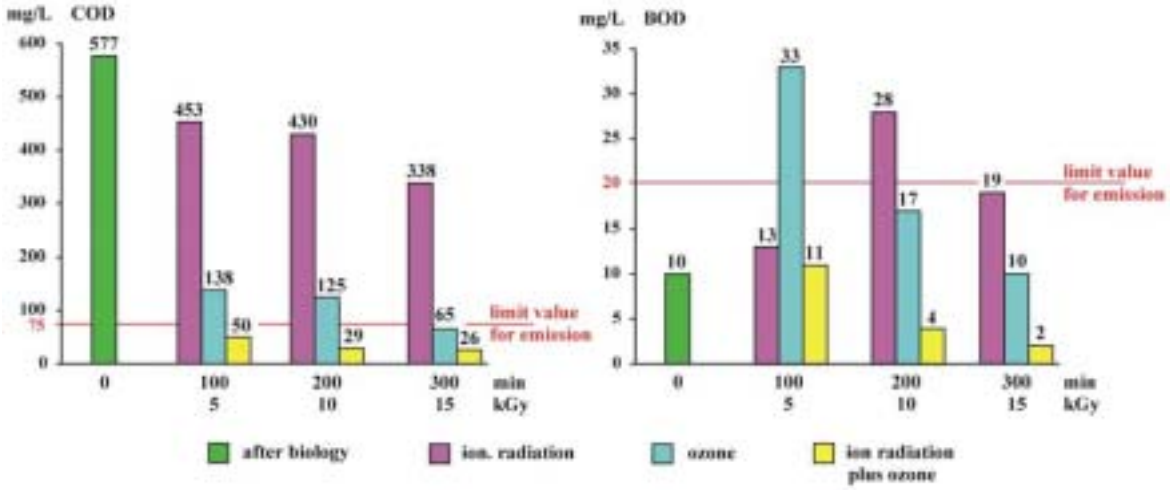

FIG. 3. Reduction of COD and change in BOD of a wastewater originating from molasses processing by different treatment processes. (Regarding time scale see Figure 1)

Again irradiation alone gave not very promising results for COD reduction, thus discussion can be focused on ozonation and the combined ozone/irradiation process as possible treatment alternatives. Both processes are quite efficient for COD reduction but resulted in different BOD values after treatment.

While the combined process kept the BOD constantly on the original value and with that clearly below the limit value of 20 mg/L regulated in Austria for discharging a wastewater into a river, ozonation increased the BOD by a factor of three and comes with that clearly above the existing limit value for BOD. Moreover, the combined process also meets the existing limit value for COD with the doses of 5 kGy and 100 minutes simultaneous ozonation, ozonation alone would need a somewhat higher ozonation dose to meet the existing requirements by applying ozonation in combination with a subsequent biological treatment (to eliminate the biodegradable substances formed by ozonation and reduce with that both the COD and BOD below the existing limit values for emission).

Consequently both processes are apt for a successful treatment of the effluent with regard to the existing regulations for discharging wastewater into a river and the data obtained in the bench scale experiments can be used now to perform a rough cost calculation of the both processes to figure out which one would be more cost-effective. Bench scale experiments have been performed with γ-irradiation, for a technical application just electron beam accelerators are possible. With such high pollutant concentrations present in the effluent a dose rate effect is not very likely, therefore, the γ-dose has been used for the missing e-beam dose for the cost calculation what is justified under the conditions given.

3. DESIGN OF THE OZONE/ELECTRON BEAM PROCESS FOR WASTEWATER TREATMENT

COD and BOD values of the process water fluctuate, of course, with time. The table below gives the actual data the cost evaluation is based on.

TABLE I. COST EVALUATION

BASIS OF COST EVALUATION	
PROCESS WATER :	COD 350 - 390 mg / L BOD 5 - 10 mg / L 50 m^3 / h
TASK :	COD reduction 70 % BOD ≤ 20 mg / L
OZONATION :	808 mg O_3 / L H_2O BOD ~ 50 mg / L
AOP :	745 mg O_3 / L H_2O 2.7 kGy * BOD ~ 18 mg / L

To treat a wastewater stream of 50 m³/h the corresponding ozone demand was calculated to be 40.4 kg/h (ozone alone) and 37.3 kg/h (ozone/e-beam), respectively. Although the ozone demand of the combined ozone/electron beam irradiation is about 8% lower than for ozonation alone a 45 kg/h ozone generator was provided for the combined process, too. The less ozone consumption and the shorter treatment time of the combined process was considered in the calculation of the operating cost (8% less oxygen as compared to ozonation alone) and in the construction of the retarding vessel.

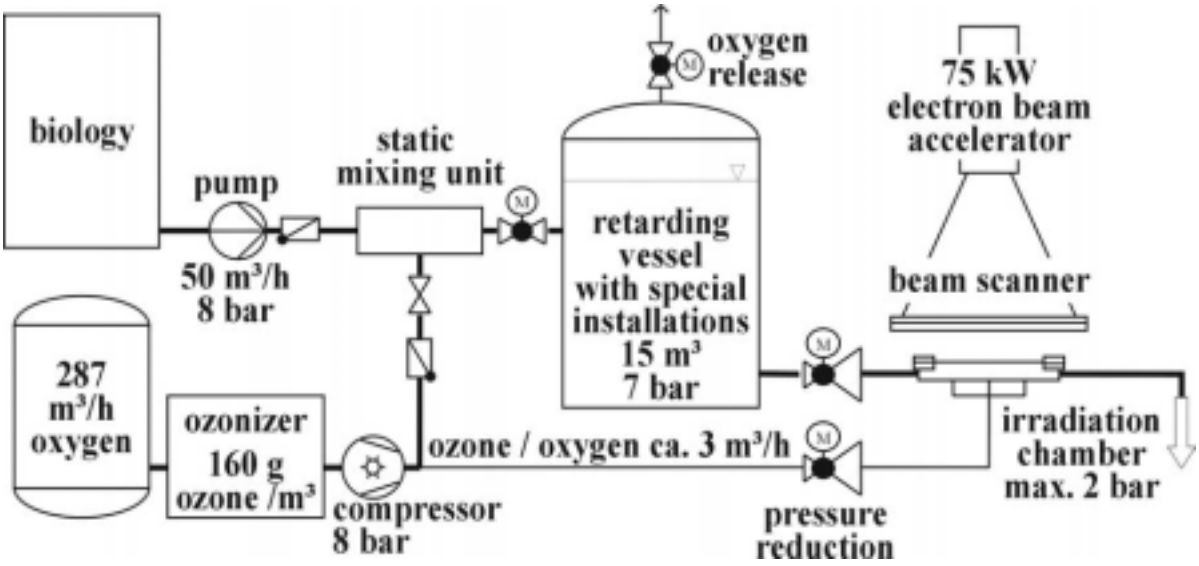

FIG. 4. Schematic view of an ozone/electron beam facility for wastewater treatment.

In our conception of the combined process (see Figure 4) ozone is introduced into the wastewater stream under a pressure of about 8 bar what significantly increases the initial concentration of aqueous ozone and accelerates by that the direct ozone reactions. Consequently the amount of gaseous ozone in the retarding vessel should be small, therefore. This is important with regard to the removal of the oxygen. The solubility of oxygen in water is rather low. For that reason and because of its large amount (gas/water ratio about 5:1 at normal conditions) almost all of the oxygen introduced is present gaseous. For technical reasons most of the gaseous oxygen has to be removed before irradiation and this should happen, of course, with a minimum loss in ozone. The retarding vessel has, therefore, special installations to avoid the formation of bigger gas bubbles and to support the ozone transfer from gas into the water phase. Moreover, oxygen release takes place continuously at the high pressure level. Under such conditions and considering the high amount of direct ozone reactions ozone losses should not exceed about 10%.

On the other hand, the acceleration of the direct ozone reactions by the elevated pressure does also influence the sizing of the retarding vessel. Since a certain amount of ozone will react already in the static mixing unit a 10 min duration of the water in the retarding vessel has been supposed to be sufficient. Accordingly the following process design results:

To irradiate 50 m³/h with a dose of 2.7 kGy a 75 kW electron beam accelerator would be necessary when a beam utilization factor of 0.5 is considered. Since under turbulent flow conditions water layers of about 3 mm have been successfully treated with a 500 keV accelerator such a machine (500 kV; 150 mA; 1.8 m scan width) has been chosen for the cost evaluation.

4. DESIGN OF THE OZONE/BIOLOGY PROCESS

A conventional process for the treatment of said wastewater could be constructed as shown in Figure 5.

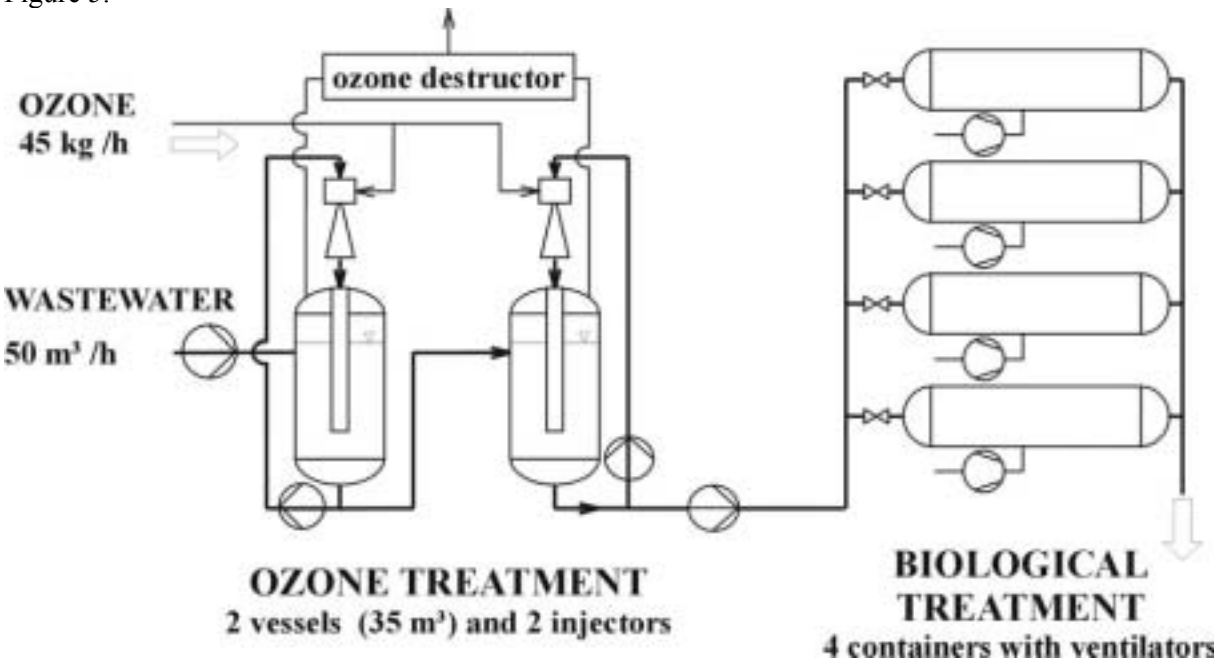

FIG. 5. Flow diagram of a wastewater treatment process based on combined ozone/biology treatment.

Dimensions and design of the both vessels for ozone treatment guarantee a sufficient contact of ozone and wastewater. After ozonation the treated wastewater is pumped to a biological treatment (activated sludge system) in order to reduce the BOD to a residual concentration below 20 mg/L. For the design of the biological stage the following data have been used: BOD 50 mg/L; NH_4-N about 10 mg/L; NO_3-N up to 40 mg/L and P-total 0.5 mg/L.

Based on these data the volume of the aeration tank was calculated for 300 m³ with an oxygen consumption of about 100 kg O_2/day. In the technical conception a container design has been chosen consisting of 4 containers, each of them has 17 m in length.

5. COST EVALUATION OF THE TWO PROCESS OPTIONS

The following table II gives once more the technical data of the main components of both process options cost evaluation is based on.

TABLE II. TECHNICAL DATA OF THE MAIN COMPONENTS

TECHNICAL DATA OF THE MAIN COMPONENTS

ACCELERATOR :	**500 kV - 150 mA - 1.8 m**
Energy consumption :	85 kW
OZONE GENERATOR :	**45 kg O_3 / h**
O_3 - concentration :	160 g O_3 / m^3 O_2
O_2 - consumption :	9.1 kg O_2 / kg O_3
Energy consumption :	529 kW
BIOLOGY :	**300 m^3 aeration tank**
O_2 - consumption :	100 kg O_2 / day

In the following Table III the capital requirement of the both processes under discussion is shown. In the costs given for the ozone/biology process pumps, ventilators all installations as well as sludge handling and sludge disposal is included.

TABLE III. CAPITAL REQUIREMENTS

CAPITAL REQUIREMENTS

OZONE / ELECTRON BEAM	in US$	OZONE / BIOLOGY	in US$
Electron beam accelerator	850 000	Ozone generator equipm.	1 380 000
Vault (concrete)	50 000		
Auxiliary equipment	150 000	Water handling and	
Transport and Installation	150 000	ozone introduction system	420 000
Water handling system			
(containing pump, compressor,		Biological processing	
mixing unit, retarding vessel,		(incl. sludge disposal)	860 000
irrad. chamber, instrumentation)	220 000		
	1 420 000		
Ozone generator (incl. cooling-circuit and ozone destructor)	1 380 000		
Total Capital	**2 800 000**	**Total Capital**	**2 660 000**

The next table IV illustrates the resulting capital costs for the two processes based on operation of 8500 hours/year.

TABLE IV. CAPITAL COST

CAPITAL COST

OZONE / ELECTRON BEAM	in US$	OZONE / BIOLOGY	in US$
Total Interest Cost		**Total Interest Cost**	
E-beam equipment (10 % over 20 years)	144 000	Ozone generator Water handling and ozone introduction (10 % over 10 years)	306 000
Ozone equipment and water handling (10 % over 10 years)	270 000	Biological processing (10 % over 20 years)	104 000
Annual charge	**414 000**	**Annual charge**	**410 000**
Total Capital Cost (8500 hr / yr)	**48.70 $/h**	**Total Capital Cost (8500 hr / yr)**	**48.23 $/h**

Finally, the operating costs and the resulting total cost of the two processes are given. (The operating cost of the biological treatment are calculated with 3.5% of the capital requirement and include energy consumption and maintenance).

TABLE V. OPERATING COST

OPERATING COST

OZONE / ELECTRON BEAM	in US$ / h	OZONE / BIOLOGY	in US$ / h
Electric Power (0.15 $ / kWh)		**Electric Power** (0.15 $ / kWh)	
E-beam equipment 85 kW	12.75	Ozone equipment 529 kW	79.35
Water handling 45 kW	6.75	Water handling 66 kW	9.90
Ozone equipment 529 kW	79.35	Biological processing (includes also maintenance)	3.54
Oxygen (0.08 $ /kg)	29.50	**Oxygen** (0.08 $ /kg)	32.05
Maintenance		**Maintenance**	
E-beam equipment	4.00	Ozone equipment	2.42
Water handling	0.40	Water handling	0.75
Ozone equipment	2.43		
Total Operating Cost	**135.18 $/h**	**Total Operating Cost**	**128.01 $/h**
Total Capital Cost	**48.70 $ / h**	**Total Capital Cost**	**48.23 $ / h**
Total Cost	**183.88 $ / h ~ 3.7 $ / m³**	**Total Cost**	**176.24 $ / h ~ 3.5 $ / m³**

Based on these data the capital requirements for both processes are almost equal the derived capital costs are, therefore, almost identical for both processes. Since operating costs just differ by a few per cent cost evaluation does not really opt for one of the two processes.

6. CONCLUSIONS

The combination of ozone with ionizing radiation is equivalent to the combination of ozonation with subsequent biology with regard to discoloration and COD reduction of a pretreated wastewater from molasses processing. Ozone/electron beam treatment would solve the problem in one single step without formation of by-products for disposal. The conventional process is a two stage process with some sludge as by-product to dispose of. A rough cost estimation favors slightly the conventional ozone/biology process.

ONGOING RESEARCH IN BRAZIL USING ELECTRON BEAM LIQUID WASTE TREATMENT

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Abstract

The objective of the research work at the IPEN is the use of the electron beam facility to study the removal and degradation efficiency of toxic and refractory pollutants (organic compounds mainly from industrial origins) and the disinfecting of pathogenic micro-organisms in wastewater, industrial effluents and sludge. The investigation are conducted in the existing wastewater treatment pilot plant at IPEN. The economical feasibility study and the results of the performed tests will be used to scale up for a demonstration plant on a commercial basis.

1. INTRODUCTION

Environmental pollution has become a significant world concern. The main causes of this contamination are industries, which generate and deliver to the environment injurious effluents often without any treatment. Most of these contaminants biodegrade very slowly, becoming dangerous for people, plants and animals. Damage to human health related to improper treatment of residues has led to strict environmental protection laws and consequently the need for research in the treatment of effluents. [1]

The variables involved in the environment's recuperation are numerous, mainly by the great variety of chemical compounds and raw materials used by industry. The most complicated industrial effluents are organic compounds, especially synthetic agents. Their degradation is difficult using conventional methods.

The quality and quantity of industrial wastes change and depending the used material and related processing technique. The aim of the conventional techniques employed is to reduce the volume and toxicity of the effluents. The available techniques are coprecipitation, adsorption on charcoal and resins, oxidation, flotation, biodegradation, incineration, radiation and recycling.

The oxidation process has attracted many researches because of the capacity to mineralise organic compounds. The most efficient oxidation is the use of OH radicals. There are various methods of generating OH radicals: the use of ozone, hydrogen peroxide, ultraviolet and the interaction of ionising radiation with water (AOP – Advanced Oxidation Process), that is the most simple and efficient method for generating OH radicals in situ. [2]

The use of ionising radiation has great ecological and technological advantages, especially when compared to physiochemical and biological methods. It breaks down organic compounds, generating substances that are easily biodegraded and it is not necessary to add chemical compounds.

The Radiation Technology Centre - CTR at the Institute for Energetic and Nuclear Research (IPEN) started in 1992 the development of an alternative technology for wastewater and industrial effluent treatment, mainly for the degradation of pollutants using the radiation from a high-energy electron beam. This technology has been extensively studied by many research centres. [3 – 5]

The objective of this programme is to use the existing wastewater treatment pilot plant that was set up in the IPEN electron beam facility, in order to study the removal and degradation efficiency of toxic and refractory pollutants (organic compounds mainly from industrial origins) and the

disinfecting of pathogenic micro-organisms in wastewater, industrial effluents and sludge. The economical feasibility study and the results of the performed tests will be used to scale up for a demonstration plant on a commercial basis. The Fig 1 shows the flowchart of this programme.

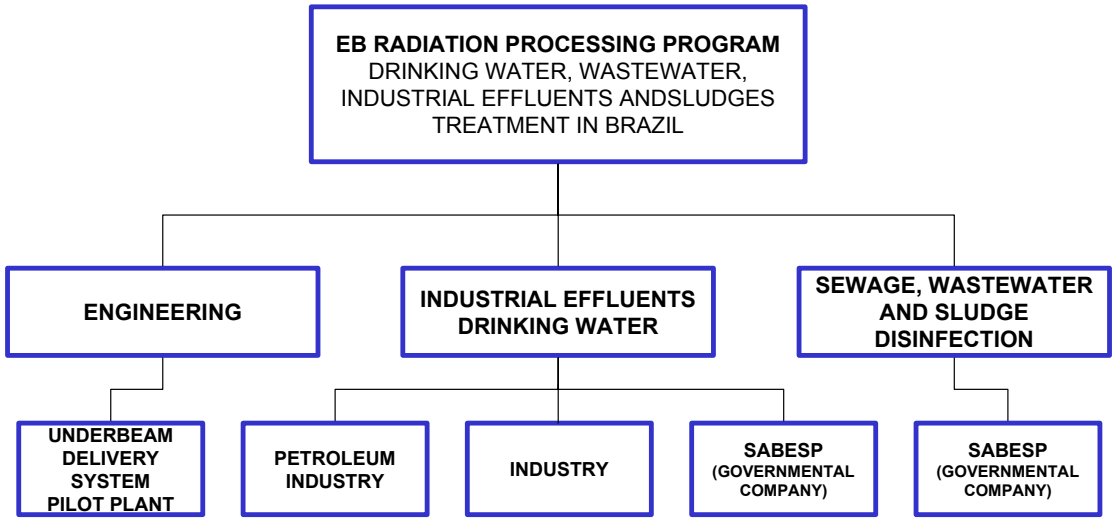

FIG. 1. Flowchart of EB radiation processing programme in Brazil

The industrial growth and population increase has resulted in the release of different pollutant compounds in the environment. Industrial wastewater without an efficient treatment is becoming a serious problem in industrialized areas, hazardous regulations are becoming more restrictive and technologies, which don't destroy these products, are becoming less acceptable. The perspective for the national market of effluent systems is demonstrated in the table I.

TABLE I. NATIONAL MARKET OF TREATMENT OF EFFLUENT SYSTEMS (IN US$ MILLION)

Type	1999	2000	2001	2002	2003
Governmental Company	34,0		38,0	40,0	42,0	44,0
Autonomous Services	4,0		5,0	6,0	7,0	7,0
Enterprises	35,0		36,0	40,0	45,0	55,0
Industry	15,0		20,0	22,0	25,0	30,0
TOTAL	88,0		99,0	108,0	119,0	136,0

A recent survey of pollutants in the rivers of São Paulo, that concentrate the main industrial activities in Brazil, reported that they were quite contaminated due to industrial waste, mainly organic compounds. Since conventional and available technologies to treat such wastes have low efficiency and high cost, the Government, through the São Paulo State Sanitation Company (SABESP) and industries are searching for alternative technologies to degrade these chemical compounds to get a better quality of water and consequently improve public health.

Considering these aspects IPEN - Institute for Energetic and Nuclear Research, started in 1992 the development of an alternative technology for wastewater and industrial effluent treatment, mainly for the degradation of pollutants submitting the material to high-energy electron beam.

The objective of this programme is to use the existing wastewater treatment pilot plant that was established in the IPEN electron beam facility, in order to study the removal and degradation efficiency of toxic and refractory pollutants (organic compounds mainly from industrial origins) and the disinfecting of pathogenic micro-organisms in wastewater. An economical feasibility study and the results of the performed tests will be used to scale up for a demonstration plant on a commercial basis.

2. ON GOING IN RADIATION PROCESSING OF WASTEWATER LABORATORY STUDIES.

2.1. Pilot Plant at the IPEN

In order to carry out feasibility studies using EB technology the stationary pilot plant set up at IPEN, was built and especially designed to study the optimisation of the process mainly of the irradiation device that governs the efficiency of the energy transfer from the electrons to the effluent, defining the requirements for the optimum operating parameters for the treatment in industry. [6]

This pilot plant can process the waste stream at a flow rate of $0.5m^3$ per hour to $7.0m^3$ per hour with an average dose rate of 5kGy. Its construction is very simple and not expensive, with the flexibility to change the dose rate, accelerating voltage of the electron beam and configuration of the irradiation device. Two tanks with 1,200 litres capacity are used for storage and collection of the treated liquid and two pumps are used to homogenize and pump the liquid through the irradiation device specially built for this purpose (Fig. 2). A sample system allows the sample collection just after and before irradiation.

The main goal of this plant is to optimise the irradiation system to get a high efficiency with low electron beam (EB) energy in order to reduce the costs of the facility including the EB machine and irradiation vault.

The hydraulic system where the water is presented to the electron beam governs the efficiency of this technology. It was developed ***of an up flow irradiation device,*** that by its configuration, theoretically alleviates the dependence of energy transfer to the stream with the beam accelerating voltage (penetration capability).

A sequence of experiments were performed in a wastewater treatment pilot plant to establish the relationships between accelerating voltage ranging from 0.5MeV to 1.5MeV; electron beam current intensity, stream flow and delivered dose, in order to optimize the operating parameters for the selection of the electron beam machine.

Three models of up flow stream irradiation device were tested; the models are represented in Fig. 3. The sequence of the development started with model 1, which was up graded, to models 2 and 3. The model 3 fitted with a 40μm titanium foil window allows the irradiation device to work as a closed system, where in this configuration hazardous liquids can be processed in a safe condition, avoiding the spread of gaseous by-products to the environment.

For each irradiation device a series of tests were carried out in different operating conditions with the purpose to determine the maximum efficiency of the system. The efficiency was determined by the relation between the absorbed dose of the stream registered in the calorimeter and the delivered dose from electron beam accelerator (without losses).[6]

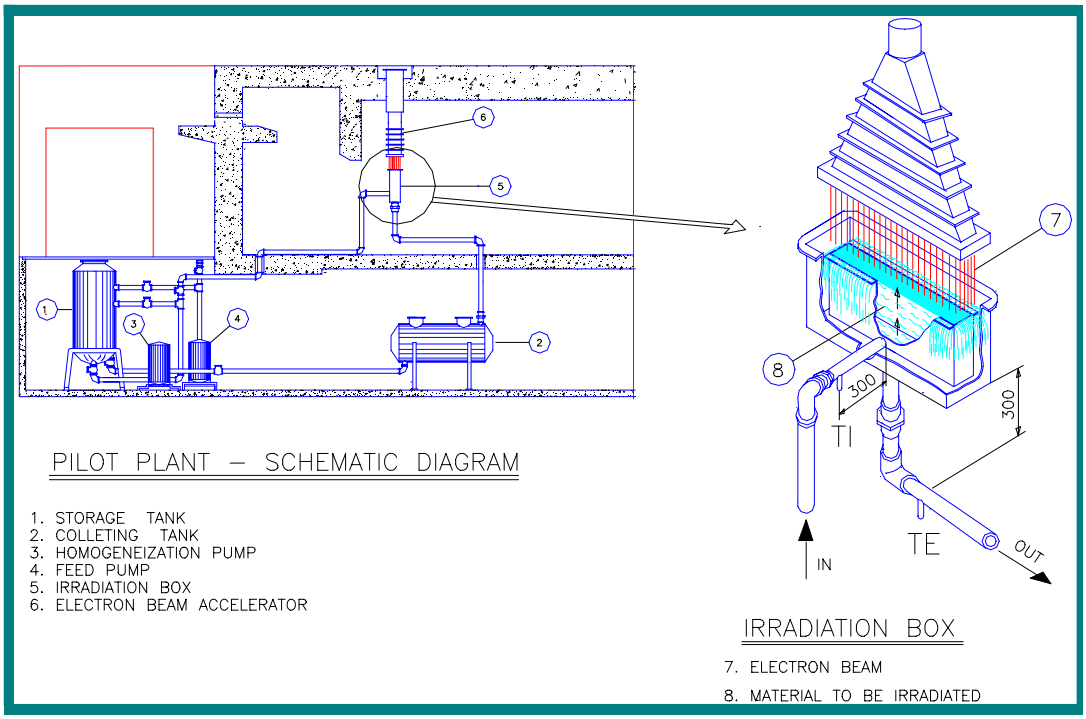

FIG. 2. IPEN's pilot plant – schematic diagram

Testing during 200 hours the IPEN's pilot plant, the best results of the efficiency for the developed irradiation prototypes is the Model 3 that becomes a versatile device when different kinds of effluents can be processed, especially hazardous wastes. The tests were performed in two configurations: without the titanium foil window becoming the hydraulic circuit opened to the environment and fitted with the foil becoming a self-contained system.

All the efficiency tests were done simultaneously with dye degradation tests. Based on these results the dose measured with the calorimetric system follows the same tendency as the color dye degradation, consistent with the evaluation of energy transfer from the electron beam to the stream. Concerning to the selection of the appropriate electron beam to be used in large-scale facility these results can be used for economical feasibility study of the process.

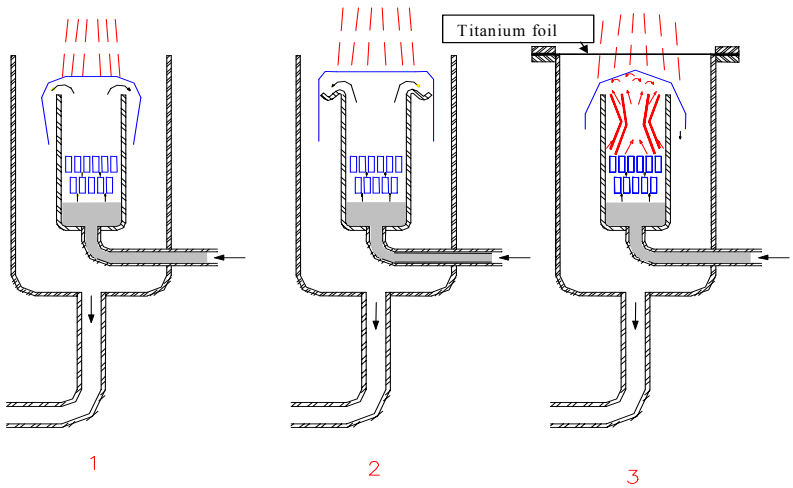

FIG. 3. Models of up flow stream irradiation devices

2.2. Dosimetric System

For a better control of parameters involved during the liquid waste radiation processing, it was developed an on line calorimetric system, where the absorbed dose is obtained by measuring the temperature difference of the water stream before and after the irradiation device.

The dosimetric system is based on two Wire Current Output Temperature Transducer, WCOTT, from Intersil (Intersil-General Electric Co.), located in the influent and in the effluent pipes respectively, separated by 35cm before and after the irradiation device. The temperature transducers are connected via an interface to a PC computer that continuously reads and records the temperatures and transforms the values to the equivalent dose delivered to the stream.

2.3. Mobile Plant Facility

A mobile EB plant is being designed to be set-up on truck flat bed trailer. With all its components including all water-processing systems, computerised control and supervision system and a diesel generator to become the plant independently operated of the public power supply system, ready to use avoiding previous preparations.

This mobile plant is expected to be concluding in 2005 and will incorporate the technology of the irradiation device developed previously in the existing IPEN´s pilot plant.

The objective of this mobile plant facility is to test and promote the use of electron beam technology for wastewater treatment and to use this facility for treatment services in the local where the liquid waste is generated and stored.

2.4. Developments

IPEN has been studying radiation improvement for effluents since 1992. There are several purposes in research and development which included: natural and artificial color reduction, organic compounds degradation (sewage and industrial wastewater), sewage and sludge disinfection, industrial effluents general improvement (organic solvents degradation, color removal), industrial and sewage detoxification. [7]

Actually the following wastewater electron beam treatment studies are:

- Comparison studies using electron beam process and granular activated carbon (GAC) to treat industrial effluents: the results showed that the organic removal efficiency was similar in the both methods, the costs using EB was higher than GAC but GAC presents a environmental problems concerning to disposal, contaminations transferred to air and the high cost for regeneration (activation).

- Studies for effluent treatment from petroleum production units for water reuse [8]: the results showed a good remotion for benzene, toluene and xylene with a dose of 100kGy for high concentration and 50kGy for lower concentration. The preliminary costs of this treatment is very expensive and this process is actually under optimization. The steps of this development are:

    - organic chemical analysis of real wastewater before and after irradiation; [9]
    - toxicity studies of raw and treated effluents; [10]
    - economic analysis of the process; [11]

- Surfactant degradation from wastewater – toxicity behavior of decomposed surfactants treated by electron beam process [12]: the toxicity studies showed that ionizing radiation from electron beam accelerators has proved to be efficient and useful for wastewater detoxification and the optimized doses from wastewater treatment are:

    - Surfactants: up to 20kGy for real sewage and from 3kGy to 9kGy for standard solutions;
    - Domestic origin: up to 1.0kGy;
    - Industrial origin: up to 20kGy;
    - Industrial effluents: from 20kGy to 50kGy;
    - Petroleum units: from 20kGy to 200kGy;

- Metals and Organic Compounds removal from industrial effluents and wastewater: the electron beam irradiation demonstrates to be a promising process on breaking down the concentration of hazardous compounds without dangerous gas by-products and reduce the sewage final volume.
- Degradation of PCB´s (started);
- Removal of odorific substances (geosmin-GEO and methylisoborniol-MIB) in drinking water with the objective to install a demonstration plant for treating these chemical compounds responsible for taste and smell problems in drinking water.
- Experiments with real effluent from industries and effluents from Municipal Wastewater Treatment (WWTP) Plants with the objective to acquire the necessary data in order to support the conclusions regarding to technical feasibility and cost studies of water treatment under optimized conditions such as:
    - data on optimized operating parameters such as electron energy, dose, flow rate, current , accelerating voltage;
    - data on wastewater composition and toxicity pre - and post – treatment;
    - technical and economical information for feasibility studies for applications at a large scale;
    - perform a model feasibility study for one particular case.

2.5. Factors which influence further development and applications

It has been shown in many laboratories that the major factor that can be pointed out is the efficacy of this technology to decontaminate or disinfect a great volume of liquid products, consolidating this technology to be applied to clean up specific hazardous waste.

Another factor to be considered is that the legislation of environmental protection is becoming more restrictive in several countries. An example is the existent law in Europe that restricts the amount of chlorine compounds in the water to be used mainly in the nutritious industry due to chlorination and related by-products. The technology with EB is perhaps the only alternative to attend with efficiency this requirement.

2.6. Remaining Problems to be Addressed for Wider Utilization of this Technology by the End-Users.

The main problem is the initial investment necessary to implant an Electron Beam facility due to the cost of the accelerator that is expensive because is not produced in large scale and the necessary shielding that elevates the cost of the building. These factors become the professionals that works in environmental area hesitant to invest a large sum in capital when they do not see a full scale facility working in an actual wastewater.

Another reason is the size of industrial commercially available electron beam accelerators that is limited in useable output EB power. Nowadays a most power EB machine is around 300 kW and using such kind of machine to disinfect the total effluent as a replacement for chlorination delivering the dose of 1 kGy in medium scale wastewater treatment plant (2,500m^3/h), it will be necessary almost 3

big machines. This quantity also makes the professional of this area hesitant about using this technology.

2.7. Additional areas of potential interest and targets of opportunity

The Electron beam irradiation process has a great potential to offer an innovative, cost-effective and flexible technology for treatment of specific aqueous streams that till this moment are not conveniently studied such as:

- decontamination of airport and hospital wastewater effluent,
- dewatering of sludge in wastewater treatment plants,
- leachates treatment from landfills
- disinfection of water as a replacement chlorination for food industry,
- reuse of specific industrial wastewater effluent (where the volume to be treated are compatible with the available EB accelerators)
- irradiation of water used as a ballast in ships. Some governmental authorities are questioning about the health safety, environmental protection of this water that is collected in one country or in one ocean and discharged in another.

2.8. Views and recommendations for future activities

The cost and size of commercially available of EB accelerators are the main reason for limiting the use of this technique on wastewater treatment, in this direction the IAEA could support or encourage the investigation of potential new applications on optimisation of water delivery device in order to reduce unit cost of the process.

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DISINFECTION OF TOTAL COLI-FORMS IN UNCHLORINATED SECONDARY EFFLUENT WITH ELECTRON BEAM

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Abstract

To investigate the disinfection of total coli-forms in the effluent of secondary sewage treatment plant with radiation, electron beam has introduced. Unchlorinated secondary effluent was irradiated at different dose of 0.2 – 1.0 kGy with 1 MeV, 40kW electron accelerator. It is observed that nearly 100% reduction in E-Coli. and total coli-forms were achieved with a dose of 0.8kGy. Even with the lower dose of 0.2kGy, the E-Coli. and total coli-forms were successfully inactivated to the level of the new guideline for discharged effluent that has been effective from 2003 in Korea. Besides disinfection of total coli-forms, approximately 50% of removal in biochemical oxygen demand (BOD) was also observed at a dose of 0.2kGy. More than 20% removal in suspended solids (SS) and turbidity was also observed at a dose of 1.0kGy. The application of electron beam irradiation appeared to be one of the options to reuse effluent from sewage treatment plant as agricultural or industrial water.

1. INTRODUCTION

Average annual rainfall in Korea is around 1,270 mm and is about 30% more than that of the world (973mm), but it varies too much with season and area to control for withdrawal. By considering the high population density (3rd in the world), the annual rainfall per capita is decreased to only 1/11 (3,000ton/yr/man) of the world average. (Fig.1) And even worse, 2/3 of those rainfalls are concentrated in 2 or 3 months in summer and hence only 24% of rainfall could be accessible for human uses. Demand for fresh water in our country increases gradually with industrialization and urbanization, but the supply has limitations in its increasing. (Table I)

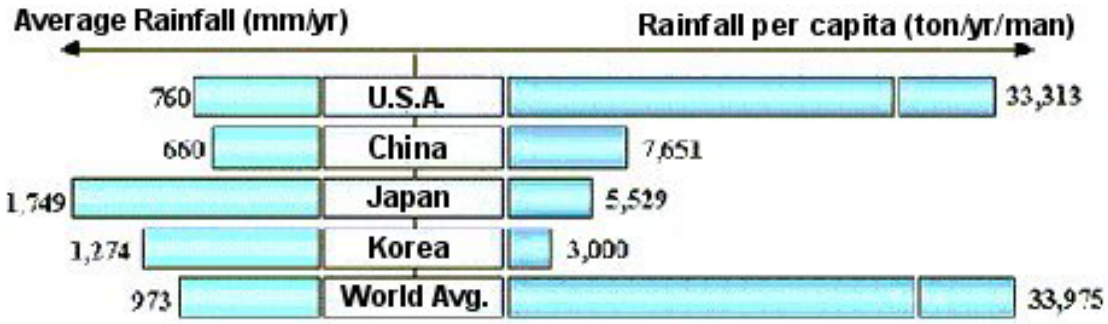

FIG. 1. Comparison of rainfalls in some countries

The treatment of municipal wastewater for re-use to industries or agricultural purposes becomes a more important subject in the field of Water Resources Management. Nation-wide in Korea, over 200 sewage disposal plants are in operation and they treat up to 20 million tons of sewages per day which covers 80% of total discharged and 95% from the main streams in the country.

Most of those existing municipal sewage disposal plants are equipped with conventional biological methods with the digestion of activated sludges, which are efficient to remove suspended solids and organic matters. However, those methods have limitations in removing nitrates and phosphates that used to be the nutrient of algae formation as well as in decreasing the number of

microorganisms in effluent. For the re-use of such effluent to industries or irrigation, not only the color, odor, and residual organics are important, but the numbers of microorganisms are also important. In Korea, starting from the 2003, new guideline of governmental authorities has been effective to control the numbers of E-coli in the effluent from sewage plants less than 3,000 numbers in 1 ml. Therefore, advanced technologies to control the microorganisms as well as to remove, color, odor etc. are required on the economical basis.

Among the many new technologies, radiation treatment is the most promising method in both economical and technical evaluation. The treatment of municipal wastewater with electron beam is actively studied in EB TECH Co.. An electron accelerator of energy 1 MeV in continuous mode is used in experiments. Applied doses in the experiments were measured with an ordinary or modified Fricke dosimeter and dichromatic dosimetry system.

TABLE I. SUPPLY AND DEMAND OF FRESH WATER IN KOREA ($10^8 M^3$/YEAR)

Year	1994	2001	2006	2011
Demand	29,901	33,640	34,991	36,652
Supply	32,219	34,290	34,541	34,655
Shortage	-	-	450	1,997

2. EXPERIMENTAL

To observe the applicability of electron beam treatment for disinfection of the effluent from municipal sewage treatment plant, the effectiveness of electron beam irradiation in the disinfection of wastewater and the improvement of the water quality were measured by determining the changes in organic matter as indicated by the measurement of BOD, COD and TOC.

The experiments were conducted with 1MeV, 40kW electron accelerator at EB-TECH.CO., LTD in Korea. The absorbed doses for all of the experiments were in the region of 0.2kGy - 1.0kGy. The effluent used for this research was from the Daejeon sewage treatment plant, and the effluent is taken after the activated sludge treatment - just prior to discharge.

Estimates of E-Coil. and total coli-forms of bacteria were determined by the membrane filter procedures EPA Method. After Irradiation, the change of characteristics in effluent was measured as BOD and COD, EPA method.

Fig. 2 shows the bench scale electron beam irradiation system used in this research.

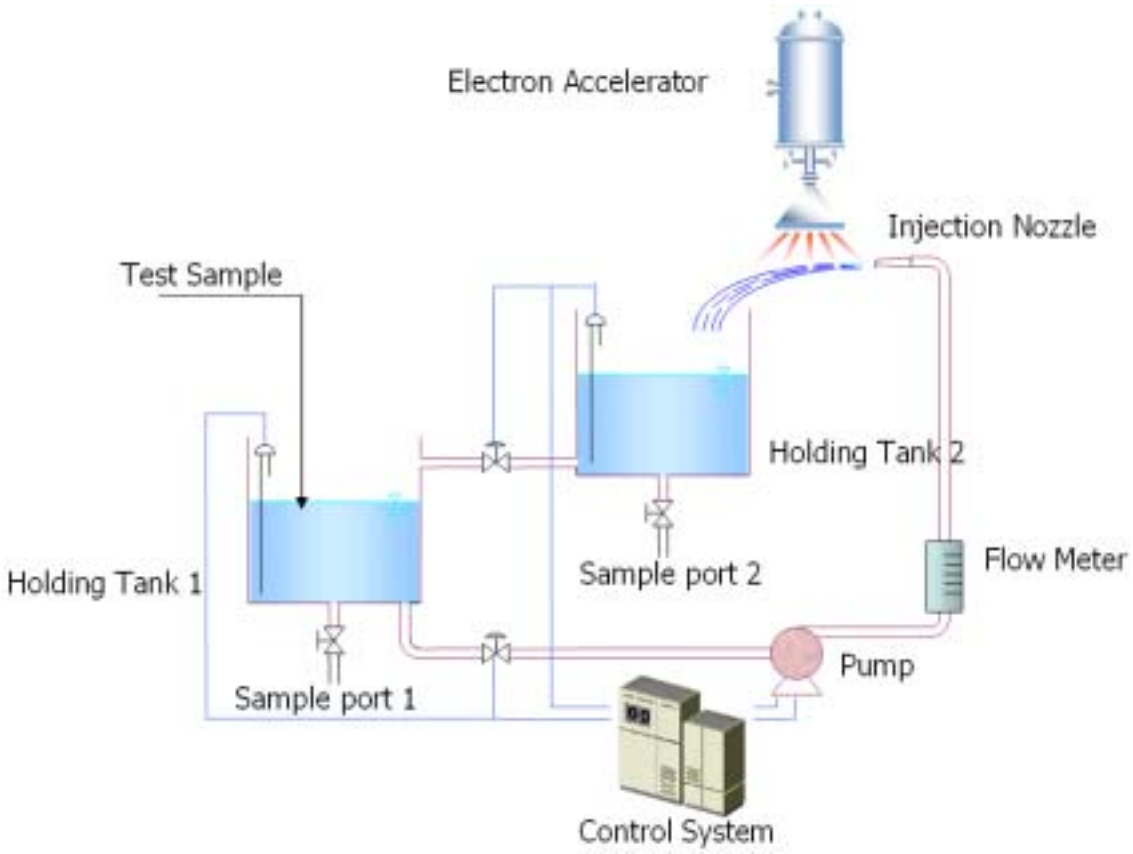

FIG. 2. Schematic diagram of experimental apparatus

3. RESULTS AND DISCUSSION

It is observed that nearly 100% of E-Coli. and total coli-forms were inactivated with a dose of 0.8kGy. Even with the lower dose of 0.2 kGy, the E-Coli. and total coli-forms were successfully inactivated to the level of the guideline for effluent discharge. Besides disinfection of total coli-forms, approximately 50% of removal in biochemical oxygen demand (BOD) was pronounced at a dose of 0.2kGy. More than 20% removal in suspended solids (SS) and turbidity was also observed at a dose of 1.0kGy.

TABLE II. CHARACTERISTICS OF SECONDARY EFFLUENT FROM A SEWAGE TREATMENT PLANT

Parameters	Max.	Min.	Aver.
	2002. 7. 8 – 2002. 9. 6 (40day)		
BOD (mg/l)	21.2	7.2	10.1
COD (mg/l)	14.8	8.8	10.8
SS (mg/l)	12.8	1.7	5.6
E-coli (CFU/ml)	14,000	800	4,200
Total coliforms (CFU/ml)	820,000	140,000	440,000

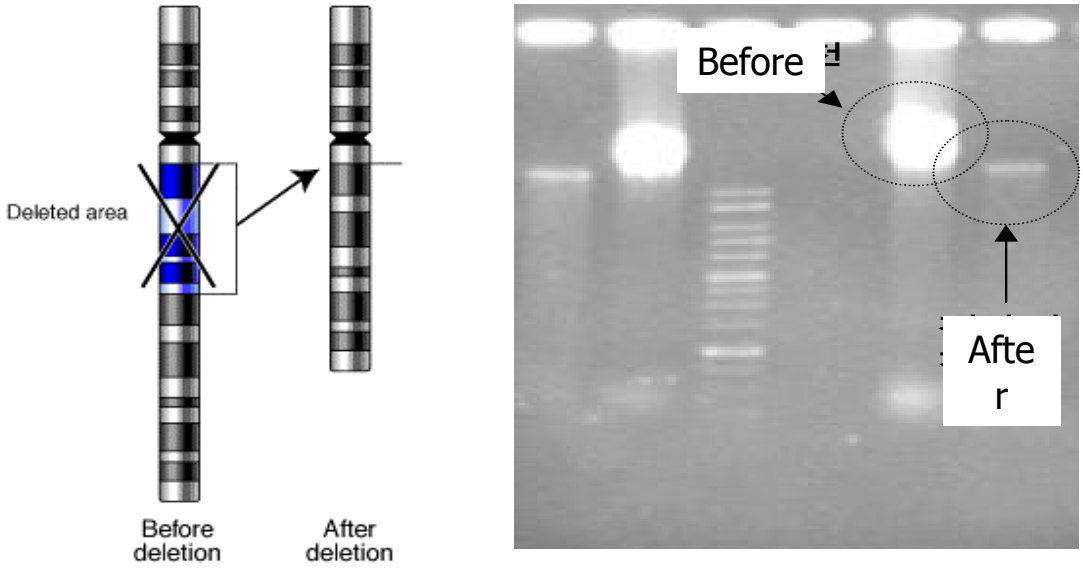

FIG. 3. Variation of DNA at E.Coli before and after irradiation (electrophoresis)

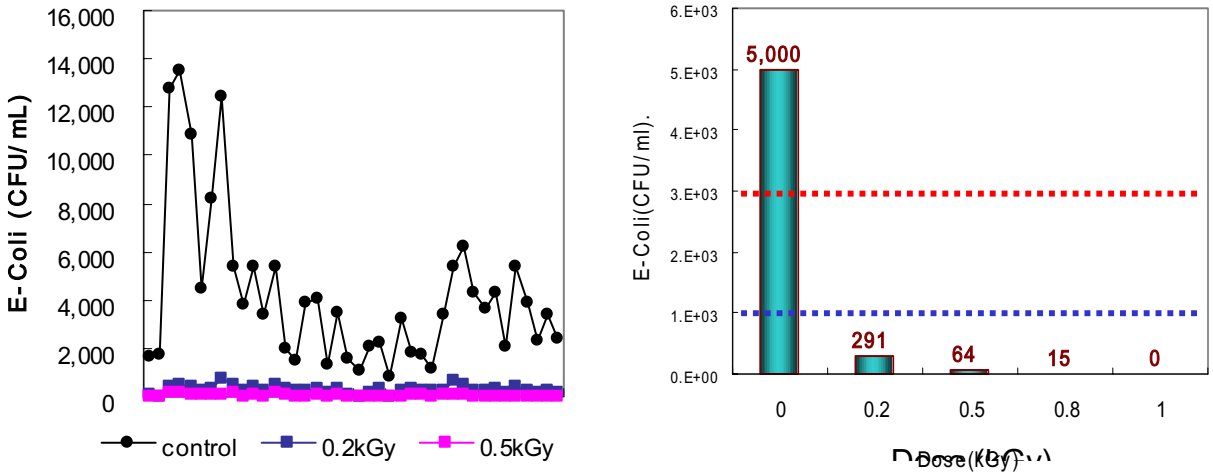

FIG. 4. Disinfection of E-Coli. with different doses

In conclusion, radiation disinfection appears to be an alternative method to replace the traditional chlorination method of treating effluent from municipal wastewater treatment plant, especially if the treated effluent is to be re-used in irrigation or industries. This would improve the economics of the disinfection process and also reduce the residual organics.

4. ECONOMICAL ESTIMATION OF COMMERCIAL PLANT

Based on the data obtained in the laboratory experiments, the suitable doses are determined as around 0.2 kGy for the flow rate of 100,000m^3 effluent per day. Therefore, accelerator with the power of 400kW is applied for economies and compactness of the plant. Cost for high power accelerator is around 2.0~2.5M$ and building, piping, other equipment and construction works could be estimated 1.0~1.5M$. Even by considering the additional cost for tax, insurance and documentation as 0.5M$, the overall cost for plant construction is approximately 4.0~4.5M$ as is stipulated in Table V.

TABLE III. CONSTRUCTION COST OF COMMERCIAL PLANT (UNIT : M$)

	Cost	Remarks
Accelerator - 1MeV, 400kW, double window	2.0~2.5	Cost for Land, R&D, Approval from Authorities are not included
Water reactor & other Raw Material	1.0~1.5	
Installation cost – welding/piping/inspection etc.		
Design		
Shield Room & Construction works		
Others - transportation, tax, insurance etc.	0.5	
Total	4.0~4.5	~ 4M$

TABLE IV. ECONOMIC EVALUATION OF COMMERCIAL PLANT (UNIT : K$)

Items		Addition of E-beam	Remarks
Operation Cost	Invest (k$)	(4,000)	
	Interest	320	8%
	Depreciation	200	20yrs
	Electricity	336	800kW
	Labor, etc.	100	3 shift
Total cost		956	~ 1M$/yr

This doesn't include cost for land, R & D and cost for the authority approval. Expected construction period includes 11 months in civil and installation works and 3 months for trial operation. To estimate the operation cost, the electricity consumption is estimated for accelerator with 500kW (80% efficiency) and other equipment in additional 300kW to the total of 800kW. Based on the year round operation (8400hr/yr), it costs 336,000$/yr when the cost of electricity (kWh) was assumed to be 0.05$. The labor cost is calculated 3-shift with one additional operator and is approximately 100,000$/yr. Thus, the actual operation cost for 100,000m^3/day plants is 436,000$/yr and if we consider the interest and depreciation of investment, the cost comes up to around 1M$/yr. It is approximately 0.12$/$m^3$ for construction and 0.03$/$m^3$/yr for operation of above re-use plant, and is inexpensive compared to other advanced oxidation techniques such as Ozonation, UV techniques etc..

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HIGH POWER ACCELERATOR ELV-12 FOR ENVIRONMENTAL APPLICATIONS

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Abstract

In the work presented here the parameters of powerful electron accelerators of continuous action are given and the main systems of the accelerator and a wide set of supplementary devices extending the application range of the accelerator is given and results of continuous operation tests are noted.

1. INTRODUCTION

BINP designs and manufactures industrial accelerators since the end of 60-s. The ELV and ILU accelerators are working in research centers and industrial facilities in Russia, Ukraine, Germany, Poland, Czechia, Hungary, Italy, India, South Korea, China, USA, Romania, Kazakhstan.

The ELV electron accelerators are DC machines purposed for wide application in various technological processes. They are designed for round-the-clock operation in industrial conditions. The ELV machines have energy range from 0.5 MeV to 2.5 MeV and beam power up to 400 kW.

TABLE I. PARAMETERS OF THE ELV ACCELERATORS

	Energy range, MeV	Beam power, kW	Max. Beam current, MA
ELV-mini	0.2 - 0.4	20	50
ELV-0.5	0.4 - 0.7	25	40
ELV-1	0.4 - 0.8	25	40
ELV-2	0.8 - 1.5	20	25
ELV-3	0.5 - 0.7	50	100
ELV-4	1.0 - 1.5	50	100
ELV-6	0.8 - 1.2	100	100
ELV-8	1.0 - 2.5	90	50
ELV-6M	0.75 - 0.95	160	200
Torch	0.5 - 0.8	500	800
ELV-12	0.6 - 1.0	400	400

2. HOW BINP PARTICIPATE IN ENVIRONMENTAL PROGRAMMES?

1) Preliminary experiments at the BINP. We have 100 kW multipurpose accelerator that is used for several kind of EB experiments.

2) Delivery of accelerators for pilot plant. It means accelerators with power up to 100 kW, consulting of reactor, accelerator location and radiation protection designing.

3) Developing of high power EB accelerators for full scale installations. (accelerators and accelerator units with some hundred kW EB power)

3. REQUIREMENTS TO ACCELERATORS FOR WASTE WATER TREATMENT

- Energy range 1.0 - 2.0 MeV
- Total power of electron beam up to some MW
- It should consist of some hundred kW units
- Efficiency – 85 – 95%
- Continuously operation
- Computer control system
- High reliability in operation

4. THE STEPS OF DEVELOPMENT HIGH POWER ACCELERATORS AT BINP.

- Increasing beam current to 100 mA. Firstly it was realized at ELV-3,
- ELV-6 accelerators.
- Increasing extracted current to 200 mA. For this purpose we developed double window extraction device and tested it with ELV-6m accelerator.
- Accelerating tube with current 1 A. To understand the behavior of accelerating tube when it accelerates the beam current about 1 A we designed special installations for recuperation of 1.0 MeV*1.0A electron beam.
- 500 kW H/V power supply. It was tested in 500 kW Torch accelerator.
- ELV-12 accelerator

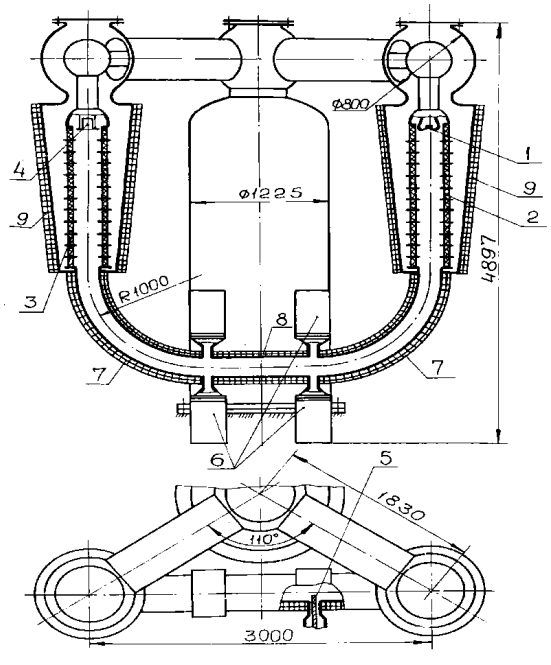

*FIG. 1. Installation for recuperation of 1.0 MeV*1.0 A electron beam (Developed and tested 1984 – 1989)*

1 - Cathode;
2 - Accelerating tube;
3 - Decelerating tube;
4 - Collector;
6 - Ion pumps,
7, 9 – Solenoids

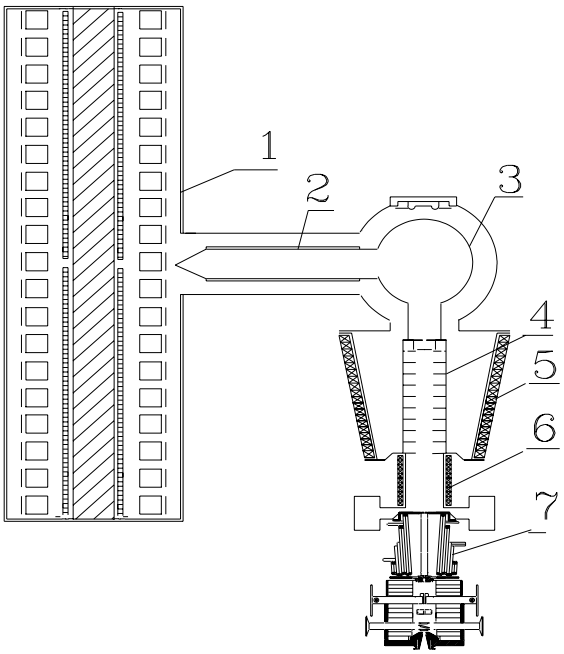

FIG. 2. 500 kW Torch accelerator (1987 – 1992)

1 - the source of accelerating voltage, 2 - gas feeder, 3 -injector control system, 4 - accelerating tube, 5,6,7 - the extraction and vacuum system.

- Max. Energy - 0.8 MeV
- Max. Current - 0.8 A
- Max. power - 500 kW
- (0.7 MeV*0.7A)

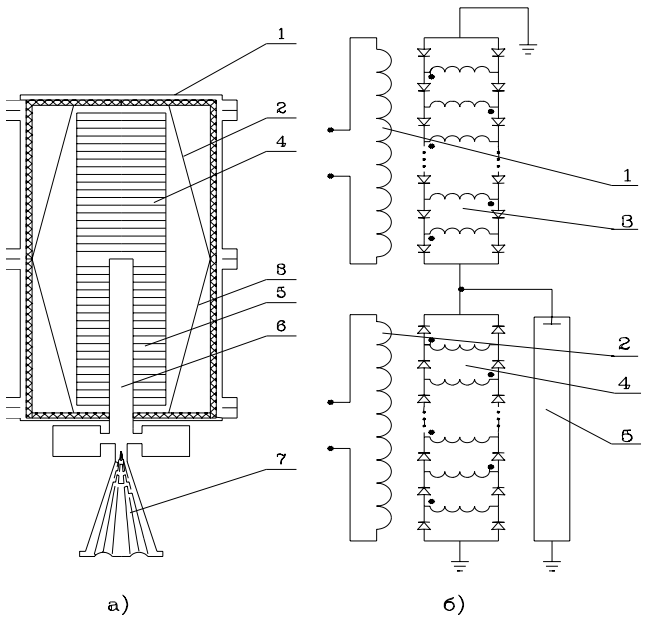

FIG. 3. ELV-6M accelerator

Max. Energy – 1.0 MeV, Max. Current - 0.2 A, Max. power - 160 kW (0.8MeV*0.2A)

- a-schematic diagram of ELV-6M.
- b - electric circuit of ELV-6M:
- 1 - tank; 2,3 – primary
- windings; 4,5 – columns
- of rectifying sections;
- 6 - accelerating tube;
- 7 - extraction device.

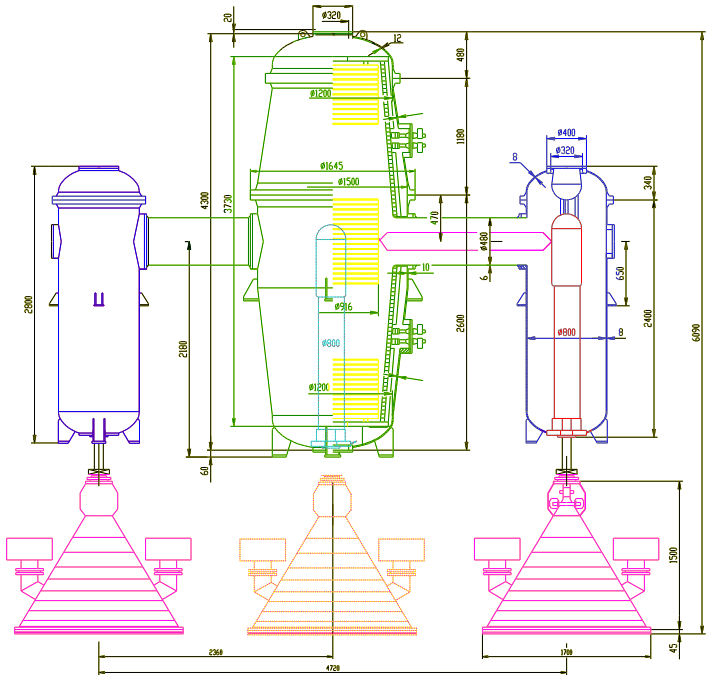

FIG. 4. ELV-12 Accelerator:

- Energy: 0.6 - 1.0 MeV,
- Max. beam power: 400 kW,
- Max beam current: 500 mA, Continuous operation, double window extraction device.

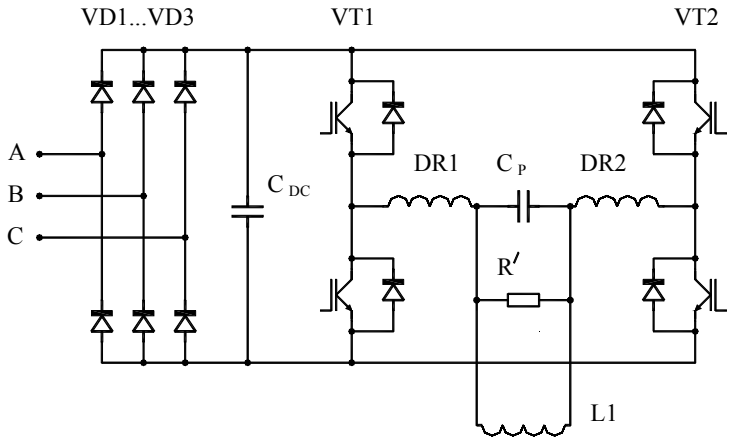

FIG. 5. Single module of frequency converter on IJBT transistors for ELV-12 power supply (125 kW, 500 - 1000 Hz)

L_1, R' means the primary winding of ELV-12 accelerator.

Frequency converter of ELV-12 consists of 4 such single modules. They are combined in pairs for upper and low primary windings. The voltage of primary windings has 90° phase shift to decrease the ripples. It includes energy stabilizer also.

Dependence of ripples as function of beam current for single and 2 phase power supply is presented in Fig. 6.

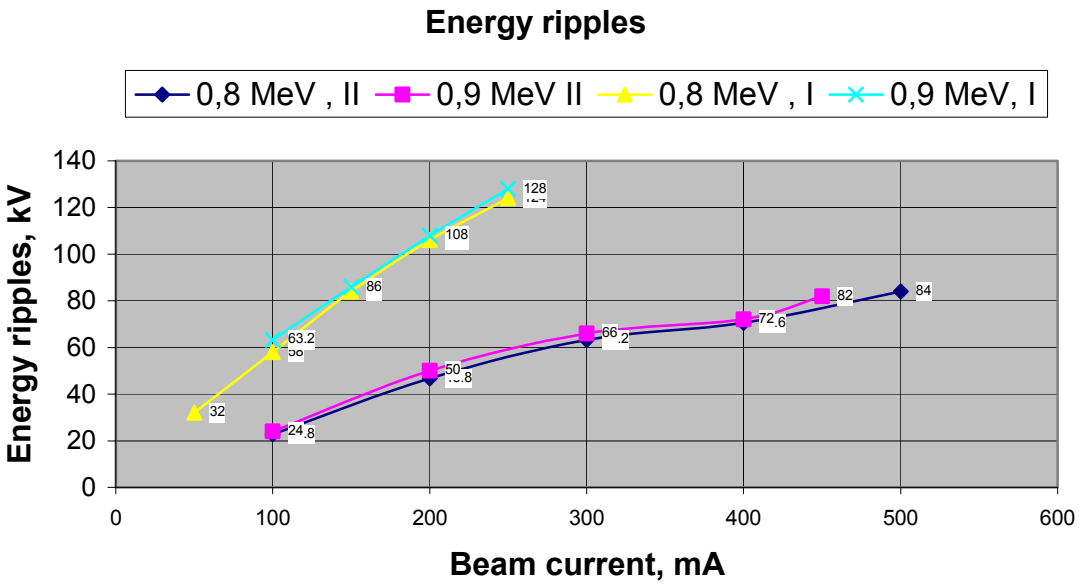

FIG. 6. Parameters of ELV-12 accelerator test

- 0.6 MeV 400 mA (240 kW)
- 0.7 MeV 500 mA (350 kW)
- 0.8 MeV 500 mA (400 kW) *
- 0.9 MeV 450 mA (405 kW) *

The duration of test at marked regimes was over 300 hours. ELV-12 is commercialized now and it is ready for delivery.

GUIDELINES CONCERNING CONSTRUCTION ACCELERATOR BASED UNIT FOR WASTE WATER TREATMENT

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Abstract

In the paper presented here the requirements to designing of wastewater treatment installations of continuous action are given and to the main systems of the accelerator and a set of supplementary devices.

1. INTRODUCTION

Usually waste water treatment installation consist of several steps. Mainly they are:

1 - Accumulate and mixing tank2 - Irradiation unit3 - Special treatment4 - Usual biological treatment, settlement, aeration, etc..

We consider the problem connected with item 2, because others units are conventional. Especially it is concerned:

- Accelerator layout
- Requirements for electron beam
- Some remarks to water transportation system
- Requirements for beam scanning system

2. ACCELERATOR LAYOUT

Accelerator produces a large amount of bremsstrahlung, so it should be placed inside of special building. This building is designed according to following requirements:

- Low level of radiation outside of building (safety for personal).
- Acceptable level of radiation inside of H/V generator room (safety for accelerator).
- Removing of ozone and others products of air radiolithis

3. THE SIMPLEST DRAWING OF BUILDING FOR ACCELERATOR.

Low level of radiation outside of building is provided by radiation shield. Radiation shield consist of enough thick concrete walls and roof.

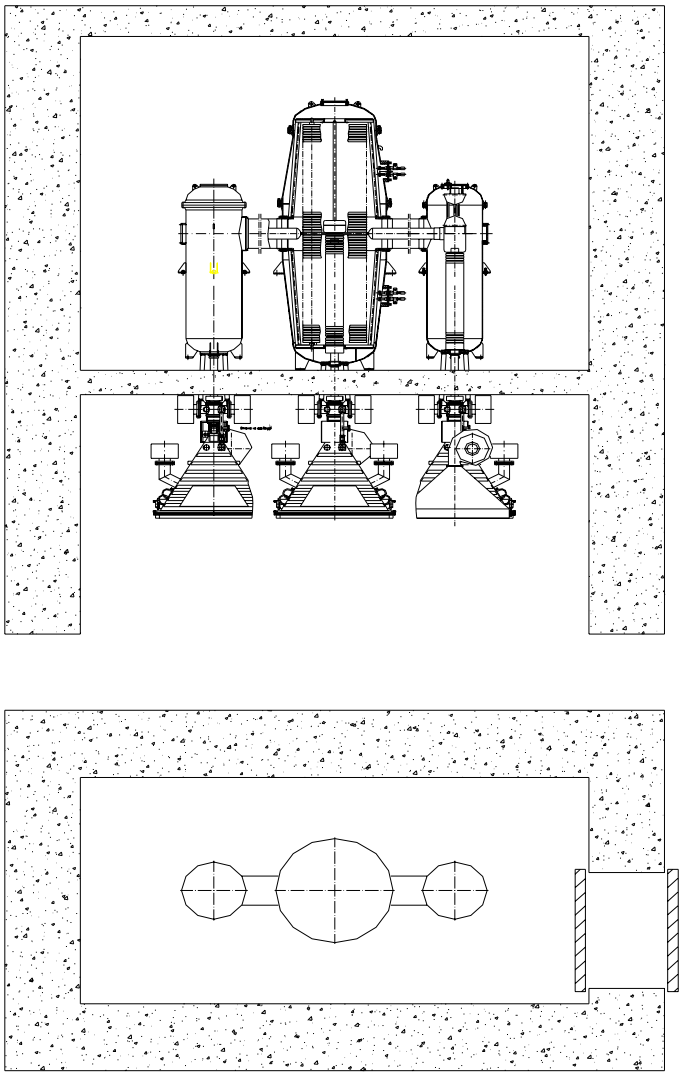

FIG. 1. Building for accelerator location

The entrance of irradiation room should be equipped by moving steel door or labyrinth. The radiation should pass out through labyrinth only after 3 reflection as minimum.

Bremsstrachlung depends from electron energy and target material. It increases both increasing electron energy and atomic number.

For example: Energy – 1 MeV, Beam power – 400 kW, 3 extraction windows with equal beam current; Distance –5m, Target material Al (similar to water), direction -90^{o}, Permitted value of leakage radiation 0.5 mkSv/h. It require reduction of radiation about $1.5*10^{7}$ times. So needed thickness of concrete wall is 130 cm.

4. BREMSSTRACHLUNG AND H/V GENERATOR

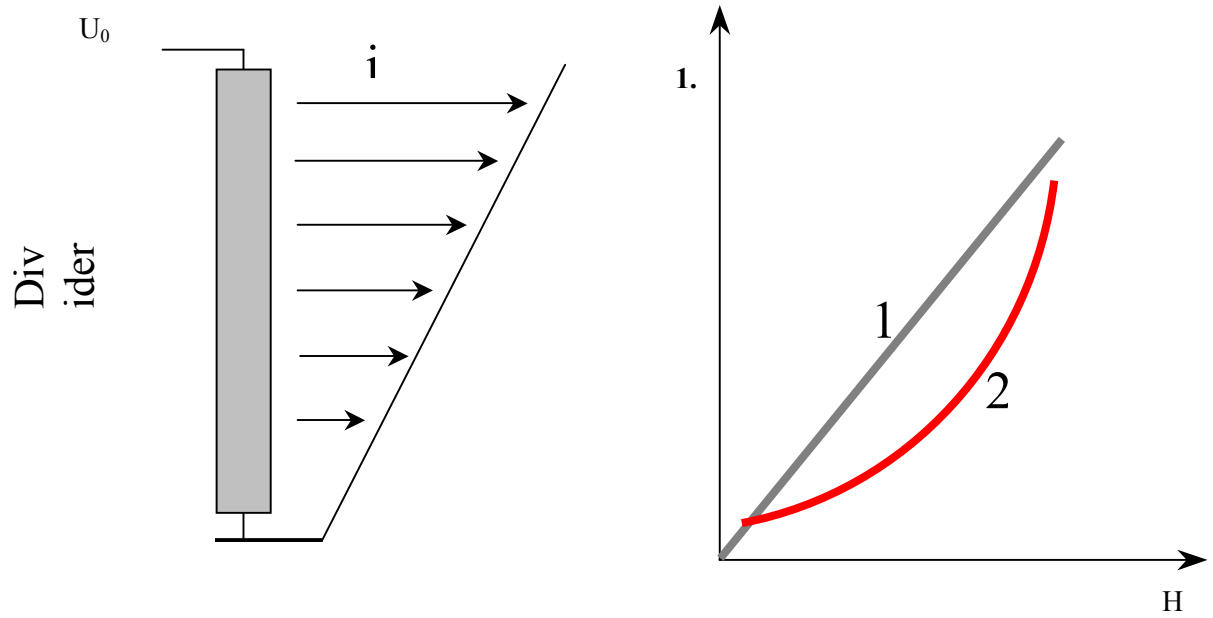

FIG. 2. Changing of potential distribution on accelerating tube due to leakage current which is produced by ionization of insulation gas.

Line 1 is normal potential distribution, line 2 — abnormal distribution.

During the operation of ELV-12 accelerator we found the decreasing of tube divider current. It was due to leakage current, which is produced by ionization of insulation gas. This leakage current changes the distributions of potential on electrodes of accelerating tube. It is shown at Fig,3. We studied this phenomena and determine the requirements for protection of H/V generator. Our estimation and experiments show that 10 – 100 times reducing is enough**.** It require 27 – 45 cm of concrete or 7 – 12 cm of steel.

5. OZONE GENERATION

During propagation of beam in air ozone and nitrogen oxides are generated. The amount of ozone can be calculated by formula:

- Moz (mg/hour)=4.2*107*I*d=42.7 kg/hour/A/m,
- Moz – amount of ozone; I – beam current (A); d – distance which beam passes in air (m)

For example: I=0.5 A; d=20 cm; Moz=4.27 kg/hour.

This estimation does not consider a radiation destruction of ozone (it's value is about 30%). If productivity of exhaust ventilation is 10000 m3/hour – output concentration is 427 mg/ m3 , 4000 times higher than permitted. So there should be install enough high exhaust tower or special devices for ozone destruction.

6. EB PROCESSING

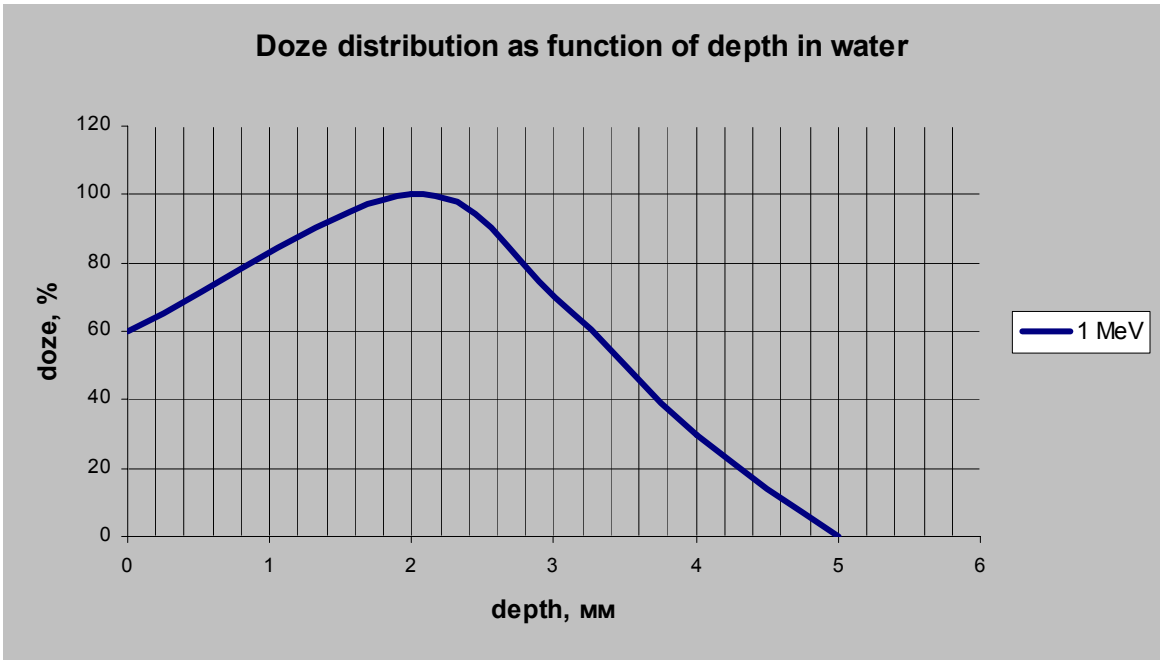

FIG. 3. Absorbed dose distribution.

The value of absorbed dose depends from depth. It is due to energy losses and scattering of electrons. There are exit two possibilities of treatment:

- single layer treatment, and
- multi layer treatment.

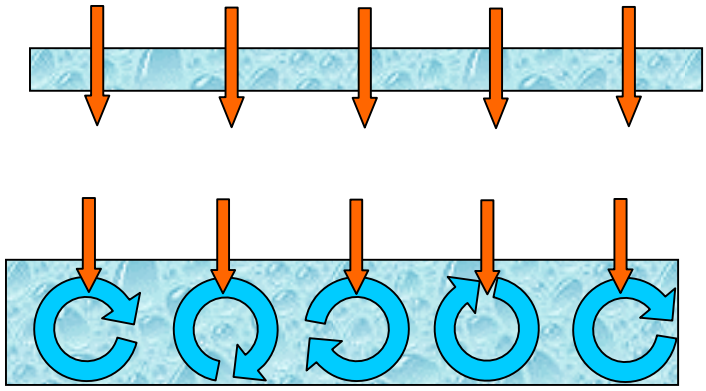

FIG. 4. Single and multi layer treatment

In case of single layer treatment the water thickness should be less than penetration depth. It should be approximately 2/3of total depth. For 1 MeV this distance is 3.5 mm

For multi layer treatment the thickness of water is some times more than penetration depth. But mixing of water or bubbling is needed.

7. REQUIRED POWER OF ACCELERATOR

The calculation of absorbed dose can be done according to formula:

$$P(kW) = M\ (kg/s)^* \ Dose(kGy, kJ/kg)^* efficiency$$

- P – electron beam power(kW),
- M mass productivity(kg/s),
- Efficiency is 0.6 for single layer irradiation
- Efficiency is 1.0 for multy layer irradiation

For example: D= 1kGy; P= 400kW; eff. = 1

M =P/D =400 (kg/s)=1440 000 kG/hour=1440 m^3/hour = 34 560m^3/day

Remarks of water flow

$$M = d^*L^*V^*\rho,$$

- M – mass productivity;
- d – thickness of flow;
- L – width of irradiation area;
- V –speed;

  ρ - density.

For example: M=400 kg/s; d=0.5 cm (single layer), d=2cm (multy layers); L=3*1.6m; ρ=1000kg/m^3:

			Single layer treatment	multy layer treatment
Flow speed:	***m/s***		***16.6***	***4.15***
Inlet pressure:	***atm***	$P= \rho V^2/2$	***1.3***	***0.1***
Pump power:	***kW***	$M^*V^2/2$	***55***	***3.5***

8. REQUIREMENTS FOR SCANNING SYSTEM

Due to scanning the electron beam treats water periodically. The maximum time between 2 irradiation (shoots) is 1/f. (f – frequency of scanning along the window)

Amount of shoots N ≅ L/a; L – width of irradiation area (in direction of water moving), a = V/f - distance that water passes between two shoots. •

Inchomogenity of absorbed dose:

$$\delta D/D \cong 1/N = V/f\ L$$

If energy 1.0 MeV, L = 0.4 m (double window extraction device); N min = 2; f =150 Hz., *Vmax. = 60 m/s*

If energy 1.0 MeV, L = 0.4m; V=16 m/s, we assume that acceptable inchomogenity can be provided by 3-4 shoots:

- f =150 Hz; N=4
- f =100 Hz; N=3

So scanning frequency along the window should be as minimum 100 Hz.WATER INSIDE OF VACUUM SYSTEM IF FOIL DAMAGE

There are special requirements to prevent the water flow in vacuum chamber if extraction foil became broken. The first is: the distance between foil and water should be about 30 cm. Second conditions - there is needed special screen plate under water jet. Due to this plate effective pressure that passes water inside of chamber became less. Other words: additional screen plate decreases difference of pressure and prevent passing of water inside vacuum system

RADIOLYTIC TREATMENT OF METHYL T-BUTYL ETHER (MTBE): PRODUCT STUDIES AND MECHANISTIC CONCLUSIONS

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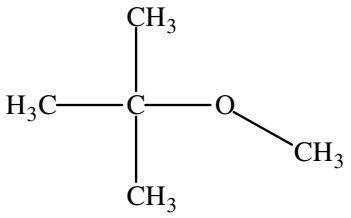
Abstract

Methyl *tert*-butyl ether, and closely related compounds have been used as gasoline additives (oxygenates) to reduce the level of volatile organic compounds from the emissions of motor vehicles. Unfortunately, large quantities of these oxygenates have been spilled into ground water and drinking water supplies creating a significant risk to the environment. Because these compounds are relatively soluble in aqueous solutions it is difficult to separate and/or treat water polluted by these additives using standard technologies. We report herein product studies from the ionizing radiation of MTBE in aqueous solutions. Based on these studies we have defined the specific reaction pathways and proposed reaction mechanisms to explain the formation and disappearance of several intermediate products.

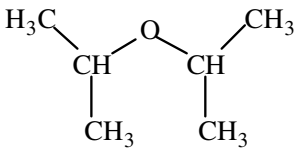
1. BACKGROUND

Alkyl ethers have been introduced into the groundwater in large quantities through leaking fuel tanks and petroleum pipelines and pose a serious environmental problem. The structure of the ethers, di-isoproproyl ether (DIPE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and methyl *tert*-butyl ether (MTBE) are illustrated in Figure 1. MTBE has been extensively used as a gasoline oxygenate to produce cleaner burning fuel in response to the federal government's demands for better air quality. But the once-championed MTBE now finds itself at the center of controversy over its potential to contaminate groundwater and its possible health risks (1). MTBE contamination has reached such high levels in Santa Monica, California that the city has to import water from other areas. The aroma of MTBE can be detected by humans in quantities lower than the levels being considered unacceptable for health reasons, down to levels as low as 13.5 ppb, thus creating additional public concern.

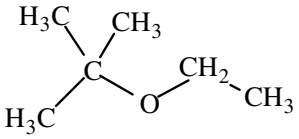
In general, the use of alkyl ethers as fuel additives is a serious problem because they are relatively soluble in water, resistant to biodegradation, travel through soil quickly and persist in the environment for long periods of time. Since these ethers do not appreciably absorb light in the near UV/visible region, direct photo-degradation by solar irradiation is very ineffective. In addition, oxidation in aqueous environments with naturally occurring hydroxyl radicals, and other oxidative processes, is too slow to yield significant decontamination. The unreactive nature of these compounds makes them especially persistent in the environment and difficult to remediate from contaminated waters using conventional techniques.



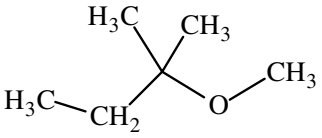
Methyl *t*-butyl ether (MTBE)



Diisopropyl ether (DIPE)



Ethyl *t*-butyl ether (ETBE)



t-Amyl methyl ether (TAME)

FIG. 1. Alkyl ethers used as gasoline oxygenates

We have demonstrated that upon treatment by the advanced oxidation processes, TiO_2 photocatalysis, sonolysis, and ionizing radiation, these fuel additives are readily degraded (2-8). Although hydroxyl radical is the predominant oxidizing species generated during TiO_2 photocatalysis, sonolysis, and ionizing radiation these processes involve significantly different reaction processes. TiO_2 photocatalysis involves the generation of hydroxyl radicals at the surface of the catalyst, sonolysis produces hydroxyl radicals during the cavitation process by homolysis of the hydrogen-oxygen bond of water, while hydroxyl radical is formed following ionization of water during electron beam treatment. Despite these significant differences in the generation of hydroxyl radical similar reaction pathways for the degradation of MTBE by these processes are observed. We present herein product studies and mechanistic conclusions for the degradation of MTBE by radiolytic techniques.

2. RESULTS AND DISCUSSION

MTBE is difficult to treat economically with conventional techniques, but it is readily degraded by radiolysis. Radiolysis of water leads to the formation of hydroxyl radicals and hydrated electrons, along with a number of other minor products, as represented below.

$$H_2O \text{ VVVV}\rightarrow (2.7)\ \bullet OH + (0.6)\ \bullet H + (2.6)\ e^- + (0.45)\ H_2 + (0.7)\ H_2O_2 + (2.6)\ H^+$$

The number in parenthesis is commonly referred to as the G-value and represents the number of species produced upon adsorption of 100 eV of energy. The reaction rate constants for hydroxyl radicals, hydrated electrons, and hydroxyl radicals with gasoline oxygenates is summarized in Table 1.

TABLE I. RATE CONSTANTS FOR THE REACTIONS OF HO•, H•, AND E_{AQ}- WITH MTBE, DIPE, ETBE, AND TAME (8).

Substrate	Rate Constants (e7 M^{-1} s^{-1})		
	HO•	H•	e_{aq}-
MTBE	200	0.4	1.8
ETBE	181	0.7	~1
DIPE	250	6.7	≤0.7
TAME	240	0.3	≤0.4

The hydrated electrons and hydrogen atoms rapidly react with dissolved molecular oxygen to yield superoxide anion radical and its protonated form, however, alkyl ethers do not react with the reducing species generated during these processes to an appreciable extent and are not susceptible to attack by superoxide anion radical. We have illustrated the predominant reactive species leading to the degradation of several aliphatic ethers with ionizing radiation is hydroxyl radical (3,4). Given hydroxyl radical is one to two orders of magnitude more reactive than hydrogen atoms and solvated electrons toward these substrates we conducted detailed product studies under conditions in which the yield of hydroxyl radicals relative to other primary reactive species is ~90 %, allowing us to selectively study hydroxyl radical reactions with MTBE. All of these reactions are run in the presence of dissolved oxygen.

Hydroxyl radicals react with MTBE by hydrogen abstraction. Two different types of hydrogens, nine "□"hydrogens and three "□" hydrogens are available for reaction with hydroxyl radical. Although abstraction of the □ hydrogen is statistically favored over □ abstraction, the □ abstraction reaction pathway is the major reaction pathway because of the stereo-electronic influence of the oxygen atom. The primary reaction products from alpha abstraction are tert-butyl formate (TBF) and tert-butyl alcohol (TBA). Aqueous solutions of TBF were subjected to gamma radiolysis under hydroxyl radical generating conditions and yield acetone as the major reaction product. It is important to note that TBF reacts rapidly with hydroxyl radical to form acetone and not TBA in the presence of molecular oxygen. Acetone is also observed from the radiolysis of TBA. Our product studies of MTBE suggest the following initial reaction sequence is operative for the hydroxyl-mediated degradation of MTBE.

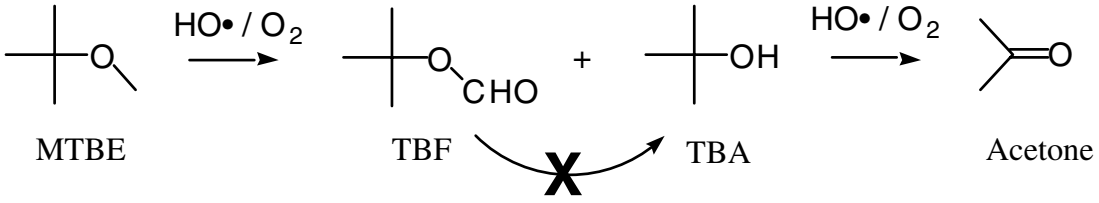


FIG. 2. Primary reaction pathway for radiolytic degradation of MTBE.

Acetone is degraded slowly relative to MTBE under radiolysis conditions. We propose the following mechanism to explain the primary reaction products observed for α hydrogen abstraction by hydroxyl radical in the presence of oxygen. The major initial reaction pathway involves hydrogen abstraction from the methyl group attached to the oxygen. This leads to a carbon centred radical which is stabilized by interaction with the orbitals of the non-bonding electrons on oxygen. Although hydrogen abstraction from the methyl groups of the *t*-butyl group is statistically favoured, t-butyl format is the major initial product indicating the hydrogen abstraction is significantly faster at the methyl group attached to the oxygen.

The resulting carbon centred radical can react with oxygen to form the corresponding peroxyl radical, which can undergo dimerization to yield the tetroxide. The tetroxide can eliminate molecular oxygen to give TBF and a hemi-acetal. While TBF is stable to hydrolysis under the experimental conditions, the hemi-acetal will readily hydrolyze to yield the observed products, TBA and formaldehyde.

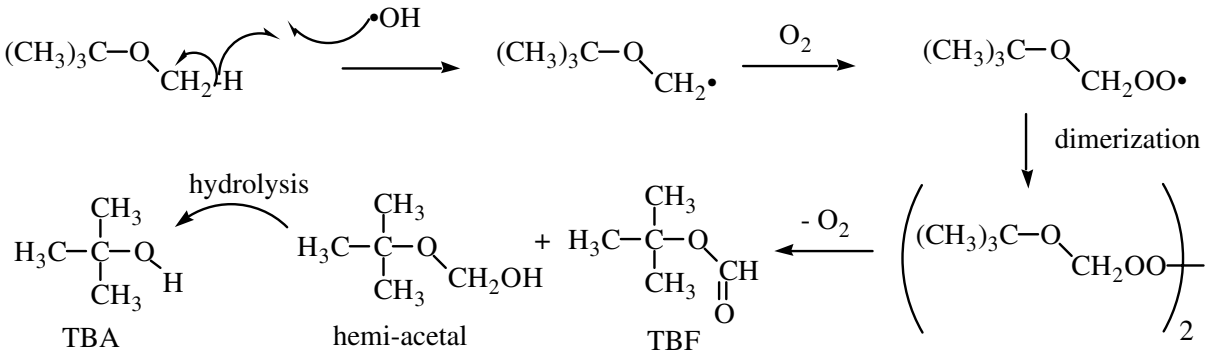


FIG. 3. Proposed reaction mechanism for the formation of TBF and TBA

We have also identified a number of products formed from β hydrogen abstraction reaction pathway. The products from β-abstraction include methyl acetate and acetone. We proposed the following reaction sequence to explain the formation of methyl acetate and acetone as products from β abstraction.

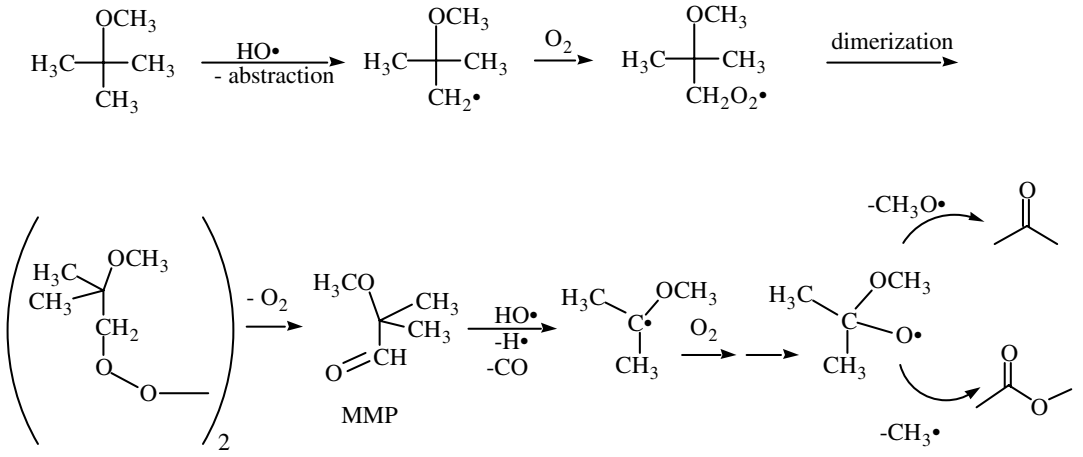


FIG. 4. Proposed reaction sequence for hydroxyl-radical mediated oxidation at the β position.

Hydrogen abstraction leads to a carbon centered radical which will undergo standard hydroxyl radical oxidation pathways. MMP will react rapidly with hydroxyl radical and thus its concentration should not build-up under our experimental conditions. Although we were unable to confirm the presence of 2-methyl-2-methoxypropanaldehyde (MMP) it could be formed but at levels below our detection limit. The reaction of MMP can lead to a carbon-centered radical, ultimately producing acetone and methyl acetate.

3. CONCLUSIONS

MTBE is readily degraded through by radiolysis to yield a number of low molecular carbonyl compounds and *t*-butyl alcohol. The reaction products are rationalized in terms of hydroxyl radical mediated pathways. In the presence of oxygen, α abstraction results in the formation of the TBF and TBA as primary reaction products. TBF does not yield TBA by hydroxyl radical mediated processes. The yields of volatile organic compounds are relatively low and can be degraded at extended irradiation times. These studies contribute to a better fundamental understanding of the reactions of hydroxyl radicals with MTBE, and the resulting oxidation products. The studies are also useful for assessing the feasibility of AOTs as applicable technologies for the decontamination of MTBE in drinking water.

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ADVANCED OXIDATION TECHNOLOGIES RADICAL PROCESSES FOR WATER TREATMENT

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Abstract

This paper provides a general overview of the use of advanced oxidation technologies (AOTs) for water purification. A comparison of AOTs, specifically radiolysis, sonolysis and photocatalysis is made and their potential applications for the specific treatment objectives are considered.

1. INTRODUCTION

There is a critical need for the development of innovative technologies for the cleanup and purification of water for human consumption and re-use. Current adsorption and air stripping water treatment methods simply transfer pollutants from one medium to another and may require additional treatment. A number of organic pollutants are resistant to bioremediation, or the longer trains of processes known as tertiary (or advanced) treatment, however radicals generated during advanced oxidation technologies can lead to the remediation of an extensive variety of organic pollutants. AOTs are characterized by the production of the highly oxidative hydroxyl radical at ambient temperatures for oxidative destruction of organic compounds, which can ultimately lead to complete mineralization with the formation of CO_2, H_2O and mineral acids (1).

$$\text{Organic pollutants -AOTs}\rightarrow CO_2, H_2O, \text{mineral acids}$$

A wide range of AOTs have been developed for the treatment of aqueous waste streams with a single treatment process or by combinations of ozonation, UV irradiation with or without catalysts such as TiO_2, ultrasonic irradiation, electron beam irradiation, γ-ray irradiation, Fenton processes and hydrogen peroxide. AOTs fundamentally rely on the production of large fluxes of hydroxyl radicals which, in the presence of complementary oxidants (e.g. ozone or H_2O_2) or upon extended treatment, can bring about (in favorable cases) complete mineralization of organic matter (2). Hydroxyl radicals can oxidize a variety of organic materials and are central to the application of AOTs for treatment of pollutants in water.

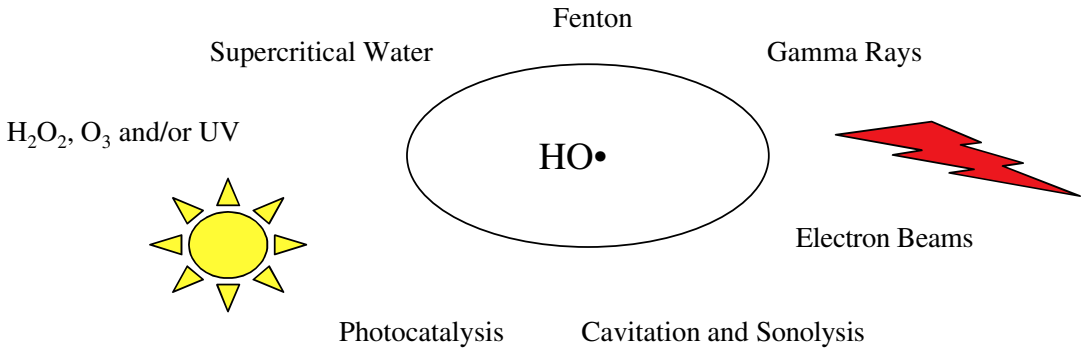

FIG. 1. Examples of advanced oxidation technologies employing hydroxyl radical.

The reactions of hydroxyl radicals with organic substrates can involve a number of competing reaction pathways, addition, electron abstraction and hydrogen abstraction being the most common, as illustrated below.

- Hydrogen Abstraction $R\text{-}CH_3 + HO\bullet \Rightarrow R\text{-}CH_2\bullet + H_2O$
- Addition $H_2C{=}CH_2 + HO\bullet \Rightarrow HOCH_2CH_2\bullet$
- Electron Abstraction $Y + HO\bullet \Rightarrow Y^{+\bullet} + HO^-$

The bimolecular rate constants for these hydroxyl radical reactions are large typically ranging from 10^8 to 10^{10} sec^{-1} M^{-1}(3). These paths usually result in the formation of free radical species that react with molecular oxygen to form peroxyl radicals and undergo standard chain oxidation reaction pathways. The typical products of such radical chain oxidation reactions are carbonyl compounds (aldehydes and ketones), organic acids, esters and alcohols which are often less toxic and more amenable to bioremediation.

Ozone is a commonly used oxidant for drinking water treatment. Comparison of reaction rate constants for ozone and hydroxyl radicals with different classes of organic compounds is provided in Table I. The reactions of ozone are dramatically slower for all the substrates listed and for all practical purposes limited to olefinic organic compounds. The formation of bromate is a concern in the use of ozone treatment for drinking water, but ozone is much more selective than hydroxyl radical and may be advantageous especially in the treatment of drinking waters containing significant levels of dissolved organics which readily consume hydroxyl radical. Regardless ozone has will be effective for the treatment of a limited number of pollutants.

TABLE I. RATE CONSTANTS FOR O_3 AND HO• REACTIONS WITH ORGANIC COMPOUNDS IN WATER.

	Rate Constant (sec^{-1} M^{-1})	
Substrate	Ozone	Hydroxyl Radical
Acetylenes	50	10^8-10^9
Alcohols	0.01-1	10^8-10^9
Aldehydes	10	10^9
Alkanes	0.01	10^6-10^9
Aromatics	0.01-1	10^8-10^{10}
Carboxylic Acids	0.001-0.01	10^7-10^9
Chlorinated Alkenes	0.1-1000	10^9-10^{11}
Ketones	1	10^9
Organo-Nitrogen	1-100	10^8-10^{10}
Olefins	1000-100000	10^9-10^{10}
Phenols	1-100	10^9-10^{10}
Organo-Sulfur	1000-10000	10^9-10^{10}

The table displays approximate rate constants for reactions between hydroxyl radical and organic compounds containing the functional groups shown. Data used to prepare the table are from the reference (3).

Chlorination of drinking water is widely used for disinfection, but the process often leads to undesirable disinfection by-products (DPBs). AOTs have the potential to be used for biological disinfection and chemical remediation without the formation of DBPs or bromate. The next section of this paper will focus on the fundamental aspects of sonolysis, photocatalysis, and radiolysis followed by concluding remarks on the potential applications of these AOTs.

2. RADIOLYSIS

Radiolysis and ionizing radiation are currently employed in a number of industrial and environmental processes, including sterilization of medical devices, cross-linking and degradation of polymers, and treatment of flue gases. The use of radiolysis and electron beam technologies for the treatment of contaminated water is based on reactive species generated during the radiolysis of water (4). Ionization of water leads to the formation of hydroxyl radicals and hydrated electrons, along with a number of other minor products, as represented below.

$$H_2O \text{ VVVV}\rightarrow (2.7)\ \bullet OH + (0.6)\ \bullet H + (2.6)\ e^- + (0.45)\ H_2 + (0.7)\ H_2O_2 + (2.6)\ H^+$$

The number in parenthesis is commonly referred to as the G-value and represents the number of species produced upon adsorption of 100 eV of energy. The hydrated electrons and hydrogen atoms rapidly react with dissolved molecular oxygen to yield superoxide anion radical and its protonated form.

$$O_2 + e^- / H\bullet \rightarrow O_2^{-\bullet} / HO_2^{-\bullet}$$

Nitrous oxide gas can be used to convert the hydrated electrons to hydroxyl radicals, although it is generally not practical for environmental applications. Hydroxyl radical scavengers such as t-butanol can be used to consume the hydroxyl radical for selectively studying hydrated electron. Hydrated electron is a powerful reducing agent and potentially could be used for treatment of halogenated compounds, but it is extremely reactivity towards molecular oxygen requiring that the solutions be deoxygenated prior to treatment, a costly prospect.

While a number of reactive species are formed during radiolysis, hydroxyl radicals are the most important for remediation and react with organic compounds to form radicals, which in the presence of molecular oxygen undergo radical chain oxidation processes. Superoxide anion radical, formed by reaction of oxygen with hydrated electrons and hydrogen atoms, can also be involved in the formation of hydrogen peroxide and radical chain processes. Radiolysis leads to the formation of hydroxyl radicals in a homogeneous environment. Under such conditions the reactions follow condensed phase reaction pathways and can be accurately predicted and modeled.

3. PHOTOCATALYSIS

Titanium dioxide is inexpensive, stable, readily available and the most extensively studied semiconductor photocatalyst for the purification of water and air (5). Photoexcitation of TiO_2 requires light with wavelengths of $\leq$ 380 nm. Upon absorption of a photon by TiO_2, an electron is promoted to the conduction band, generating what is commonly referred to as an electron-hole pair, shown below.

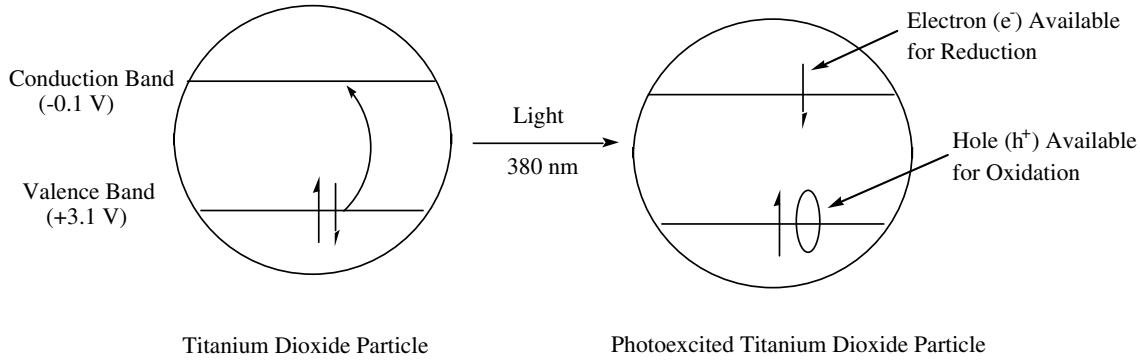

FIG. 2. Photoexcitation of titanium dioxide.

The conduction band election is available for reduction and the valence band hole available for oxidation, unfortunately under ambient conditions rapid recombination of the electron with the hole leads to very low quantum yields. Use of electron scavengers, like oxygen can trap the electron prolonging the lifetime of the hole.

$$O_2 + e^-_{cb} \rightarrow O_2^{-\bullet}{}_{abs}$$

The hole can subsequently react by electron transfer with a substrate to form a radical species or hydroxide (water) to form hydroxyl radical. In condensed oxygenated aqueous media the surface of TiO_2 is completely hydroxylated and upon photoexcitation generates hydroxyl radical in an adsorbed state,

$$h^+_{vb} + HO_{abs} \rightarrow HO\bullet_{abs}$$

subsequent reactions require diffusion of a substrate to the adsorbed hydroxyl radical (active site) or diffusion of the hydroxyl radical into the solution or across the catalyst surface. These reactions occur at or near the liquid-solid interface and are subject to heterogeneous mass transfer limitations and diffusion constraints. In the case of extremely strongly adsorbed substrates direct oxidation by the hole may compete with the formation of hydroxyl radical.

4. ULTRASONIC IRRADIATION

Ultrasonic irradiation of aqueous solutions can result in the growth and collapse of gas bubbles (cavitation) producing high transient temperatures (up to 7,000 K in aqueous phase) and pressures (up to 1,000 atm), which leads to the formation of free radicals via the homolysis of water (6).

$$H_2O))))) H\bullet + \bullet OH$$

Ultrasonic irradiation has shown promise for the purification of contaminated water and involves at least in significant part standard hydroxyl radical mediated chain oxidation processes 6,7).

Hydrogen atom reacts with oxygen or undergoes termination and is generally not considered to be important in the degradation of organic substrates during sonolysis. The sonochemical treatment of a variety of organic pollutants yields low molecular weight carboxylic acids as the final products.

Three regions, gas phase, gas-liquid interface, and bulk liquid solution are present during cavitation, illustrated below. The most extreme conditions are generated in the gas phase, commonly referred to as the hot-spot. Significantly high temperature and pressure conditions produced at the gas-liquid interface can accelerate hydrolysis, eliminations, low temperature pyrolysis and supercritical water oxidation processes that are not observed from other AOTs. Changes to the bulk solution are relatively insignificant.

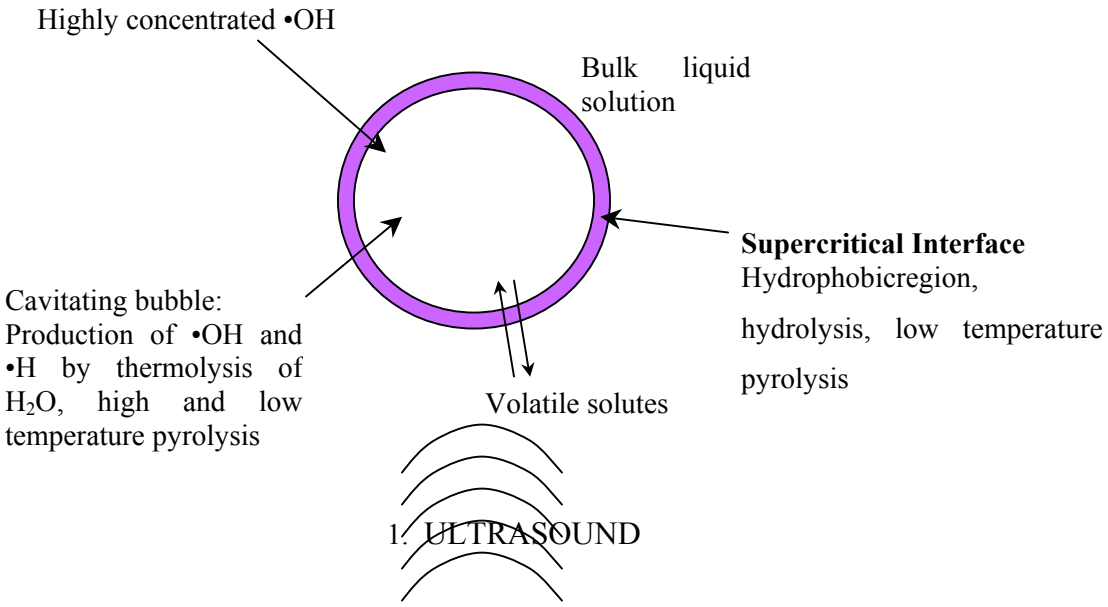

FIG. 3. Schematic illustration of cavitation caused by ultrasonic irradiation.

Ultrasonic technology is well advanced and used for a number of industrial applications (*i.e.,* for cleaning, pigment dispersion, etc). Versatility of ultrasonic irradiation should make it adaptable for the removal of problematic contaminants in aqueous phase. Despite the tremendous interest in the ultrasonic irradiation induced degradation of pollutants, much of the fundamental understanding and characterization of these complex processes are still at the preliminary stages.

5. CONCLUSIONS

Ultrasonic irradiation and radiation technologies, have been developed for a number of industrial applications, can provide high fluxes of hydroxyl radical in aqueous media and are highly attractive for the remediation of organic contaminants from water. While these technologies can be used to degrade a variety of contaminants, actual application will likely require a combination with other treatment methods such as bioremediation to afford economical solutions for large-scale wastewater treatments.

Electron beam (EB) technologies offer excellent conversion of electrical power for the production of hydroxyl radicals compared to other AOTs and are attractive for treatment of large volumes of contaminated water, however there are large costs associated with the construction of EB treatment facilities.

Ultrasonic treatment systems are available for a variety of treatment capacities, but involve relatively poor conversion of electrical energy for treatment purposes. Volatile organic compounds are concentrated during the compression-expansion cycles of ultrasonically induced cavitation resulting in more effective treatment.

Ultrasonic irradiation is also applicable for solutions, which contain solids, and/or are turbid which cannot be effectively treated by AOT methods involving UV or visible light because of light scattering and absorption. Photocatalysis generates relatively low fluxes of hydroxyl radicals and has limited application to dilute contaminants or substrates, which exhibit good surface adsorption. While detailed studies of the different AOTs are required for the evaluation and ultimate application of AOTs treatments for specific treatment criteria, electron beam irradiation and other means of ionizing radiation appear to be one of the most promising technologies for general economical treatment of a variety of contaminated waters.

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A STUDY ON THE REMOVAL OF COLOR IN DYEING WASTEWATER USING ELECTRON BEAM IRRADIATION

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Abstract

In this research, experiments of electron beam irradiation have been carried out for the wastewater from different types of dye industry, and for the reactive dye, for the acid dye and for the disperse dye which are commercially widely used with respect to industrial dyeing process. At the electron beam irradiation dose of 2.34KGy, the efficiency of color removing was higher than that of usual chemical treatment for the reactive dye and for the acid dye. Wastewater from printing dye industry showed the highest measuring value of color among the wastewater from different types of dye industries, which are polyester, cotton T/C, printing, yarn dyeing, and nylon dye industry. Electron beam irradiation tests have been performed for the wastewater from different types of dye industries. Color removing rates by electron beam irradiation were higher than those by general chemical treatment for the wastewater from cotton T/C dye industry and from yarn dyeing industry, and whose dispersive dye contents are low. EA (electron beam irradiation + activated sludge) process and CA (chemical treatment + activated sludge) process have been tested for removing color and organic substance in wastewater from different types of dye industries. EA process showed better results in color removing rate for the wastewater from cotton T/C dye industry and yarn dyeing industry. However, CA process showed better results in color removing rate for the wastewater from polyester, printing, and nylon dye industry. CA process were predominant in COD_{Mn} removal rates compare to EA process for the wastewater from different types of dye industries. However, both CA and EA processes showed less than 80mg/L of BOD_5, which is the legal effluent guideline.

1. INTRODUCTION

It is presumed that water usage for 1 metric ton of production is about 300～400 ton in dye industry. Industrial water is directly used for size removing, refining, bleaching, and for washing process. In process classification more than 80% of the water is used for pre-treatment and for washing. The problem of organic pollutant and color is originated in dyeing process, and which intimidates the productivity of dyeing industry. Since color is easily detected, even though the effluent is good enough for the regulation, it is still serious point of argument.

Dyes causing color problem in dye processing industry are classified into direct dyes, acid dyes, disperse dyes, and reactive dyes according to the subject material. Different dyes are widely used in the category of dye process. In the category of polyester disperse dyes are mostly used. In this category of blended fabric with value added to the original subject, a mixture of reactive dyes and acid dyes is used. In the category of cotton, and T/C water-soluble reactive dyes are mostly used. In the category of polyester and nylon mixture, disperse dyes and acid dyes are blended. In the category of nylon reactive dyes, disperse dyes, acid dyes are mixed by a certain ratio. Dyes used for process industry, like this, are various according to the ways, and to the categories. The amount and concentration of wastewater from those industries are much different.

However, effective and economic wastewater treatment system, which consider the characteristics of wastewater from different types of dye industries, is not fixed ,yet. Cost increase in wastewater treatment due to combined facilities of unit operation, makes weak competitiveness. Thus, economic ways of wastewater treatment is acutely demanded. Recently advanced researches, which try to solve problems of existing wastewater treatment facilities and to meet consolidated regulations relating to dye wastewater, are actively performed in electron beam irradiation, electrolysis, chemical oxidation by chlorine and ozone, advanced oxidation by UV-catalyst-hydrogen peroxide-ozone).

There are special points and merits, demerits in those methods by the ways of application. However, economic aspects of operating cost and maintenance cost in real field are mostly important. In this aspect, wastewater treatment by electron beam irradiation can be one of very possible ways.

In the wastewater treatment process by electron beam irradiation, aqueous electron, hydrogen and OH radicals produced from electron beam irradiated to the wastewater decompose organic pollutants in the wastewater. Active researches are currently carried out in the areas of industrial wastewater treatment, drink water purification, sludge reduction in Japan, USA, and Russia.

Due to the different sources of pollutants and operating conditions of facilities, commercial plants are not operating, yet. It is known that electron beam irradiation process is highly economic, since no chemicals and no catalysts are needed. It is expected that many advantages like small areas of facilities, safety, no secondly pollution problem, continuous operation, automatic control, can solve the problems of existing wastewater treatment facilities.

Since 1995 an electron beam irradiation facility has been operating for the dye wastewater from reducing weight operation. And the operating cost including chemicals, electricity, sludge dumping is reported half of the cost for the conventional plant. Regardless of many advantages, commercial plants of electron beam irradiation are not built, yet, due to the incompletion of operating conditions for the wastewater from different types of dyes and categories. Thus, much studies should be continued.

In this study, relating to dye processing, comparison of wastewater treatment between chemical and electron beam irradiation methods. Color removing efficiency by above methods for three different types of dyes, such as reactive dyes, disperse dyes, acid dyes, which are widely used in dyeing industry have been studied.

2. APPARATUS AND METHODS

2.1. Material

Dyes used for the experiments are selected according to the commercial dyes applied to the subjects produced from the companies in D-Dye Industrial Park. Those are reactive, disperse and acid dyes. And three different colors, such as red, blue, and yellow are prepared for the three different types of dyes, respectively. The concentration of each dyes for the experiments are decided under the bases of wastewater color from each unit operation. Prepared color is 3,000(degree), and Table 1 illustrates the details.

The wastewater used for the electron beam irradiation experiment are prepared from a random company of the D-Dye Industrial Complex. The experimental purpose is to find color removing efficiency for the different types of dyes. The original wastewater from polyester, cotton T/C, printing, yarn, nylon dye industries are directly used for the experiments. Table 2 shows the characteristics of wastewater from each companies in D-Dye Industrial Park.

2.2. Apparatus

2.2.1. Electron Beam Irradiation Facility

Electron Beam Accelerator is ELV-4 type, with 0.95MeV Energy and 40kW Power, which has been currently operated in the Wastewater Treatment Center of D-Dye Industrial Complex. Figure 1 shows electron beam irradiation facility.

2.2.2. Batch reactor

Batch reactor used for electron beam irradiation experiments of artificially made dye solution and wastewater of different types of dye industry was a quadrangle of 37.5cm×24.5cm×5.3cm, and was made of Pyrex. For bubbling Pyrex glass tube of inner diameter 7mm was made inside of the reactor. Inside this tube several tens of crevice with less than 1mm inside diameter were manufactured to give enough air supply. Air pressure was set as 3psi to give enough air throughout the reactor.

2.2.3. Sample transfer Unit

Batch reactor was set on the top of the experimental sample transfer unit established in the lower part of the electron beam bell mouth. Transfer speed of the tray was controlled to 3.0m/min, and the number of transfer was once. Time for electron beam irradiation was about 1second to 2 seconds, after considering the actual size of the bell mouth where electron beam is coming out. The irradiation distance between sample and electron beam bell mouth was 11cm.

3. EXPERIMENTAL METHOD

Electron beam irradiation experiments of artificially made dye solution and of wastewater from different types of dye industry were performed at batch reactor. Batch reactor was set to be transferred once at speed of 3.0m/min under the bell mouth of electron beam accelerator, and current was controlled to change electron beam dose. Prepared samples were dye solution and wastewater from different categories of dye industry. Sample depth injected to the batch reactor was 4mm. This depth is based on the capacity of electron beam accelerator of D-Dye Industrial Complex, which has a 0.95MeV energy and 40kW power. Electron beam currents are changed 15mA, 30mA, 40mA, 50mA. The absorbing dose for these currents are 1.17KGy, 2.34KGy, 3.12KGy and 3.90KGy, respectively. Samples before and after electron beam irradiation are analyzed in the area of color, COD_{Mn}, BOD_5, Wavelength Scan (Perkin Elemer, LAMBDA18).

4. RESULTS AND DISCUSSION

2.1. Dye wastewater treatment by electron beam irradiation for different electron beam dose

Fig. 2 shows the electron beam irradiation results for different dose applied to the wastewater of D-Dye industrial Park. The wastewater used for the experiments are wastewater mixture from individual companies in D-Dye Industrial Complex. The wastewater mixture contains very diverse organic pollutants, and average value of the COD_{Mn} is 670mg/L, of the BOD_5 is 1,200 mg/L, of the color is 1,000(degree).

As shown Fig. 2, with increasing electron beam dose, color is strongly decreased and COD_{Mn} is more or less increased. It might be explained that TPA(Telephthalic Aicd) and EG(Ethylene Glycol) which are well known hardly destructive material in dye wastewater are changed into somewhat easily destructive material after electron beam irradiation. BOD was slowly decreased according to the increase of electron beam dose.

Electron beam dose for dye solution and for dye wastewater from different categories of dye industry was decided as 2.34kGy (electron beam current 39mA), after considering the above test results, electron beam accelerator capacity, amount of wastewater for treatment, economic aspect of cost, active sludge method after electron beam treatment, and etc.

2.2. Electron beam irradiating treatment for different dyes

For the artificially made dye solution shown at Table 1, color removing test results, by electron beam irradiation at the electron beam dose of 2.34kGy in the case of air injection of 3psi pressure or no air injection, are illustrated at Table 3. As shown at Table 3, color removing efficiency of dye solution by electron beam irradiation was very high. On the contrary, in the case of C.I. Disperse Red 60, which is dispersive dye, color became higher by electron beam irradiation. It is estimated that lower solubility of C.I. Disperse Red 60 became higher after electron beam irradiation. Meanwhile, Choi, and etc,. reported more than 50% of color removing efficiency for one of the dispersive dyes of C.I Disperse Red 152 at electron beam dose of 5 ~ 25kGy with air bubbling. But, air bubbling effect for the color removing from dye solution by electron beam irradiation was revealed to be insignificant in this study. It is estimated that electron beam irradiation dose in this study was relatively lower and absolute color degree of the dye used for this study was 2.5 times higher.

2.3. Results of electron beam irradiation treatment for the blended dye solution

Reactive dye mixture solution (reactive red 120:reactive blue 160:reactive yellow 84=1:1:1(wt%)), acid dye mixture solution (acid red 336:acid blue 350:acid orange 67= 1:1:1(wt%)), and dispersive dye mixture solution (disperse red 60: disperse blue 56:disperse yellow 54=1:1:1(wt%)) has been prepared by using of dyes at Table 1. Color removing tendency by performing electron beam irradiation for the prepared dye mixture solution has been studied, and this was compared to the results of chemical treatment (Jar Test). Fig. 3 shows the comparison. Electron beam irradiation was carried out for the dye mixture solution at the dose of 2.34kGy without air bubbling. Cohesive chemicals and concentrations are as follows; sulphuric acid 1,450mg/L, poly ferrous sulfate 1,400mg/L, calcium hydroxide 1,200mg/l, polymer (K-320) 1mg/L.

As shown at Fig. 3, color removing efficiencies by electron beam irradiation in the case of reactive dye mixture solution and acid dye mixture solution was about 90%. Color removing efficiencies by electron beam irradiation in the case of dispersive dye mixture solution was less than 65%. Thus, color removing efficiency by chemical treatment was a little higher than electron beam irradiation treatment.

It seems to be the characteristics of the dispersive dyes which has low solubility at water. UV spectrum for the acid dye mixture solution was shown at Fig. 4 under conditions before and after electron beam irradiation.

2.4. Electron beam irradiation for the wastewater from different categories of dye industries

Changes in color, $COD_{Mn,}$ BOD_5 of wastewater from different categories of dye industries by electron beam irradiation have been studied. The results were compared to the chemical treatment (Jar-test), and were shown at Fig. 5 ~ 7. Table 2 shows characteristic of wastewater from different categories of dye industries used for the experiments. Electron beam irradiation condition and Jar-test experimental condition was same as section 3. Fig. 5 illustrates color removing results for the wastewater from different categories of dye industry by electron beam irradiation and by chemical treatment. Average color degree was 920, 930, 2,400, 1,400 and 670units for the polyester, cotton T/C, printing, yarn and nylon, respectively. Color of wastewater from printing operation was the highest.

Color removing efficiency by electron beam irradiation was better than by chemical treatment in the case of wastewater from cotton T/C and yarn dyeing industry. Color removing efficiency by

chemical treatment was better than by electron beam irradiation in the case of wastewater from polyester, printing and nylon dyeing industry. It is understood that dispersive dyes with low solubility's are used mostly in polyester, printing dye industry, and reactive dyes with relatively higher solubility's are mainly used in cotton T/C and yarn dyeing industries. It is confirmed that color removing efficiency of wastewater from printing dye industry is lowest because of dispersive dye with low solubility. COD_{Mn} and BOD_5 changes for the wastewater from different types of dye industries by electron beam irradiation and chemical treatment are shown at Fig. 6 and 7. As shown at Fig. 6, the overall removal efficiency of COD_{Mn} is greater in electron beam irradiation treatment than in chemical treatment.

In the case of wastewater from polyester and printing dye industry, COD_{Mn} is higher from the results by electron beam irradiation than from the raw wastewater. It is assumed that hardly destructive material like TPA and EG of wastewater from polyester dye industry, and like size and PVA(Poly Vinyl Alcohol) of wastewater from printing dye industry could be changed into easily destructive material. Fig. 7 compares the removal rate of BOD_5 by electron beam irradiation with the removal rate of BOD_5 by chemical treatment. It shows the opposite results for the different types of dye industry.

2.5. Biological treatment for the different types of dye industry

In this section the characteristics of processes treated by electron beam irradiation plus active sludge and by chemical reaction plus active sludge for the wastewater from different types of dye industries are compared. The results of COD_{Mn}, BOD_5 removal rate are shown at Fig. 8 ~ 10. The same methods of electron beam irradiation and of chemical treatment (Jar-test) are performed through the experiment. At the evaluation of biological treatment for the wastewater from different types of dye industries, two biological active sludge reactors are operated at the same time. The results were compared to find the changes in concentration and etc,.

One reactor is for the process of electron beam irradiation plus biological active sludge treatment, and the other reactor is for the process of chemical treatment plus biological active sludge treatment. The volume of active sludge reactor is 40 liter, respectively. Bubbler and temperature controller were installed at both bio-reactors. Active sludge of D-Dye Industrial Park was used for both bio-reactors.

MLSS concentration of inside two reactors was maintained as average of 2,800mg/L, and DO concentration of the reactors was maintained as average of 0.6 ~ 1.8mg/L. HRT of the reactor was 24hr, F/M ratio was maintained as 0.49, and sludge return ratio was maintained as 60%. The volume of sedimentation was 10L, and HRT was 6hr.

Fig. 8 shows comparison of the color removing results for the wastewater from different types of dye industry treated by the combined EA process, of electron beam irradiation plus active sludge, and by the combined CA process, of conventional chemical treatment plus active sludge. The average color degree for the wastewater from polyester, cotton T/C, printing, yarn, and nylon dyeing industry was 905, 960, 2,600, 2,050 and 915 Units, respectively.

EA process was better in the color removing efficiency for the wastewater from cotton T/C, yarn dyeing industry. In the case of wastewater from polyester, printing, and nylon dyeing industry the color removing efficiency of CA process was better. EA process showed about 50% of color removing efficiency for the wastewater from printing dyeing industry. CA process showed about 80% of color removing efficiency. At Fig. 9 COD_{Mn} removal efficiency for the wastewater of different types of dye industry was better in CA process. Fig. 10 shows BOD_5 removal efficiency by the process EA and process CA for the wastewater of different types of dye industry. BOD_5 of both process were less than 80mg/L of effluent regulation.

Overall, CA process showed better removal efficiencies of color and organic pollutants than EA process under conditions for the experiments. The results were opposite to the kinds of dyes and to the different types of dye industry.

Possible treatment of dye wastewater by electron beam irradiation were confirmed. However, power of the electron beam accelerator should be increased, and dose control of the electron beam accelerator should be studied to the smallest detail. Also, electron beam irradiation process study should be carried out in future to overcome the limit of irradiation depth (currently 4mm) which is related to economic evaluation and accelerator capacity. Reactor design should be performed in future to give even distribution of irradiation inside the reactor.

Even though EA process showed a little worse results compared to CA process for dye wastewater treatment, EA process was much better than CA process for operating and managing cost of the facilities like chemical cost and sludge dumping cost. If several ways of inducing efficiency increase by the electron beam accelerator such as multi bell mouth type (3 beam or 6 beam type), decreasing irradiation distance between bell mouth and irradiating objects, better reactor design, etc,. are prepared, electron beam accelerator process will be expected to solve many problems of conventional dye wastewater treatment.

5. CONCLUSION

Many experiments were carried out for various dyes and wastewater from different types of dye industry by using electron beam accelerator with 0.95MeV energy and 40kW power 0.95MeV. The results were as follows.

1) At 2.34 kGy of electron beam irradiation dose, for reactive dyes and acid dyes, color removal efficiency by electron beam irradiation treatment were better than by chemical treatment

2) Wastewater from printing dyeing industry showed highest analysis result in color among other wastewater from polyester, cotton T/C, yarn, nylon dyeing industry. For color removing efficiency of wastewater from different types of dye industry, electron beam irradiation treatment showed better result than chemical treatment in cotton T/C and yarn dyeing industry. For color removing efficiency of wastewater from different types of dye industry, chemical treatment showed better result than electron beam irradiation treatment in polyester, printing, nylon dyeing industry.

3) In the case of COD_{Mn} removal efficiency chemical treatment showed better result than electron beam irradiation treatment. But, BOD_5 removal efficiency showed opposite results according to the types of dye industry.

4) In the case of color removal efficiency EA process showed better result than CA process in cotton T/C and yarn dyeing industry. But, the result was opposite in the case of polyester, printing, and nylon dyeing industry.

CA process showed better results in COD_{Mn} removing efficiency, and both CA and EA processes showed less than 80mg/L of BOD_5 analysis value.

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TABLE I. NAMES OF DYE

Dyes	C.I. Generic Names	Commercial Names
Reactive dye	C.I. Reative Red 120	Suncion Red H-E3B
	C.I. Reative Blue 160	Suncion Blue H-ERN
	C.I. Reative Yellow 84	Suncion Yellow H-Z4RN
Acid dye	C.I. Acid Red 336	Nylosan Red N-2RBL
	C.I. Acid Blue 350	Nylosan Blue N-BLN
	C.I. Acid Orange 67	Nylosan Yellow N-3RL
Disperse dye	C.I. Disperse Red 60	PALANIL Red FD-BFY
	C.I. Disperse Blue 56	DZANIX Blue E-R
	C.I. Disperse Yellow 54	PALANIL Yellow 3GZ

TABLE II. CHARACTERISTICS OF DYEING WASTEWATER FROM DIFFERENT TYPES OF DYE INDUSTRY (UNIT : MG/L EXCEPT FOR PH)

Types of dye industry	Constituents	Concentration
Polyester	pH	12.5 ~ 13
	COD_{Mn}	910 ~ 930
	BOD_5	1,700 ~ 1,800
	Color (PtCo Color)	900 ~ 910
Polyester/Cotton	pH	12 ~ 13
	COD_{Mn}	1,070 ~ 1,200
	BOD_5	850 ~ 870
	Color (PtCo Color)	920 ~ 1.000
Printing	pH	8.2 ~ 9.5
	COD_{Mn}	650 ~ 680
	BOD_5	370 ~ 400

Printing	Color (PtCo Color)	2,500 ~ 2,700
Yarn Dyeing	pH	9.0 ~ 9.5
	COD_{Mn}	450 ~ 470
	BOD_5	900 ~ 920
	Color (PtCo Color)	2,000 ~ 2,100
Nylon	pH	9.3 ~ 9.5
	COD_{Mn}	470 ~ 530
	BOD_5	800 ~ 1,200
	Color (PtCo Color)	900 ~ 930

TABLE III. VARIATION OF COLOR IN DIFFERENT DYES BEFORE AND AFTER ELECTRON BEAM IRRADIATION

C.I. Generic Names	Color (Units)		
	Raw	Irradiation Dose (2.34 KGy)	
		No bubbling	Air bubbling
C.I. Reative Red 120	3,070	105	100
C.I. Reative Blue 160	3,090	900	870
C.I. Reative Yellow 84	3,010	138	130
C.I. Acid Red 336	3,120	800	780
C.I. Acid Blue 350	3,040	64	60
C.I. Acid Orange 67	3,110	130	124
C.I. Disperse Red 60	2,630	2,624	2,750
C.I. Disperse Blue 56	3,200	260	250
C.I. Disperse Yellow 54	3,100	146	140

FIG. 1. Electron beam irradiation apparatus.

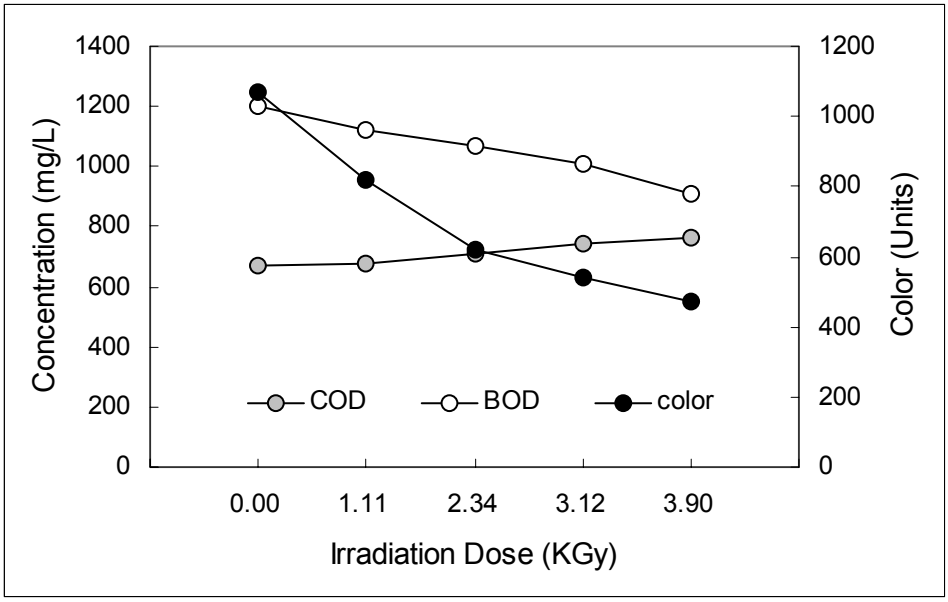

FIG. 2. Variation of color, COD and BOD in the dyeing wastewater as a function of electron beam irradiation dose.

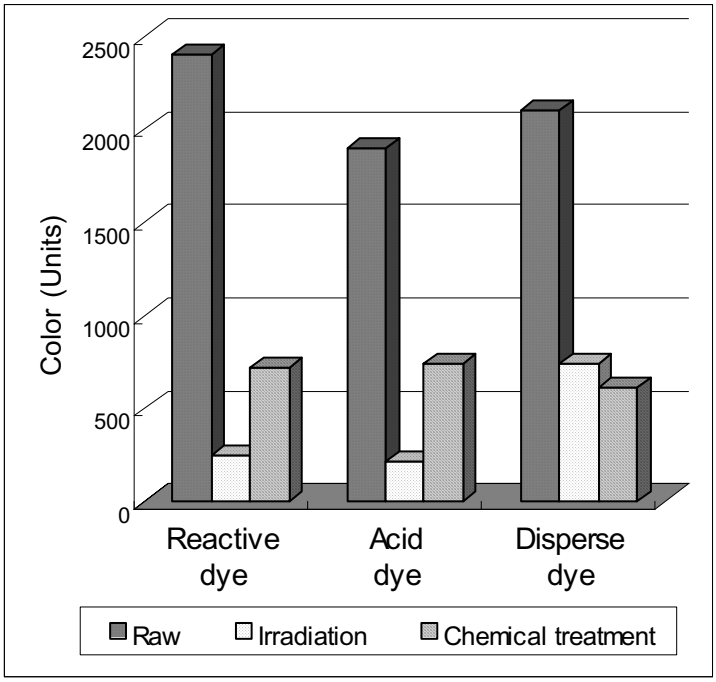

FIG. 3. Color removing for the mixed dye solutions by electron beam irradiation.

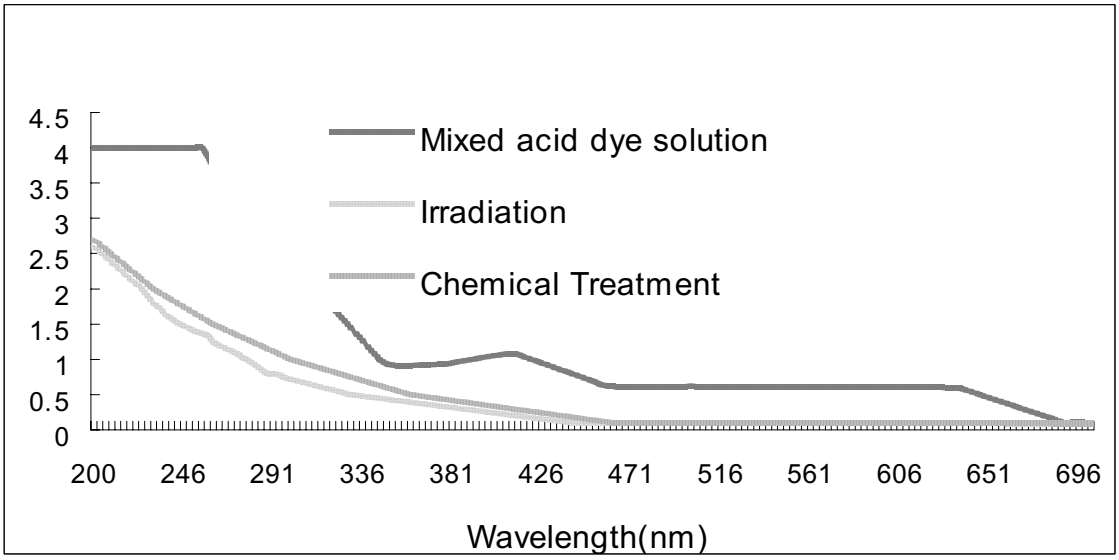

FIG. 4. UV spectrum of the mixed acid dye solution before and after electron beam irradiation.

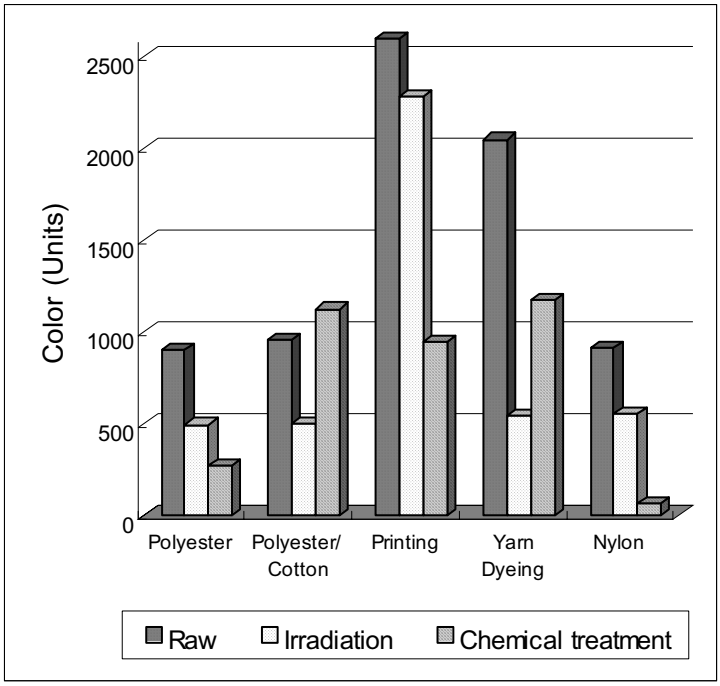

FIG. 5. Color removing by electron beam irradiation for wastewater from different types of dye industry.

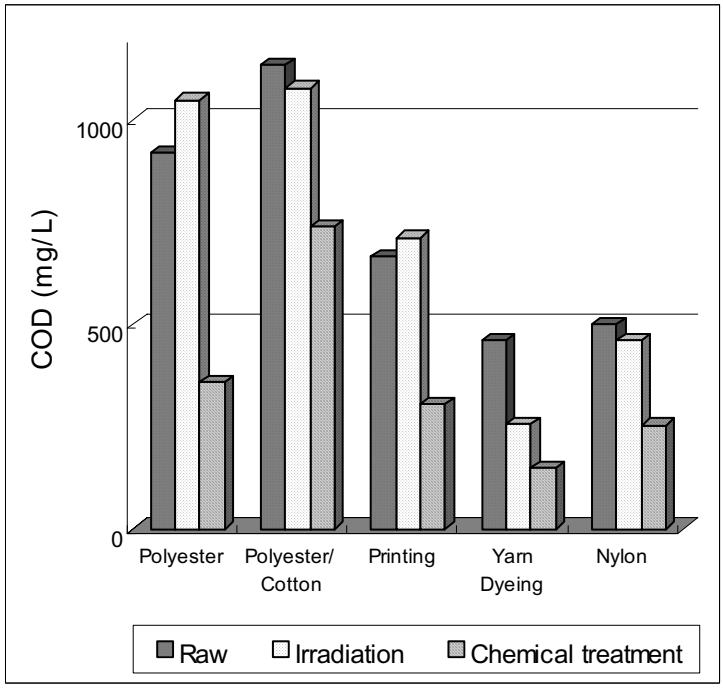

FIG. 6. COD_{Mn} removing by electron beam irradiation for wastewater from different types of dye industry.

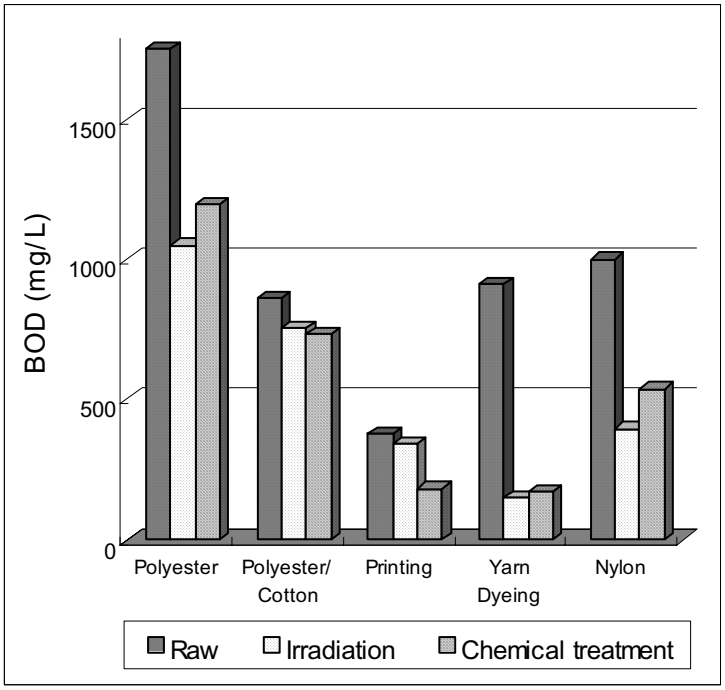

FIG. 7. BOD_5 removing by electron beam irradiation for wastewater from different types of dye industry.

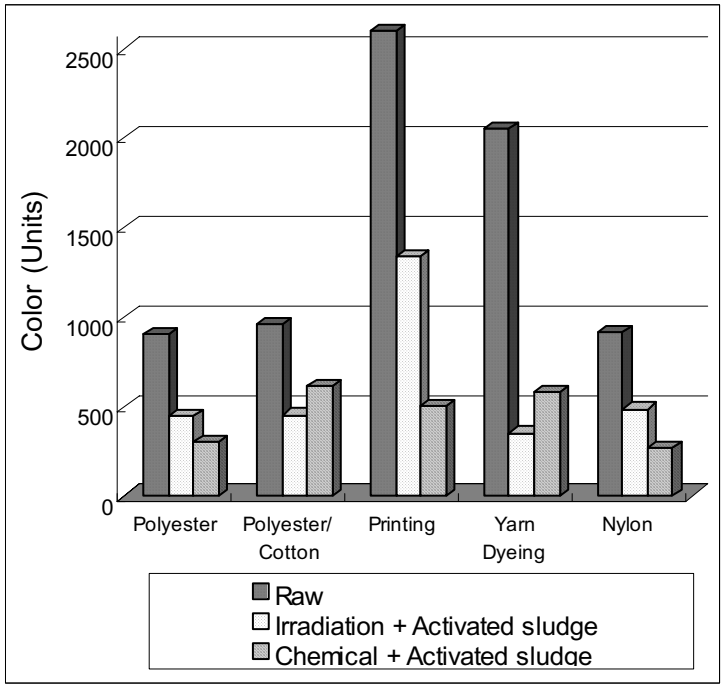

FIG. 8. Comparison of Color removing efficiency for wastewater from different types of dye industry.

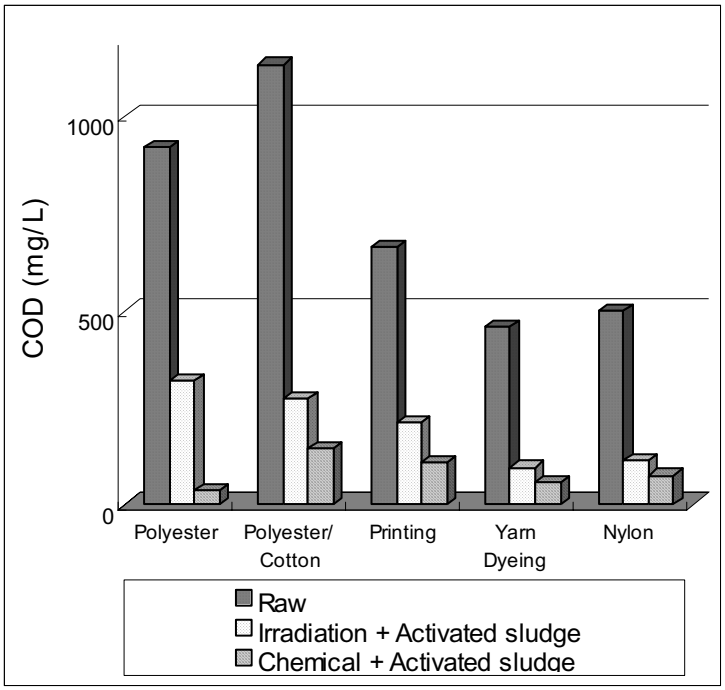

FIG. 9. Comparison of COD_{Mn} removing efficiency for wastewater from different types of dye industry.

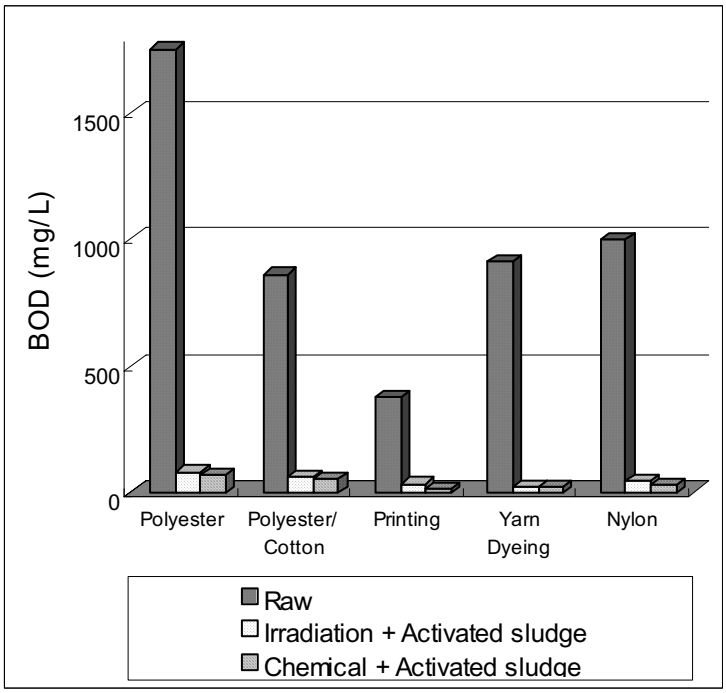

FIG. 10. Comparison of BOD_5 removing efficiency for wastewater from different types of dye industry.

GAMMA RAYS TREATMENT OF GROUNDWATER POLLUTED BY TCE AND PCE

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1. BACKGROUNDS AND PURPOSE

A serious drinking water shortage motivates us to find new water sources. Groundwater can be one of the possible drinking water sources. However, the contamination of groundwater with some organic pollutants such as chlorinated ethylene is becoming serious and it is not decreasing due to increased industrialization and poor groundwater conservation. Many techniques have been proposed for the treatment of pollutants. However, they just remove the contaminants but do not destroy them. An attractive solution for chlorinated ethylenes treatment is radiation-induced decomposition. The organic pollutants can be completely decomposed by gamma-ray or electron-beam irradiation. In this study, decomposition of chlorinated ethylenes and the behaviour of the by-products were investigated including several experimental factors in a continuous gamma irradiation reactor.

2. MATERIALS AND METHOD

Synthetic groundwater polluted with PCE and TCE was prepared. Radiation dose, pH, anion and ozone as experimental factors were adapted in order to investigate the effect on decomposition of PCE and TCE by irradiation. Experiments were carried out with synthetic groundwater (γ-rays alone and O_3 only) and ozone-saturated synthetic groundwater (around 3 mg O_3/L, γ-rays/O_3) .The radioactivity of the gamma source was around 100,000 Ci. The inside of the irradiation vessel with a 15L volume was equipped with 3 baffles in order that water solution would be uniformly irradiated. The figure shows schematic a diagram of the experiment. The experimental systems are consisted of mainly an irradiation vessel(R), synthetic groundwater(CGW), TCE and PCE stock solutions(OC) and an ozone generator(OG). For the gamma-rays/O_3 experiment, ozone saturated water and synthetic groundwater meet in the feeding line before irradiation.

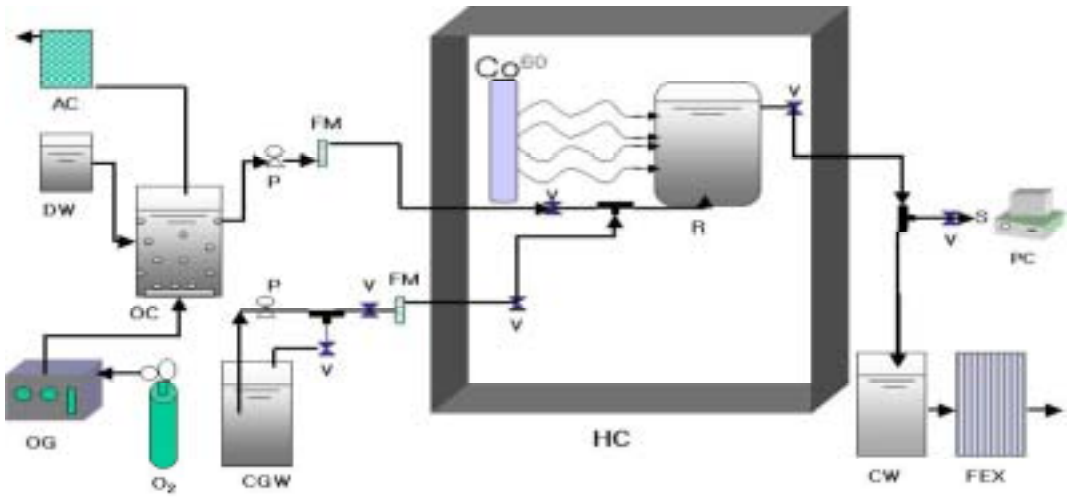

FIG. 1. Schematic diagram of experiment for decomposition of organic pollutants in groundwater by irradiation

TCE and PCE and the by-products contents after gamma-irradiation were measured by an HP 5890 II gas chromatograpy equipped with an electron capture detector. The column was a 30-m HP-5

(cross-linked 5 % phenyl methyl siloxane) from Hewlett Packard. A HPLC and IC meter were also used for the determination of other by-product concentrations. For the measurement of hydroxyl radicals, a nitron spin-trapping reagent, DMPO (5,5-dimethyl-pyrroline-N-oxide, Aldrich) was used. Immediately after irradiation, around 25 μl of the sample solution was transferred into a capillary tube, and the EPR spectra were recoded on the X-band of a Bruker EMX spectrometer at room temperature.

3. RESULTS AND DISCUSSION

2.1. Radiation Treatment

There was significant difference on the decomposition of TCE and PCE between O_3, gamma-rays and gamma-rays/ozone as a function of irradiation dose. The process of gamma-rays/ozone was shown to be the most efficient. The removal efficiency of ozone was less than 2%. The combined process of gamma-rays/ozone could remove all the TCE and PCE at 20Gy and it showed a 80% higher removal efficiency than that of gamma-rays alone.

The removal of TCE and PCE by the gamma-rays/O_3 system is higher than that of gamma-rays system at the irradiation dose below 40Gy. It is suggested that the generation of hydroxyl radicals was increased due to the synergic effect by O_3 after irradiation. Differences of removal efficiency between combined process and O_3 process was decreased at the irradiation dose over 50Gy. It insinuated that the oxidants generated by O_3 was minor than the radicals produced by irradiation at the condition of high level gamma-rays.

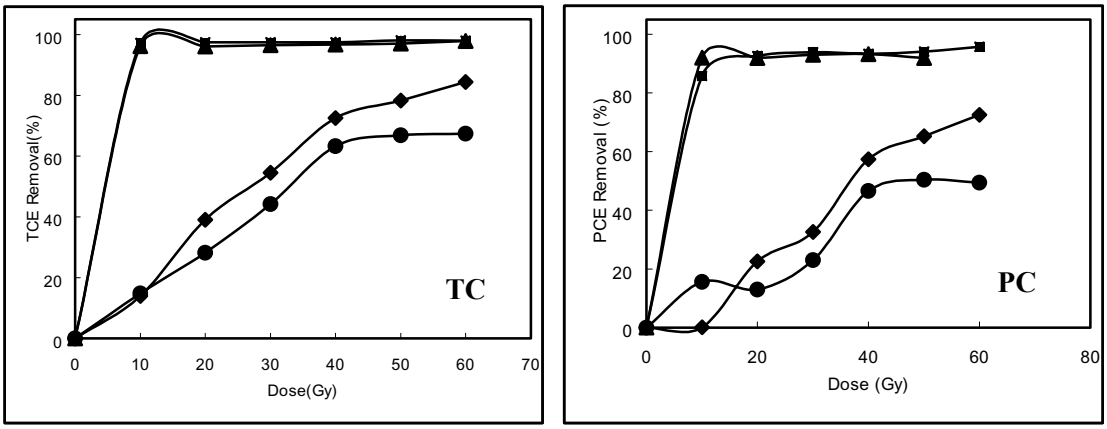

FIG. 2. Effect of O_3 on decomposition of TCE and PCE in synthetic groundwater (□ : demi-water + gamma-rays, ● : synthetic groundwater + gamma-rays, ▲ : demi-water + gamma-rays + Ozone, ■ : synthetic groundwater + gamma- rays + ozone)

2.2. Effect of the Carbonate Ion

The decomposition efficiency of TCE and PCE was decreased when the concentration of carbonate ions was increased. Fig. 3 showed decomposition efficiency of TCE and PCE. The reason was that the carbonate ion acted as a scavenger of hydroxyl radical.

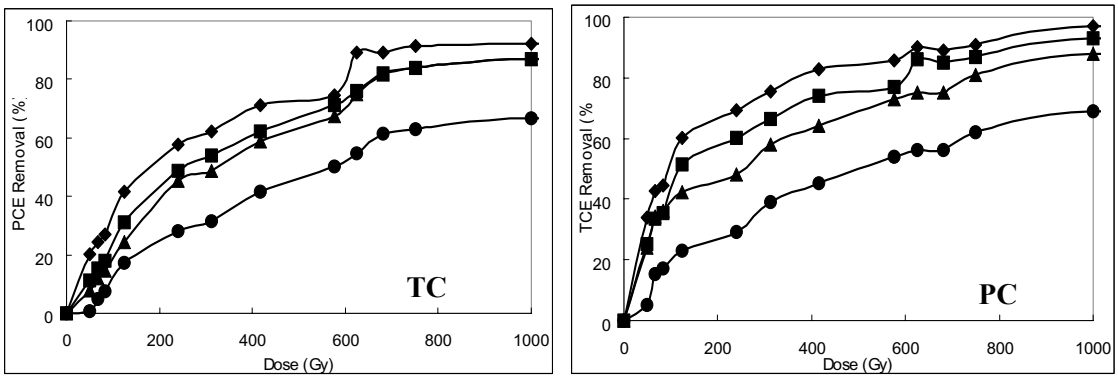

FIG. 3. Effect of carbonate ions on decomposition of TCE and PCE in synthetic groundwater (□ : 0 M, ■ : 10^{-3} M, ▲ : 5×10^{-3} M, ● : 10^{-2} M)

2.3. EFFECT OF H_2O_2

There was no relation between removal efficiency of TCE, PCE and the addition of H_2O_2 (Fig. 4). The reason was considered that the hydroxyl radicals produced from the decomposition of H_2O_2 with irradiation were recombined with each other instead of reacting with TCE and PCE. Effect of H_2O_2 on decomposition of TCE and PCE was measured by using EPR/spin-trapping method. Fig. 5 shows that EPR signal intensity of DMPO-OH signal was increased in accordance with the irradiation dose though difference between the processes was not observed.

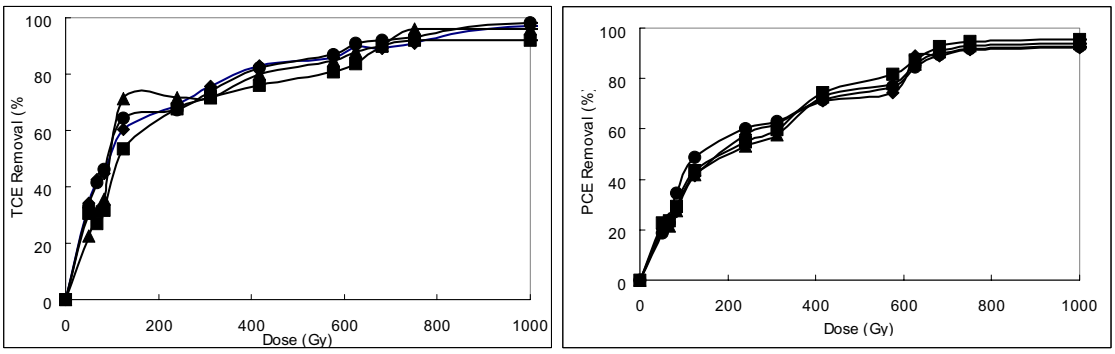

FIG. 4. Effect of H_2O_2 on decomposition of TCE and PCE in synthetic groundwater (□ : 0 M, ● : 0.18 mM, ▲ : 0.30 mM, ■ : 0.42 mM)

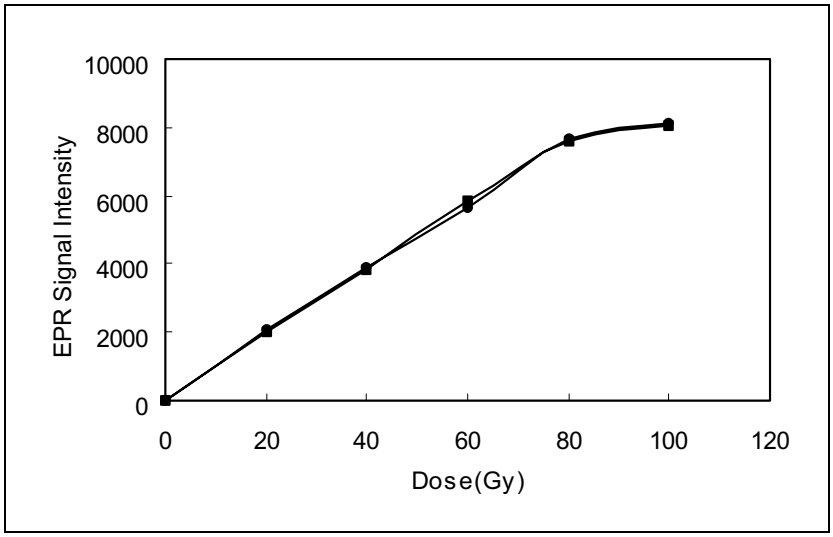

FIG. 5. EPR signal intensity of DMPO-OH as a function of irradiation dose (● : gamma-ray process, ■ :combined gamma-ray/H_2O_2 process)

2.4. BY-PRODUCTS

MCAA(mono-chloro acetic acid), DCAA(di-chloro acetic acid), TCAA(tri-chloro acetic acid), formic acid and oxalic acid were detected with irradiation (Fig. 6). The concentration of TCAA and DCAA in the gamma-rays/ozone were rapidly increased as the irradiation dose was increased. This means that gamma irradiation in the presence of ozone oxides make PCE and TCE easily decomposed because of the abundant hydroxyl radical produced from combined gamma/O_3 process.

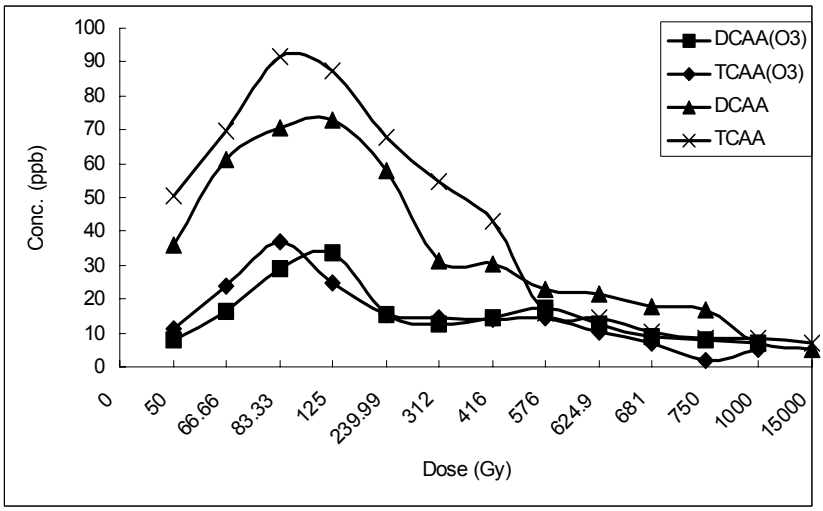

FIG. 6. Effect of O_3 on removal of TCE and PCE by-products in synthetic groundwater

2.5. EPR STUDY

Hydoxyl radicals were measured by the EPR/spin-trapping method since the radicals have a dominant role in the decomposition of TCE and PCE. Fig. 7 shows the EPR signal of trapped DMPO-OH which was represented the peak ratio of 1:2:2:1. Gamma-rays/ozone increased the DMPO-OH signal around 20 % compared to the ozone alone (Fig. 8).

This directly indicates that gamma-rays enhanced the production of hydroxyl radicals from water radiolysis, and thus increased the decomposition of TCE and PCE. Indeed added O_3 accelerated the decomposition of the pollutants because O_3 boosted the generation of OH radicals.

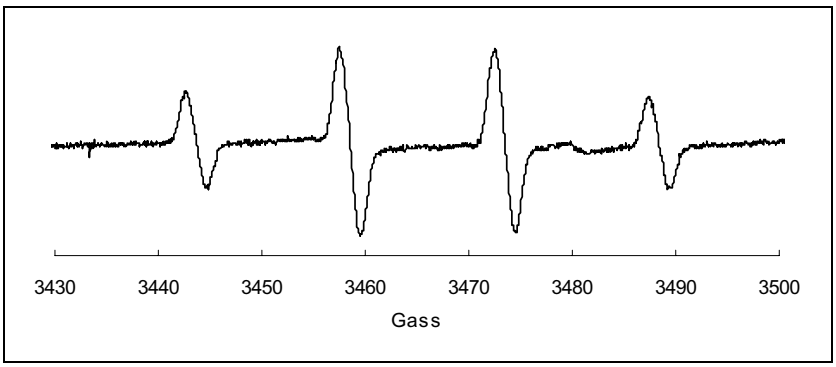

FIG. 7. EPR spectra of DMPO-OH

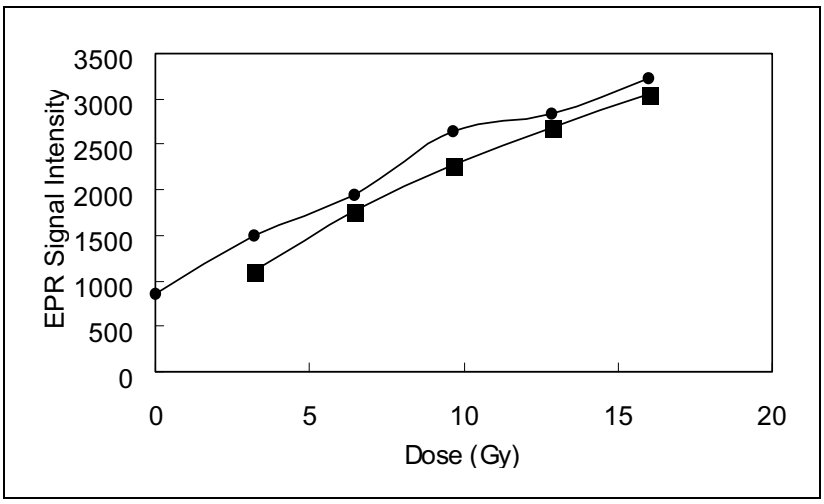

FIG. 8. EPR signal intensity of DMPO-OH as a function of irradiation dose (■ : gamma-ray process, ● : combined gamma-ray/O_3 process)

4. CONCLUSIONS

The radiation treatment of TCE and PCE in the presence of O_3 removed the pollutants by nearly 100 %. By-products and hydroxyl radicals were characterized by gas chromatography and EPR spectroscopy. Anion effect on the decomposition of TCE and PCE was also examined. This information will be helpful for the application of radiation treatment to contaminated groundwater.

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FEASIBILITY TEST TO CONTROL ALGAL BLOOM USING ELECTRON BEAM IRRADIATION

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Abstract

Efforts were made to assess the feasibility to control algal growth using electron beam irradiation. Fresh water algae (e.g. Chlorella sp., Scenedesmus sp., Microcystis sp., Anabaena sp., Oscillatoria sp.) and sea water red algae (e.g. Procentrium minimum, Lingulodinium polyedra, Cochlodinium polykrikoides, Scrippsiella trochoidea, Procentrium micans) were cultured in laboratory and irradiated at different dose of 1.0-10kGy by ELV-4 model electron beam accelerator. The results indicated that in spite of low dose, electron beam irradiation have a great effect on the algal photosynthetic activity; especially for sea water red algae, approximately 40% reduction in chlorophyll-a concentration was observed right after electron beam irradiation at 1.0kGy. Decrease in photosynthetic activity of sea water red algae was more pronounced than that of fresh water algae. With regard to fresh water algae, blue green algae(e.g. Microcystis sp., Oscillatoria sp.) was more vulnerable to electron beam exposure than green algae(e.g. Chlorella sp., Scenedesmus sp.). It is interesting to observe that complete bioflocculation marked by cell aggregation and rapid settling of fresh water algae occurred within 2days after electron beam irradiation. Continuous mixing was one of the important factors to induce algal bioflocculation. Algal removal and settleable matter production were found to be proportional to irradiation dose and mixing intensity. It is likely that electron beam irradiation damages cell contents including chlorophyll-a, releasing extracellular biopolymer that can be used for inducing bioflocculation.

1. INTRODUCTION

Technique applied for controlling algae consists of physical, chemical and biological treatments or disposals; aeration, use of microstrainer, chemical flocculation, use of algicides, floatation, use of predator, dark sedimentation, use of clay, use of AOP(Ozone, Ultrasonic) etc. Most of these techniques appears successful in laboratory or small scale algal ponds but not in field scale operation.

The goal of this research was to assess the feasibility of controlling algae by using electron beam irradiation. In this study efforts were made to cultivate algal cultures in laboratory and then the algal culture was irradiated by electron beam accelerator in order to disintegrate or damage algal cells. It was postulated that a large amount of soluble protein leached out from the algal cells damaged or disintegrated as a result of electron beam irradiation, leading to the release of intracellular biopolymeric substance that eventually resulted in algal bioflocculation.

2. METHODS

2.1. Selection of algae

The dominant algal species encountered in algal blooming in lakes and coastal water in Korea were tested in this study; *Chlorella* sp., *Scenedesmus* sp., *Microcystis* sp., *Anabaena* sp., *Oscillatoria* sp for fresh water algae and *Prorocentrum micans(P.mican), Prorocentrum mininum(P.mini), Scrippsiella trochoidea(S.t), Lingulodinium polyedra(L.p), Cochlodinium polykrikoides(C.p)* for sea water red algae.

2.2. Electron beam irradiation to algae

Prepared algal cultures were irradiated by ELV-4 model electron beam accelerator(EB-TECH Co.). Electron beam dose increased from 1.0 to 10kGy.

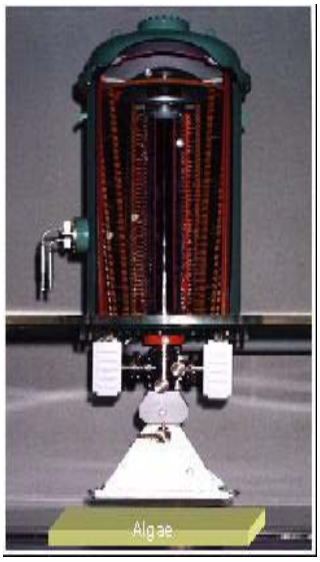

FIG. 1. Schematic diagram of electron beam accelerator used for algae treatment

3. RESULTS AND DISCUSSION

Results indicated that approximately 40% reduction in the photosynthetic activity of blue-green algae, Microcystis sp. was obtained right after electron beam irradiation at 3kGy. However, sea water red algae required lower dose of irradiation (approx. 1kGy)to reach the same magnitude in chlorophyll-a reduction. This was due to the different cell structure and composition between two algal species.

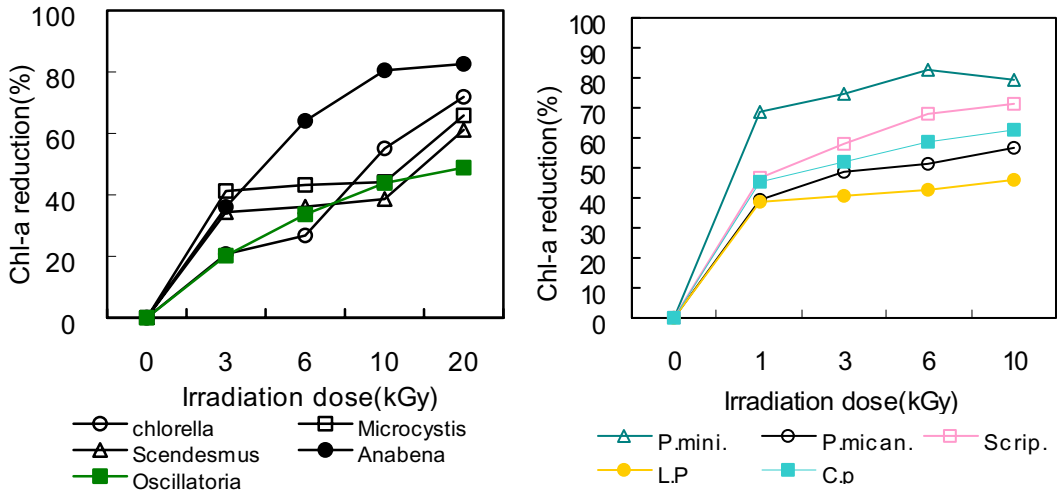

FIG. 2. Chlorophyll-a reduction of fresh water algae and sea water red algae right after irradiation.

As a result of electron beam irradiation to the fresh water algal cultures, a large amount of soluble-protein leached out from the damaged algal cell leading to the release of intracellular biopolymeric substance that eventually resulted in algal bioflocculation. Complete bioflocculation marked by algal cell aggregation and rapid settling of electron beam irradiated culture occurred within

2 days in the mixed cultures. In contrast, the control(no irradiation) showed no sign of bioflocculation. Chlorophyll removal in the electron beam pretreated *Microcystis* sp. culture mixed at $20sec^{-1}$(G value) reached 82%.

TABLE I. CHLOROPHYLL-A REDUCTION OF IRRADIATED *MICROCYSTIS* SP. AT DIFFERENT MIXING INTENSITY ANDIRRADIATION DOSE(A: NO MIXING, B: $10SEC^{-1}$, C: $20SEC^{-1}$, D: $40SEC^{-1}$, E: $60SEC^{-1}$)

Time(day) / dose	1					2					3				
	G Value (sec^{-1})					G Value (sec^{-1})					G Value (sec^{-1})				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
1kGy	23	24	35	26	28	34	39	46	34	46	41	43	56	45	57
3kGy	29	27	52	51	30	35	51	60	57	62	51	59	64	64	62
6kGy	42	45	66	56	46	45	59	64	62	64	57	64	64	66	79
10kGy	55	55	66	63	61	59	67	77	69	61	64	72	64	73	62

TABLE II. CHLOROPHYLL-A REDUCTION OF IRRADIATED *CHLORELLA* SP. AT DIFFERENT MIXING INTENSITY AND IRRADIATION DOSE (A: NO MIXING, B: $10SEC^{-1}$, C: $20SEC^{-1}$, D: $40SEC^{-1}$, E: $60SEC^{-1}$)

Time(day) / dose	1					2					3				
	G Value (sec^{-1})					G Value (sec^{-1})					G Value (sec^{-1})				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
1kGy	39	56	70	65	59	59	62	79	71	70	56	63	62	69	71
3kGy	53	66	76	74	70	63	75	62	60	77	66	72	62	76	77
6kGy	59	73	63	70	79	66	76	66	75	62	70	76	67	75	61
10kGy	67	74	60	77	60	72	74	90	62	64	74	77	90	61	64

It is likely that electron beam irradiation to algae followed by bioflocculation with extrabiopolymer is a promising means of controlling algae in eutrophic lakes.

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