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# Radiation Technology for Cleaner Products and Processes

## *Proceedings of the Technical Meeting on Deployment of Clean (Green) Radiation Technology for Environmental Remediation*

IAEA
International Atomic Energy Agency

# RADIATION TECHNOLOGY FOR CLEANER PRODUCTS AND PROCESSES

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# RADIATION TECHNOLOGY FOR CLEANER PRODUCTS AND PROCESSES

## PROCEEDINGS OF THE TECHNICAL MEETING ON DEPLOYMENT OF CLEAN (GREEN) RADIATION TECHNOLOGY FOR ENVIRONMENTAL REMEDIATION

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2016

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# FOREWORD

Environmental issues such as increased emissions of greenhouse gases and other gaseous pollutants in the atmosphere, pollution of water resources due to emerging organic contaminants such as pharmaceuticals, insecticides, surfactants and endocrine disruptors are a result of the increasing industrialization and urbanization, which today affect the entire world. Developing appropriate green technologies capable of reducing the use and release of such pollutants to meet the tightening environmental regulations being implemented for industrial and municipal authorities will ensure environmentally sustainability development.

Radiation technologies have a demonstrated history of innovating new products and processes that are environmental friendly. For example, radiation sterilization of medical devices alleviated the use of toxic ethylene oxide gas, surface curing using radiation processing, besides being energy efficient, also enabled users to comply with restrictions on the emissions of volatile organic compounds which can form greenhouse gases. Processes based on radiation cross-linking of polymers have led to the production of products which are free from toxic chemical additives. Radiation technologies are being explored for developing products based on natural polymers to produce value added environment friendly products. Radiation technologies have also been successful in directly treating industrial pollutants such as nitrogen oxide and sulphur dioxides present in flue gases, effluents from the textile dye industry, hygienization of sewage sludge for agricultural applications and the treatment of polychlorinated biphenyls present in transformer oil. Recently, studies have also focused on investigating radiation initiated degradation of organics to transform various pollutants into less harmful substances or to reduce them to the levels below permissible concentrations.

The Technical Meeting on Deployment of Clean (Green) Radiation Technology for Environmental Remediation was held 16–20 June 2014 at the IAEA Headquarters, in Vienna. The meeting revisited the global, regional and national level initiatives for the development and use of radiation technologies for developing environment friendly processes and products. It provided a forum for sharing practical experiences in the use of radiation technologies for the treatment of environmental pollutants, lessons learned and formulated the way ahead for integrating this technology with conventional technologies on a large scale.

The IAEA acknowledges the valuable contributions of all the participants at this Technical Meeting. The IAEA officer responsible for this publication was S. Sabharwal of the Division of Physical and Chemical Sciences.

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# EXECUTIVE SUMMARY

## 1.1.BACKGROUND

Environmental changes occurring in an increasingly globalized, industrialized and interconnected world constitute a major factor in increasing risks and diminishing opportunities for the advancement of human well-being. A variety of environmental issues today affect the entire world. Environmental issues such as increase of greenhouse and other pollutants in the atmosphere, pollution of water resources due to emerging organic contaminants (EOCs) such as pharmaceuticals, insecticides, surfactants and endocrine disruptors are caused by the increasing industrialization and urbanization. The past few decades have seen efforts in developing appropriate “Green” technologies, covering both product and process developments that can ensure environmental sustainability and meet the tightening environmental regulations.

Radiation technologies have a successful history of innovating new products and processes that are environmental friendly. The unique ability of high energy radiation to induce profound chemical and biological effects on substrates at room temperature and often without requiring presence of chemical additives has been a major factor in bringing environmental and societal benefits in many commercial ventures. For example, while radiation sterilization of medical devices alleviates the use of toxic ethylene oxide gas, surface curing using radiation processing, besides being energy efficient, also enables users to comply with restrictions on the emissions of volatile organic compounds (VOCs) which can form greenhouse gases. The development of the process of radiation cross-linking of polymers has led to inception and growth of an entirely new industry to produce polymeric products which are free from chemical additives and possess unparalleled physical and chemical characteristics. Such technologies are widely used to produce wires & cables, heat-shrink materials, foamed materials, rubber products and packaging materials. Another novel application of radiation technologies has been in the area of developing products based on natural polymer to produce value added environment friendly products. Radiation technologies have also been successfully deployed for directly treating industrial pollutants such as NOx and SOx present in flue gases, effluents from textile dye industry, hygienization of sewage sludge for agricultural applications and treatment of PCBs present in transformer oil. Recently, studies have also focused on investigating radiation-initiated degradation of organics to transform various pollutants into less harmful substances or reduced to the levels below the permissible concentrations. Studies in several Member States have demonstrated the usefulness and efficiency of radiation technology for development of such environment friendly products and processes.

IAEA has been at the forefront of recognizing the need to developing appropriate technologies to meet the challenges task of evolving environmental issues. It has pursued development, demonstration and deployment of radiation technology through a number Coordinated Research Projects (CRPs). These include:

- Radiation Treatment of Wastewater for Reuse with Particular Focus on Wastewaters Containing Organic Pollutants.
- Radiation Curing of Composites for Enhancing their Features and Utility in Health Care and Industry.
- Application of Radiation Technology in the Development of Advanced Materials for Food Products.

Despite radiation technology being a multi-billion dollar industry, its full potential and the capabilities yet remain unfamiliar to large number of stake holders especially to professionals engaged in addressing issues related to environmental conservation. The lack of appropriate interaction with the practicing end users, decision makers or coordinators of implementing programmes related to environmental technologies has also been a contributing factor for lack of interest by the industry in this technology. Hence, there exists a need to create a forum for interaction between the stakeholders and the radiation technologists to discuss the potential of radiation technologies in mitigating the environmental challenges faced by various industries, assess and evaluate the techno-commercial feasibility of applying radiation technologies to address these issues and where possible, to develop a pathway for implementation of radiation technologies.

## 1.2.OBJECTIVES OF THE MEETING

The technical meeting was aimed at presenting the recent development as well as revisiting global, regional, and national level initiatives for development and use of radiation technologies for developing environment friendly ‘Green’ processes and products. During this meeting, status of these initiatives was discussed and critically evaluated. The meeting focused on presenting new concepts and practical utilization of such techniques with an aim to evolve strategy for deployment of these technologies and identify further needs of further scientific and technological development in this area. It provided a forum for sharing practical experiences in use of radiation technologies for treatment of environmental pollutants, lessons learned and formulates the way ahead for integrating this technology with conventional technologies on a large scale. Finally, it targeted to strengthen contacts and fostering cooperation between technology providers, facility operators, administrators, coordinators of programmes in addressing environmental issues and the end-users.

The meeting focused on the following major topics:

- Applications of radiation technologies for developing “Green” products and processes.
- Environmental and commercial benefits of using radiation technologies.
- Recent developments in using radiation technologies for manufacturing sustainable materials.
- Radiation technologies for treatment of gaseous pollutants, industrial waste waters, municipal waste water, sludge and very toxic pollutants like PCBs.
- Operational experiences of radiation facility operators for treatment of various pollutants.
- Reliability of radiation technologies for environmental remediation.
- Economic aspects of treatment of environmental pollutants vis.-a-vis. conventional technologies.
- Radiation induced degradation of emerging organic pollutants.
- Suitability of radiation technologies to meet the emerging stringent regulatory requirements.

## 1.3.HIGHLIGHTS OF THE PRESENTATIONS

### Radiation technology for treatment of industrial wastewater

With an estimated 10,000 different dyes and pigments with a total annual worldwide production of over 0.7 million tons, of which nearly 200,000 tons gets discharged as effluents every year, dye wastewater remains a source of environmental pollution problems as most of these dyes escape conventional wastewater treatment processes and persist in the environment as a result of their high stability against light, temperature, water, detergents, chemicals, and microbial attack. The status of the technology and the current developments were presented by Republic of Korea and China. The successful operation of an industrial scale electron beam facility integrated with conventional biological process for treatment of 10 000 $m^3$ of textile dye waste water in Republic of Korea for over last 5 years, has conclusively established the techno-commercial viability of the effectiveness and efficiency of the radiation treatment process. China has now set up a pilot-scale electron beam facility in December 2013 for treatment of textile and dyeing wastewater treatment plant to treat 2,000$m^3$/d and work out the techno-commercial aspects of the process and eventually establish an industrial-scale wastewater treatment by electron beam (EB) (10 000$m^3$/d).

Another potential area where radiation technologies can play an important role is in petroleum industry where during the offshore oil production large volumes of aqueous waste with high salinity are produced. The produced water originates mainly from the oil-bearing formation but may also include seawater, which has been injected to maintain reservoir pressure. This water is normally separated from oil on the platform generating aqueous effluent with metal ions, sulphite, ammonium, and organic compounds. The conventional treatment used includes filtration, flotation, ionic change, and adsorption in activated charcoal, but the high salinity of this water decreases the efficiency of those treatments. Radiation induced degradation of organic impurities present in these waters has been extensively investigated in Brazil.

### Radiation technology for treatment of municipal sewage

Disposal of enormous amounts of sewage sludge being produced as a by-product in waste water treatment plants continue to pose challenge for its disposal despite the fact that it can be beneficially used in agriculture to improve the physical, chemical and biological properties of soils which may enhance crop growth by providing appropriate nutrients and micro-nutrients which are not commonly restored in routine agricultural practice. However, achieving this objective needs shifting the focus of sludge management from just disposal to its measured application in agriculture for recycling nutrients and to restitute organic matter to soils with appropriate regulations to ensure health and safety of environment, animals and humans. The potential threat is the presence of a wide variety of pathogens in sewage sludge which can be infectious and may survive for a remarkable period of time in sludge and the environment. The US EPA has approved a variety of methods including irradiation as a means of producing "Class A" sludge that is safe. However, the perceived risks irradiation technology and perception of irradiation being a high costs technology has been a hindrance in growth of this technology. The various aspects of the technology were presented by India, Republic of Korea and United States of America. The successful operation of a cobalt-60 gamma radiation based facility for sludge hygienization of liquid sludge since 1989 in India has continuously provided valuable information about the techno-commercial aspects of the process.

The experience of this facility has shown that technology is easy to integrate with the existing plants and the hygienized sludge is useful natural manure. Recent studies in Republic of Korea are focused on transferring an electron beam technology for the preparation of highly qualified fertilizer mixed with sewage sludge and a starfish to the industry.

**Radiation technology for treatment of air pollutants**

Electron beam (EB) flue gas treatment technology for purification of gaseous effluents from coal fired boilers, after testing in Japan, the USA, Germany, Poland, China and Bulgaria has been implemented in industrial scale in Pomorzany Power Plant, Szczecin, Poland. The present state of the technology, new developments like the use of mobile facility to conduct the demonstration experiments at end user facilities and identifying potential areas of application of the technology were presented by Republic of Korea and Poland. The successful demonstration of the technology at Pomorzany Power Plant, Szczecin, Poland using more than 1 MW power of electron accelerators of 700 keV has proved the reliability of the process. In a recent study jointly carried out by EB Tech Korea, and INCT, Poland. A mobile electron beam plant (MEB) was utilized for a pilot scale demo plant for flue gas treatment from the power plant at Saudi Aramco in Jeddah, Saudi Arabia. It is now planned to design a demo plant in a larger scale (60,000 ~ 200,000 Nm$^3$/h) together with Saudi Aramco, INCT (Poland) and EB Tech. The emission of pollutants from big cargo ships by the year 2020 is expected to exceed than those from stationary on-shore sources. Development of appropriate treatment process for on-board treatment of flue gases provides an opportunity to utilize the electron beam technology.

**Radiation technology for treatment of persistent organic pollutants (POPs) including Poly chlorinated biphenyls (PCBs) and emerging organic pollutants**

Persistent Organic Pollutants (POPs) pose a risk of causing adverse effects to human health and the environment of the whole globe. The international community has now, at several occasions called for urgent global actions to reduce and eliminate these chemicals through effective treatment approaches. The Stockholm Convention prohibits any new production and use of PCBs. The parties to the Convention are required to eliminate the use of PCBs in existing equipment by 2025 and ensure environmentally sound waste management of them by 2028. The potential of PCBs entering the environment by leaks or releases from electrical transformers containing PCBs, release from contaminated sites or their release into the environment by the burning of some wastes in municipal and industrial incinerators continue to pose considerable risk with adverse health effects on the immune system, reproductive system, nervous system, and endocrine system. PCBs treatment in transformer oils using electron beam accelerator on a pilot scale has been established in republic of Korea. Studies are now planned for field demonstration work with a mobile electron beam accelerator for the treatment of PCBs contained in waste transformer oil in the area of Africa with support of IAEA and UNIDO. Feasibility studies are also envisaged in Slovakia to evaluate the possibility of treatment of large river bed sediments contaminated with PCBs using a transportable electron beam.

It is also now well understood that many pharmaceutically active compounds pass through the human body are transferred to wastewater and subsequently to receiving waters and drinking waters, owing to incomplete removal of these compounds by conventional treatment processes. The radiation induced degradation behavior of a wide range of pharmaceutical compounds has been studied at Centre for Energy Research, in Hungary and the results have indicated that such drugs also can be effectively degraded by using irradiation technology. Toxicity after irradiation in most cases has a maximum value: first increases than decreases probably caused by the hydrogen peroxide produced during water radiolysis and also by the degradation products (phenolic type compounds) which are in most cases more toxic that the original compounds. Complete mineralization can be achieved by applying appropriate doses; however, usually it is not required as the purpose is to improve the biodegradability of the solutes and to decrease the toxicity of both the compounds and their metabolites.

### Development of radiation processed environment-friendly products

Development of products that possess the intended life time but subsequently degrade easily under the natural biosphere conditions is emerging as a cherished goal of material scientists for sustainable development. Radiation processing techniques have been successfully applied for developing many such products for particular applications such as

- Crosslinking of Poly-lactic acid to improve thermal deformation of Dummy Lens: PLA is so transparent and hard that the promising applications are thermally molded products such as optical lens, cabinets of electrical applicants, and regeneration medicine which require the property of high thermal stability. However, PLA thermally deforms at temperature higher than its glass transition temperature of 60°C in spite of high melting point of 175°C. Radiation crosslinking techniques have been successfully applied commercially to improve the heat resistance of PLA for making them useful as dummy lenses in Japan.
- Decomposed marine polysaccharides such as chitosan from crab and shrimp shells play role of the plant growth promoter (PGP) in shoot elongation and harvesting yield. Low molecular weight chitosan called oligo chitosan can be degraded by acid hydrolysis and enzymatic reaction. However, the oligo chitosan prepared by radiation-induced degradation shows higher activity than that obtained by acid hydrolysis and enzyme reaction as radiation processed oligo chitosan has larger portion of pyranose rings than that prepared by non-irradiation methods. In the field test for crops and vegetables such as rice, chili, potato, carrot, etc., foliar spray of oligo chitosan solution induced 30–60% increase of harvesting yield in Asian countries such as Japan, Thailand, Indonesia and Vietnam, thus offering significant economic benefits to the farmers besides being environmental friendly. Currently, commercial success on a limited scale has been achieved for such products.
- Radiation-processing methods have also been successfully used to prepare super water absorbent (SWA) which has the property of absorbing large amount of water. Such materials can be applied as super water absorbent (SWA) for soil conditioner in arid area. Sandy soil in arid area has too low capacity to keep rain water in the soil. Studies conducted by Japanese researchers have shown that by addition 3 % dry SWA to sandy soil in arid area, available soil water content increased 2 times in irrigation system of tomato culture resulting in tomato fresh yield increased from 19 to 31 Mg/ha when fresh yield was normalized by drained water. This application revealed the potential of combining SWA and drip irrigation system to significantly enhance efficiency of water utilization in tomato culture. Trial of semi-field test using SWA conducted in Thailand showed reduced irrigation requirement for Marigold plants and increased production of baby corn.

- The development of biodegradable materials from natural polymer such as cassava starch waste can be obtained by using radiation-induced copolymerization with other natural polymer and synthetic polymers. Tests to be made a variety of environmentally friendly plastic products such as plastic bag, dish, hanger, *etc.* is being conducted in collaboration with industries to the possibility of mass production if irradiator is available. It is a more promising clean/green technology, and can be more easily public-accepted.

**Development of radiation processed materials for specific applications**

The importance of rapid and reliable methods for analysis of pollutants at site cannot be overstated. There is always demand towards developing, sensitive, reliable, fast responding and cheap analytical systems for quick and if possible on-site monitoring, determination of pollutants in aqueous systems. Polymer thin film electrodes have been developed jointly by Turkey and France for determination of $Pb^{+2}$ in water down to 0.1 ppb using radiation-induced RAFT-mediated grafting of poly(acrylic acid) into the Nano channels of track-etched PVDF membrane. Atrazine imprinted polyethylene/polypropylene (PE/PP) nonwoven fabrics were prepared by simultaneous surface grafting and crosslinking of poly(meth acrylic acid). RAFT grafting was shown to impart significant improvement in atrazine recognition properties of the polymeric matrices developed.

**Development of new accelerator systems**

The success of radiation technology applications in industry can be attributed to simultaneous development of a very diverse array of industrial accelerators with many designs customized for specific commercial end use applications. The emerging technologies related to environmental applications demand high accelerators with beam power upward of 500 kW. The success of such applications will equally depend on new technologies to produce reliable, high power and cost effective electron beam accelerators .Illinois Accelerator Research Centre (IARC) is a new U.S. Facility to develop industrial applications of accelerator technology developed in pursuit of basic science and a plan to launch a large program of cooperative work with industry including but not limited to accelerator applications for Energy & Environment The proposed facilitates are under construction with 1st availability for the program expected in 2015. The focus will be on high impact applications that can have transformative impacts on the way mankind generates and uses energy. Examples of technologies under consideration include Flue Gas Treatment (EBFGT); Water and Sludge treatment, Gas to liquids conversion including biogas and Flare Gas Recovery; accelerator Driven Systems; for energy and nuclear waste destruction, Carbon reduction via Highway Life Extension and Accelerator Technology (SC magnets) applied to Wind Power. Each program will have a business plan that insures technical success results in widespread adoption of the technology.

In the Republic of Korea, a mobile electron accelerator mounted on a trailer has been developed by EB TECH Co. Ltd. This mobile electron beam irradiation system with self-shielded structure of steel plate and lead block is designed for the individual field application. Shielding of radiation of mobile electron accelerator of 0.7 MeV, 30 mA has been simulated by Monte Carlo technique (MCNP code), actual measurement of leakage radiation was under the regulation. This mobile unit will be used for on-site test of liquid waste and gaseous waste in U.S. by PELE Technology Inc. and EB TECH Co. Ltd. This unit could treat up to $500m^3$ of liquid waste per day at 2kGy or 10,000 $Nm^3$ of gases at 15kGy per day.

**Radiation technologies for conservation and preservation of cultural heritage artifacts**

Ionizing irradiation conservation of Cultural Heritage artifacts has been successfully established as a viable alternative for highly toxic (and not environmental friendly) chemical treatments, preventing health hazards for museum curators, restorers, investigators, and visiting public in Romania. .

## 1.4.CONCLUSIONS

- **Radiation treatment of PCBs:** In the case of transformer oils, PCB inventory for countries are being documented in national implementation plans of the Stockholm convention. Radiation Technology to treat oils containing up to 1000 ppm is available today requiring about 700 kGy of radiation using fixed electron beam equipment. Technology to decontaminate associated equipment installed in the transformers is also available. Despite the engineering solutions being available for integrating with other needed technologies to meet country specific requirements, there exists a need to be explore the flexibility of the electron beam technology under actual field conditions. Evaluation of pros and cons of mobile versus installed technology will allow appropriate technology to be deployed for this application. The treatment of the PCBs in river sediments still is at an exploratory stage as dredging as well as radiation treatment methodologies remain challenging and need to be assessed more rigorously for appropriate engineering solutions.
- **Radiation treatment of industrial wastewater:** Technology for treatment of textile dye wastewater has been demonstrated at industrial scale for textile dye wastewater and is now at the threshold of large scale implementation. Since the textile industry has moved to locations in developing countries, establishing joint strategies with other stakeholders to enhance the visibility of radiation technologies to the end users, is needed As regards the treatment of wastewater containing other organic pollutants, though the preliminary results of studies look promising, more R&D efforts are needed to establish techno-commercial benefits of radiation technologies over alternative technologies.
- **Municipal wastes, pathogens**: technology to decrease pathogens and convert to enriched soil conditioner is well researched and demonstrated specially using gamma radiation facility. The cost-benefit analysis worked out at an operational level indicate that such a technology can be more beneficially carried out using high powered electron beam facility. However, presently no electron beam facility is operational in the world to demonstrate this application, although such facilities have been conceptually conceived. Decision makers, environment regulators, private consulting companies, general contractors, involved in waste water treatment as well as financing bodies have to be involved for encouraging its acceptance by municipal authorities.
- **Treatment of $SO_X$ and $NO_x$ present in flue gases:** the electron beam technology for the simultaneous removal of $SO_X$ and $NO_x$ present in flue gases is a matured stage for the conventional coal fired boilers. The reliability of electron beam facility to treat up to

300 000 $Nm^3$ $h^{-1}$ over long periods of time has been successfully tested. Committed efforts are now needed to assure the stakeholders regarding the efficacy of this technology for adoption. Work on treatment of flue gases from oil fired plants are still at pilot scale while flue gases emission from diesel engines on ships is still relatively at an early stage and subject of future investigation.

- **Radiation modified "green" products for environmental remediation**: A variety of environment friendly radiation processed products such as bio-degradable polymers, super water absorbents based soil conditioners, plant growth promoters PGP and elicitors have been successfully commercialized and/or tested in many Member States. These success stories need to be documented and advertised. International financing entities to stimulate the creation of innovation and commercialization centers in developing countries need to be explored.
- **Emerging research needs**: Research effects on degradation of various emerging pollutants like pharmaceutical compounds, surfactants, pesticides etc. has been a subject of scientific study in recent years. The studies have shown promising results as many of these pollutants of environmental significance can be easily degraded in aqueous solutions. Combination of electron beam irradiation with other AOP techniques to reduce dose requirements could help in developing cost effective technologies for remediation of such pollutants. An important aspect that needs meticulous study is to identify the by-products formed and assess their toxicity behavior. This will be essential to critically evaluated and assess the developed process in a comprehensive manner the potential toxicity and ecological risks to environment. New organic pollutants such as perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) its salts, and its precursor compound, perfluorooctane sulfonyl fluoride (PFOSF), have been officially added into the list of the "Stockholm Convention" and their production banned in many countries. Nevertheless they are still ubiquitous in the environment. The potential of ionizing radiation to treat these emerging new which may be present in water bodies and are resilient to conventional methods of degradation needs to be investigated. Nanoparticles also have been recently recognized as hazards, for example, nanoparticles appear to be responsible for the fouling of membranes used for water treatment. Radiation technologies may be investigated to remove nanoparticles from such solutions.
- **Emerging technology needs**: Development and design of new compact high energy (> 5 MeV) and high beam power (> 100 kW) accelerators with assured reliability should form a priority area for the accelerator developers and/or vendors. The availability of easily transportable, mobile and modular electron beam machines for demonstrating applications to the end users will go a long way in achieving commercial breakthrough of the developed technologies.

# REPORTS OF THE PARTICIPANTS IN TECHNICAL MEETING

# 2. OVERVIEW OF THE R&D ACTIVITIES ON ENVIRONMENTAL APPLICATIONS OF RADIATION PROCESSING IN ALGERIA

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**Abstract**

To cope with the constantly increasing problems of environmental pollution, that conventional technologies cannot support, advancement in science and technology has contributed to the development of so-called green technologies, which might help to solve some of the environmental issues that the world is facing. Among these technologies, radiation processing technology based on electron-beam radiation and 60Co $\gamma$-radiation has reached a high level of development. The applications are many and varied; they concern the treatment of all forms of effluents before their release into the environment, the synthesis of adsorbent materials for organic pollutants and metal ions removal from wastewaters and other applications that allow the elimination of chemicals in industrial processes, and agriculture. In Algeria, although the commercialization stage of radiation processing has not yet been reached, a special attention is given to research in this area. A number of studies have been conducted, which concerned the development of polymer based adsorbents for environmental purposes, and the use of gamma irradiation for wastewater treatment with the emphasis on persistent organic pollutants. The results of some of these studies are presented below.

## 2.1.INTRODUCTION

The environmental degradation caused by human activities constitutes a serious problem, which has attracted increasing concern throughout the world. The increasing urbanization due to the rapid growth of the global population, together with the increased development of agriculture and industry it engenders, have led to the generation of large quantities of polluted effluents that pose a real environmental threat. Wastewaters generated by some industries, such as mining, galvanic and foundry industries, contain dissolved heavy metals, such as cadmium, lead, chromium, copper, mercury, nickel and zinc, which accumulate in soil and are eventually transferred to the human food chain, leading to health problems [2.1].

Besides the contamination by heavy metals, of particular concern are the effluents containing organic pollutants, pesticides, dyes, pathogenic bacteria, parasites and viruses, and in some cases pharmaceuticals and endocrine disruptor compounds, many of which, the conventional wastewater treatment processes are often not successful for their remediation [2.2].

Green technologies have emerged as an important trend and development which might help to solve some of the environmental issues that the world is facing. Among these technologies, radiation processing technology based on electron-beam radiation and $^{60}$Co $\gamma$-radiation has reached a high level of development [2.3]. According to IAEA, in 2008, Worldwide, over 200 gamma irradiators are in operation for a variety of purposes in 55 countries [2.4].

Concerning e-beam technology, over 1400 high-current industrial electron accelerators are in operation, worldwide, for commercial and industrial purposes and there are also approximately 1000 low-current accelerators used for research purposes [2.5]. This large number of industrial units denotes the growing importance of radiation processing technology and its integration into the industrial sector worldwide. The successful development of this technology is governed by a number of factors related to the benefits it provides in comparison with conventional technologies, including those related to environmental protection.

The irradiation technology is used in a wide range of applications for environmental protection or remediation. Among the known applications, we can distinguish those which consist of direct contributions to protecting the environment, and those whose impact is as effective in terms of environmental protection, but in an indirect way. Among the new techniques explored for wastewater treatment, the utilization of ionizing radiation seems to be an effective and economical issue. Radiation-initiated degradation of organics helps to breaks down organic compounds, generating less harmful substances that are easily biodegraded or reduce their content to the levels below the permissible concentrations [2.6]. Ionizing radiation such as, gamma and electron beam is an effective tool for removal or inactivation of various microorganisms and parasites in water and wastewater. Radiation treatment is also applicable for the hygienization of sewage sludge to produce pathogen-free sludge, which can be further upgraded to produce bio-fertilizers.

In addition to these applications that directly contribute to environmental protection or remediation, there exist other applications that contribute indirectly. These include the use of ionizing radiation for the synthesis of adsorbent materials for removal of metal ions, dyes and persistent organic pollutants from liquid effluents.

In Algeria, although the commercialization stage of radiation processing has not yet been reached, a special attention is given to research in this area. A number of studies have been conducted, which concerned the development of polymer based adsorbents for environmental purposes, and the use of gamma irradiation for wastewater treatment with the emphasis on persistent organic pollutants. The results of some of these studies are presented below.

## 2.2.RADIATION SYNTHESIS OF CHITOSAN BEADS GRAFTED WITH ACRYLIC ACID FOR METAL IONS SORPTION

A wide range of physical and chemical processes is available for the removal of toxic metals from wastewater, among them adsorption is a common method for the removal of metals from wastewater [2.7]. Several low cost adsorbents, mainly biopolymers, which are obtained from renewable sources, adsorb selectively metallic ions [2.8]. Chitosan which is described as an excellent metal adsorbent by many investigators, forms chelates with almost all the metal ions [2.9] thanks to the presence of a large number of amino groups [2.10].

However the utilization of the chitosan in the adsorption processes is confronted with some limitations, such as poor mechanical properties and poor heat resistance, solubility in acidic media, high swelling ratios, and limited sorption capacities for some metal ions. To overcome the first four limitations, crosslinking could improve the stability of chitosan, while for the last one, grafting of polymer with functional groups to the chitosan would increase its sorption capacity.

In this study, raw chitosan beads have been suitably modified by crosslinking with glutaraldehyde to increase their resistance to chemical and biological degradation and then modified by radiation grafting reaction introducing carboxyl groups to increase their sorption capacity. The efficiency of modified and unmodified chitosan beads to adsorb cadmium and lead ions was investigated.

Chitosan solution was prepared by dissolving 2 g of chitosan powder into 60 ml of 5% (v/v) acetic acid solution. The chitosan solution was sprayed into a precipitation bath containing 0.5 M NaOH, which neutralized the acetic acid within the chitosan gel and thus coagulated the chitosan gel to spherical uniform chitosan gel beads.

Crosslinking of the chitosan beads was performed with 0.7% glutaraldehyde solution. The grafting of acrylic acid onto chitosan beads was performed by irradiating with $^{60}$Co gamma source the beads into 30% acrylic acid solution at a dose rate of 20.64 Gy/min.

The characterization of synthesized beads was performed by the measurement of the grafting yield, swelling rates, infrared spectra spectroscopy, and batch adsorption experiments.

The radiation dose of 4 kGy and dose rate of 20.64 Gy/min resulted in the production of chitosan beads with a grafting rate of 81%. The grafting degree increased with the increase in radiation dose (Fig. 2. 1).

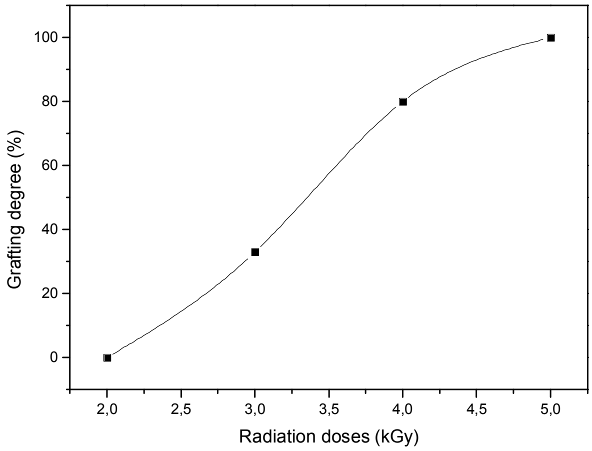

*FIG. 2.1 Influence of radiation dose on grafting degree of acrylic acid on chitosan*

The natural chitosan beads have shown a higher degree of swelling than the grafted ones (Fig. 2.2 and 2.3). The unmodified chitosan beads showed a pH dependent swelling behavior. The degree of swelling decreased from 1000% at pH 3 at almost 700% at pH7 and pH9. This is due to the high ionization degree of chitosan in acidic media (pH 3) since its pKa is 6.3. For Chitosan-AAc, the observed pattern indicated an initial rapid mass uptake more pronounced at pH 9 than at pH 3 and 7, followed by mass stabilization over a 30 min period at the three pH values studied at almost the same swelling rate (220%) at pH values 7 and 9 and 185% at pH 3.

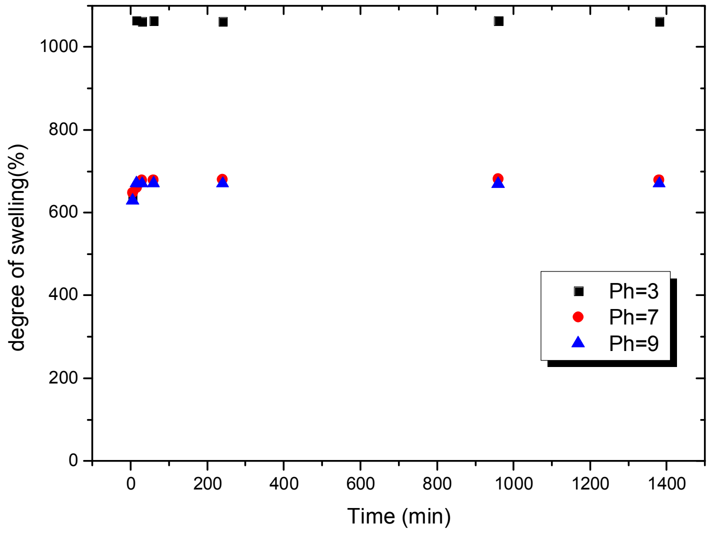

*FIG 2.2. Swelling kinetic of Chitosan at different pHs and ambient temperature.*

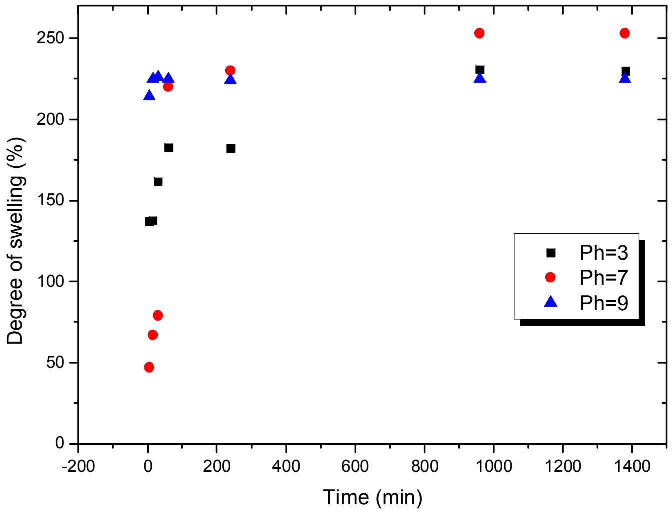

*FIG 2.3. Swelling kinetic of Chitosan-AAc at different pHs and ambient temperature.*

The effect of grafting degree on the sorbent capacity to adsorb metal ions at the same initial concentration (200 mg/l) is represented in Fig. 2.4. The general trend is that, with the increase in grafting rate, the adsorption capacity of the sorbent increased. It is understandable that the increment in the adsorption capacity may be attributed to the increase in carboxylic groups, which appear to play an important role in the ability to adsorb metal ions.

It was observed that the adsorption capacity of metal ions by Chit and Chit-AAc was almost constant for over a wide pH range, though the adsorption was lesser at pH 3 for Chit and almost zero for Chit-AAc (Fig. 2.5). The optimum pH for Cd and Pb uptake is between 4 and 7 for both metal ions.

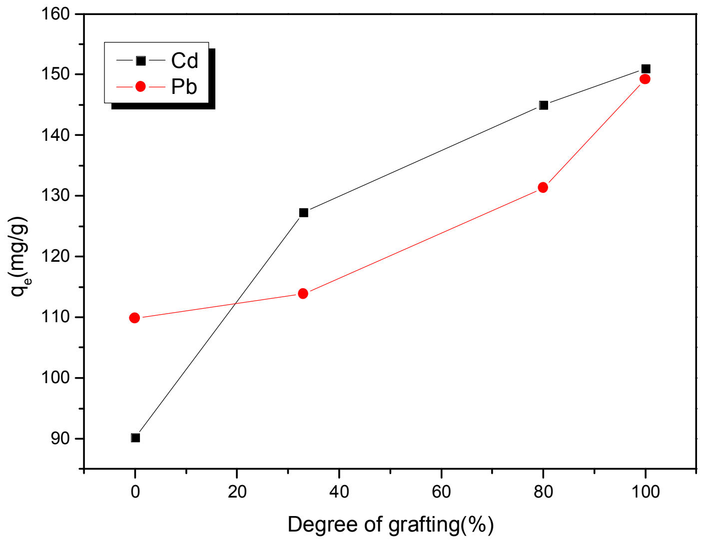

*FIG. 2.4. Effect of grafting degree on adsorption capacity of Cd and Pb (initial concentration 200 mg/l, ambient temperature).*

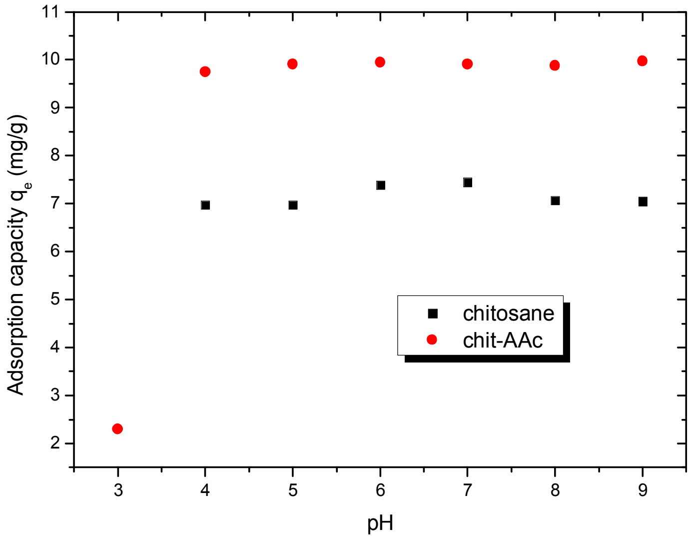

*FIG 2.5. Effect of pH on the sorption of Cd onto Chitosan and Chitosan-AAc. Initial concentrations of 10 mg/l, ambient temperature.*

Kinetic data were successfully fitted to the pseudo-second-order equation. It was observed that for both metals Qmax values are higher for Chit-AAc than Chit based sorbent. The grafting of new groups increased the number of sorption sites in chitosan, leading to the increase in adsorption capacity.

Chitosan seems to be among the inexpensive, effective and readily available materials, which can be used in place of activated carbon or ion-exchange resins for the removal of heavy metals from solution. Because chitosan may be considered as ‘‘low cost’’, such as it needs a little processing, it is abundant in nature, it is a by-product (or a waste) from another industry [2.12].

## 2.3.ADSORPTION OF DYES AND METAL IONS BY ACRYLAMIDE-CO-ACRYLIC ACID HYDROGELS SYNTHESIZED BY GAMMA RADIATION

The objective of the present work is to synthesize a hydrogel based on acrylamide and acrylic acid, and to determine its efficiency in removing dyes and metal ions, such as methyl violet, Congo red and cupric ions respectively, from aqueous solutions.

The monomer solutions were prepared in a composition consisting of 15/85 mole ratio acrylamide/acrylic acid. A dose of 8kGy was delivered to the samples at dose rate of 24.5 Gy/min.

The swelling kinetics was followed gravimetrically at 25°C and pH ranging from 3 to 9. Equilibrium adsorption measurements were conducted in solutions containing respectively 50 mg/l of methyl violet (MV), 200mg/l of red congo (RC). Adsorption of $Cu^{2+}$ ions by the hydrogel was followed in aqueous solutions of $CuSO_4$ (2000 ppm) at pHs ranging from 1 to 5. The mass of $Cu^{2+}$ ions uptake per unit mass of adsorbent ($qe_{Cu2+}$, mg/g) was calculated. The concentrations of the solutions were measured at 810 nm.

It is observed, that in acidic medium, the swelling of the gel does not exceed 200%. At neutral and basic initial pHs the swelling rate becomes much higher, reaching 6000% at pH 8. This may be explained by the fact that at higher pHs, the deprotonation of carboxyl groups leads to the presence on the polymer of high concentration of carboxylate anions.

The same pattern as in water is observed in MV solution; the swelling rate is higher at higher pHs. The swelling rate at low pHs is nearly the same as in distilled water. But at initial neutral pH the swelling rate at equilibrium in MV solution represents 50% of that in distilled water. At initial pH 8 the swelling rate represents 92% of that in distilled water.

The swelling behavior of the hydrogel in 200mg/l CR solutions at initial pH 3, 5, 7, 8 and 9 showed that at lower initial pHs (3-5), the swelling rate is more sensitive to pH changes than with methyl violet and water. By increasing the initial pH from 3 to 5 the swelling rate at equilibrium increases by three times, passing from 200% to almost 600%. At neutral pH it reaches 800%. At initial basic pH the swelling rate continue increasing to reach 1500% at pH 8, and then it reaches 3300% at pH 9. In basic medium, the excess of hydroxyl ions leads to more deprotonation of the acidic groups of the bounded acrylic acid, generating more carboxylic anions. Compared with MV, the swelling rate in CR solution is much less pronounced. This may be explained by the existence of repulsion between the anionic groups of the copolymer and the anionic groups of the dye. The pH effect on swelling behavior of the hydrogel is summarized in Fig. 2.6 for the two dye solutions and water. We can observe the similarity in swelling at initial pHs below pH 5 for the three systems. But a notable difference appears above pH 5.

Diffusion of water and methyl violet solution within the hydrogel was found to be non-Fickian in character. The parameter $n$ obtained from the plot of $lnF$ vs $lnt$ in water, MV and RC solutions (Fig. 2.7) ranged from 0.43 to 0.48. This type of diffusion is mainly observed in glassy polymers at temperature below Tg. Below Tg, the solvent diffusion rate and the polymer relaxation are about the same order of magnitude[13], because the macromolecular chains are not sufficiently mobile to permit fast penetration of the solvent in the hydrogel core.

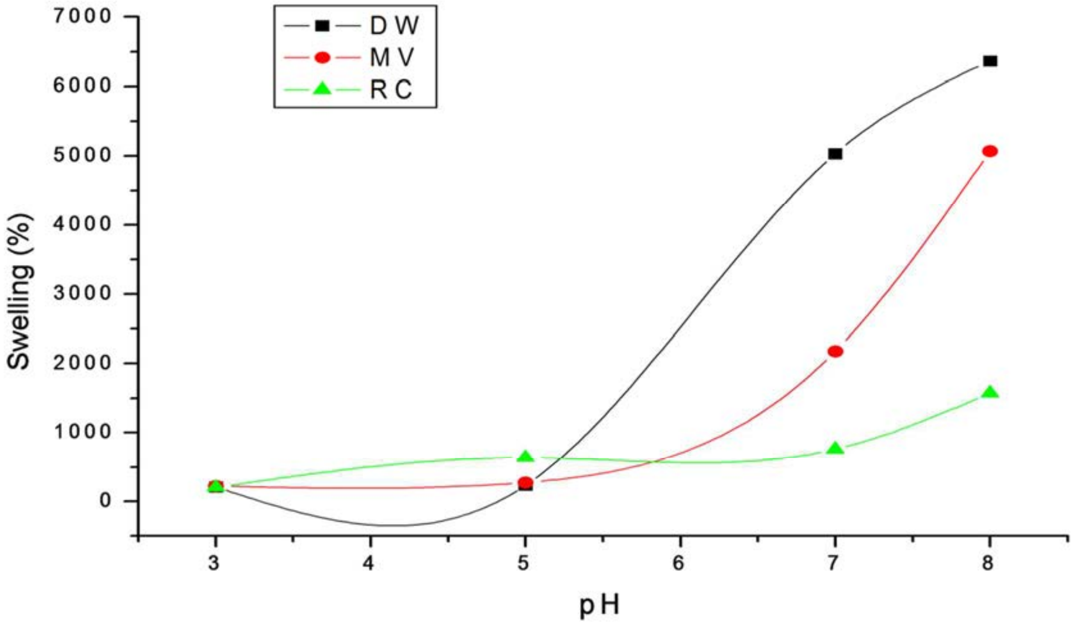

*FIG. 2.6. Effect of initial pH on swelling of the poly (AAm-Co-AAc) hydrogel in distilled water anmethyl violet solution and Congo red solution at 25°C.*

The poly (AAm-co-AAc) has different structures in acidic and alkaline media. Due to the deprotonation of carboxylic groups, it becomes more negative (COO-) in alkaline media, and more positive (COOH) in acidic media. A quasi reverse situation is observed with the charges of MV dye; the amine groups become more protonated at lower pHs. So the dye adsorption is governed by the equilibrium between the deprotonation of the carboxylic groups of the copolymer and the protonation of amine groups of the dye. At pH<5 better adsorption is observed due to the higher protonation of amine groups of the dye. On the other hand a better adsorption is expected at pH>5, due to the high deprotonation of carboxylic groups of the copolymer.

In Fig. 2.8, *qe* is plotted as a function of the initial pH of the solution, so the shape of the curve does not reflect the expected results, which consist in an increase of *qe* above pH 5. But in fact, the pH values at equilibrium are much lower than the initials. The protonation of the carboxylic groups of the copolymer lowered the pH of the solution, in such a way, that all final pHs were acid (Table 2.2).This may explain the decrease in cationic dye (MV) adsorption onto polymer with the increase of pH.

TABLE 2.1. VARIATION OF INITIAL PH OF MV SOLUTION AFTER ADDITION OF AAM-CO AAC HYDROGEL

| Initial pH | 3 | 5 | 7 | 8 | 9 |
|---|---|---|---|---|---|
| Final pH | 1 | 2 | 3 | 4 | 5 |

For poly(AAm-co-AAc) it is reported that the pKa is 4.5 [2.14], so the surface of the adsorbent will be positively charged below pHi, and beyond this it will be negatively charged. Since the CR is an anionic dye, maximum adsorption is carried out below pHi. Above pHi a decrease in adsorption take place due to repulsion between anionic dye molecules and negatively charged adsorbent surface (Fig. 2.9).

It was observed, that adsorption of $Cu^{2+}$ ions in the gels is strongly dependent on the pH (Fig. 2.10). The maximum adsorption value (211mg/g) was obtained at pH 3.3. At this pH the dominant charge in the gels is the carboxylate ions in the acid form. An increase in solution pH from 1 to 3.3 caused a significant increase of the amount of Cu2+ adsorbed.

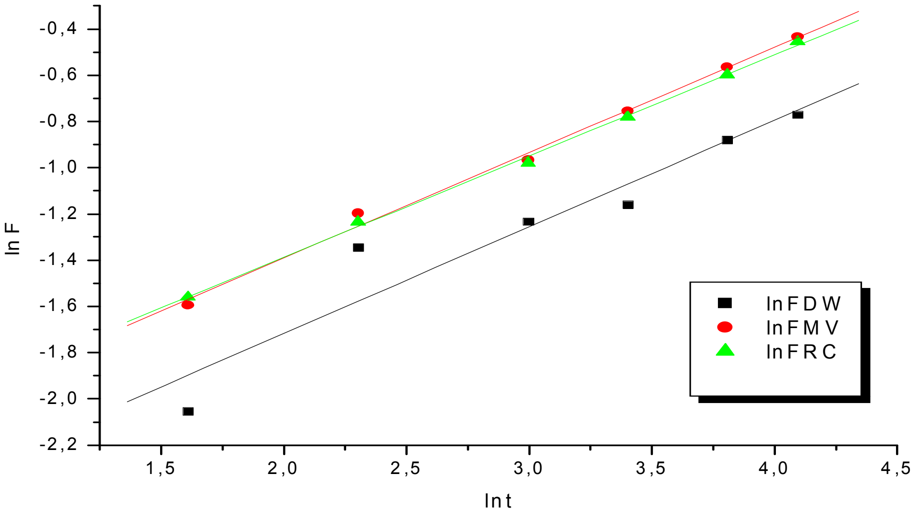

*FIG. 2.7. Plots of ln F versus lnt of poly (AAM-coAAc) hydrogel at pH 3 in methyl violet, Congored and distilled water.*

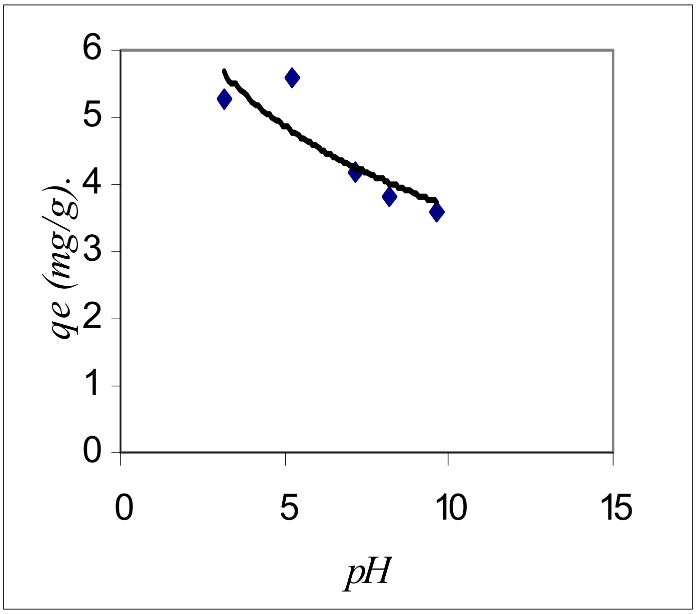

*FIG. 2.8. Effect of initial pH on adsorption of Methyl violet solution (50 mg/l) by poly (AAM-co-AAc) hydrogel.*

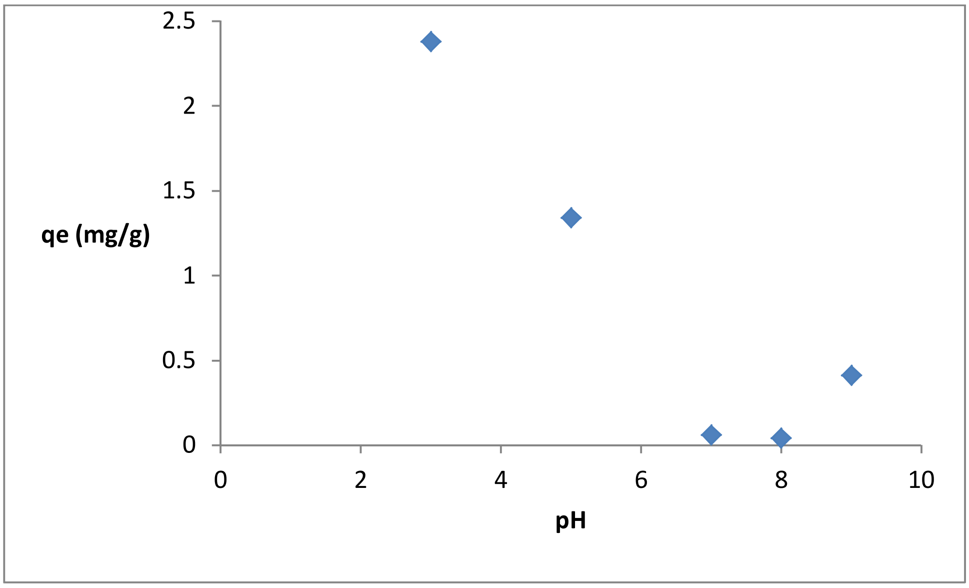

*FIG 2.9. Effect of pH on the adsorption of Congo red solution (200 mg/l) by the poly (AAm-co-AAc) hydrogel.*

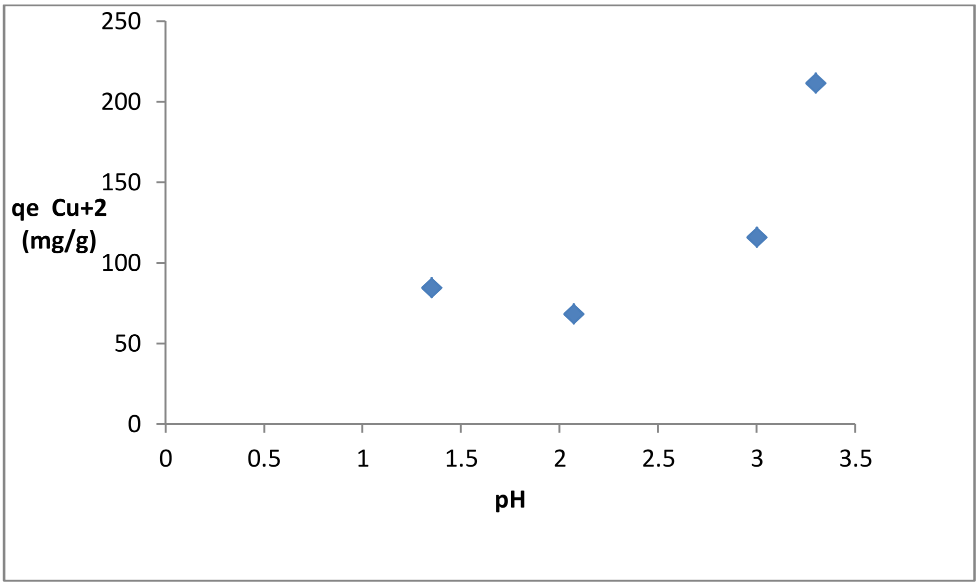

*FIG. 2.10. Effect of pH on the adsorption of Cu2+ ions in the CuSO4 solution (2000 ppm) by poly (AAm-co-AAc) hydrogel.*

## 2.4.APPLICATION OF GAMMA RADIATION FOR REMOVAL OF ORGANIC POLLUTANTS FROM WASTEWATER

Recent decades have witnessed increases in the levels of contamination of water with toxic organic compounds. Among those highly toxic compounds dissolved in water are pesticides, which through their extensive use have become increasingly present in water. Consequently, the pesticide pollution of environmental waters is a pervasive problem with widespread ecological consequences.

The present study is focused on the use of gamma radiation to reduce organic compounds concentration in wastewater. The effect of gamma radiation on organic pollutants contained in wastewater was studied, first on a synthetic aqueous solution of fenitrothion (FNT), which is an organophosphorus pesticide, then on a real sample of wastewater. In Algeria it is used in agriculture for controlling cereals, fruits trees, and vegetables and also used in public health programs (sewer) to fight against the larvae of mosquitoes.

On a synthetic solution, the study was conducted with a concentration of 150ppm of FNT submitted to gamma rays of $^{60}$Co to absorbed doses varying from 15 to 50kGy.The results showed that the pesticide concentration decreased with dose increasing. The HPLC analysis has shown that 90% of the FNT contained in the solution was degraded at the dose of 50kGy. Some by-products formed during irradiation were identified using the identification program of NIST library, these are: phosphothioico, o-dimethyl-o-3methyl-4-methylsulfonyl, and fenitrooxon, with a fit value higher than 75%.

The study on wastewater was conducted on real samples collected from a purification plant influent that receives industrial and domestic wastewater. Samples were irradiated in 2 -12 kGy dose range. The results showed that gamma radiation at the dose of 12kGy reduced by 46%the COD of the influent. The degradation was followed by HPLC and GC-MS. The results revealed the presence of trace of fenitrothion in the influent control sample; the corresponding peak disappeared in the sample irradiated at 2kGy. The chromatographic profile of the control solution of FNT revealed the characteristic peak of FNT at the retention time (Rt) of 3.44min (Fig. 2.11).

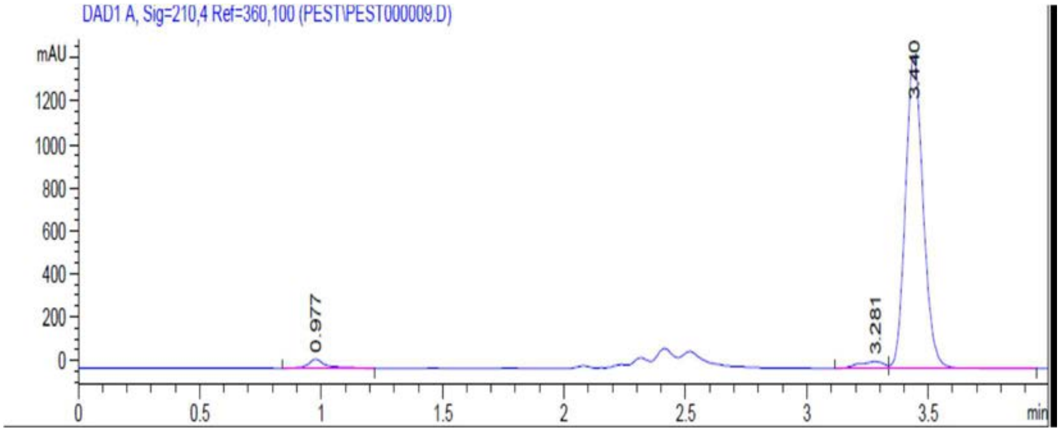

*Fig. 2.11. Chromatogram of FNT control solution analyzed by HPLC.*

After irradiation at a dose of 50kGy the chromatographic profile showed a decrease in the peak area of TNF that appeared at Rt 3.44min. (Figure 2.12).

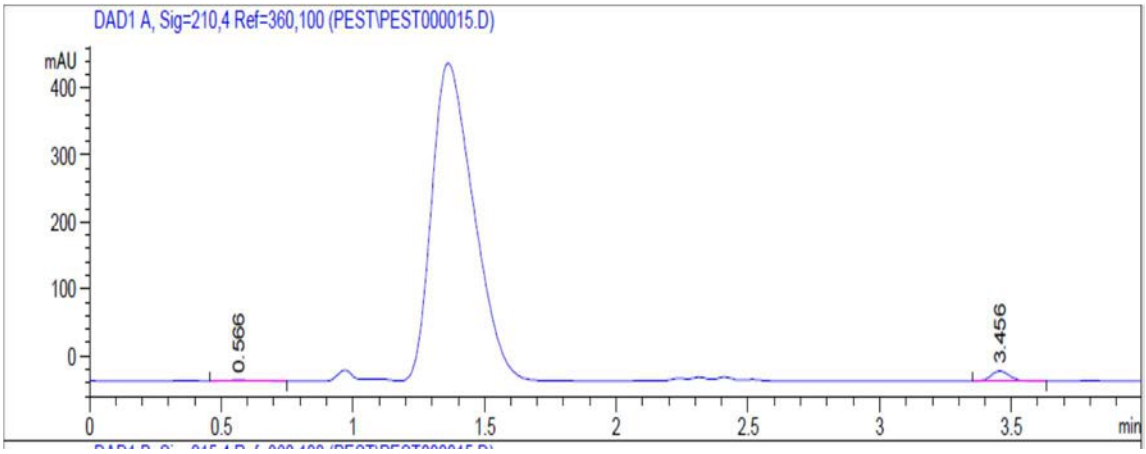

*Fig. 2.12. HPLC chromatogram profile of irradiated solution of FNT*

The concentration of FNT solution irradiated at various doses is illustrated on Figure 2.13. The decrease of the concentration with the increase of the dose showed that irradiation is an effective technique for the degradation of this molecule.

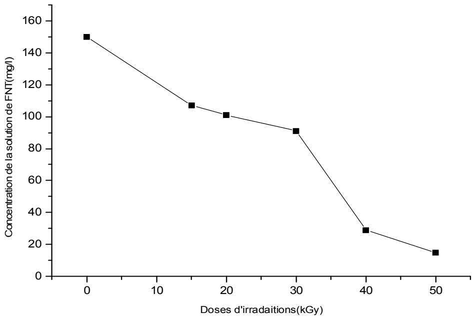

*FIG. 2.13. Radiation effects on irradiated FNT solution.*

GC-MS analysis showed the presence of trace of FNT in both the synthetic and the real solutions before irradiation. No trace of FNT was observed in the samples irradiated at 2 kGy.

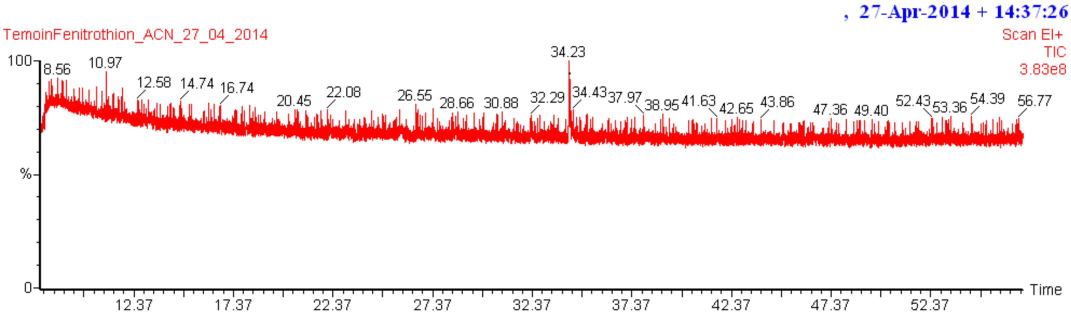

*FIG. 2.14. Analysis of the fenitrothion synthetic solution by GC-MS.*

On Figure 2.14 is shown the GC-MS profile of FNT synthetic solution, the peak appeared at retention time of 34.23 min. The NIST library has identified a FNT with a fit value higher than 90%. The GC-MS profile of the influent control sample is shown on Figure 2.15, where the fenitrothion peak which appeared at retention time of 34.25minutes.

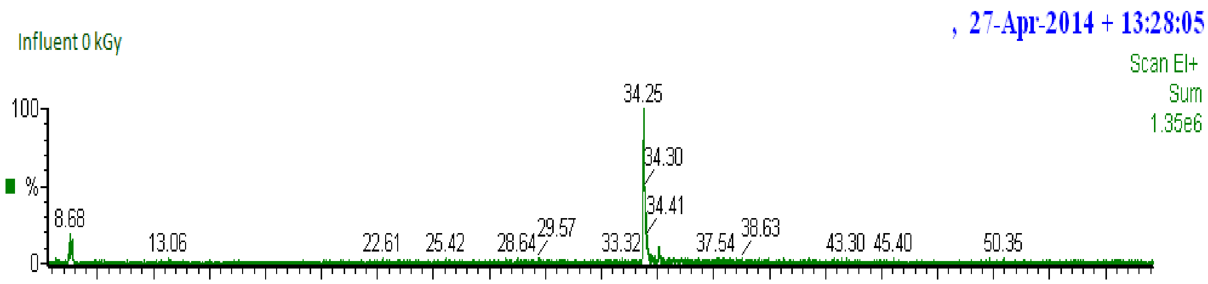

FIG. 2.15. Analysis of influent control sample by GC-MS.

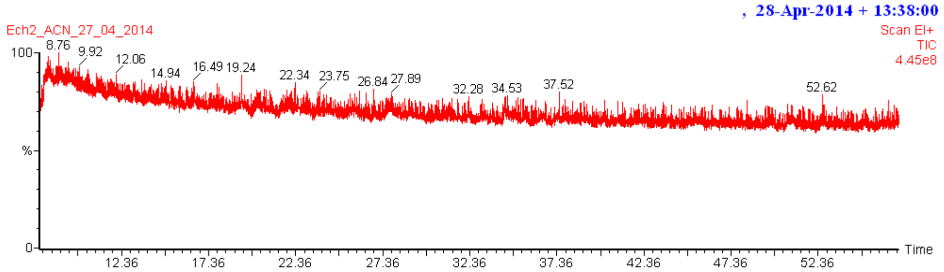

FIG. 2.16. GC-MS chromatogram, of the influent samples irradiated at 2 kGy.

The chromatogram obtained by GC-MS analysis show the no existence of the FNT in the irradiated influent sample (Fig 2.16) compared to the control influent sample, where the peak appears at the retention time of 34.25min. The irradiation of the influent showed a reduction of chemical oxygen demand (COD). On figure 2.17 it is shown that the COD for the control influent sample, decreased from 693 mg/l to 375 mg/l with a percentage of reduction of 46% when 12kGy doses was applied.

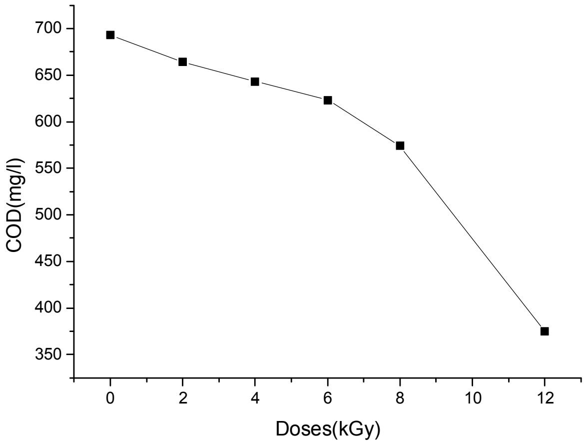

FIG. 2.17. COD Vs irradiation dose of influent sample

## 2.5.IMMOBILIZATION OF BACTERIA ON RADIATION CROSSLINKED POLY (VINYLPYRROLIDONE) HYDROGEL: APPLICATION TO THE DEGRADATION OF POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) are considered as environmental pollutants due to their recalcitrance, their potentially deleterious effects as well as their toxicity. Among PAHs, both naphthalene and anthracene are classified by the US Environmental Protection Agency (EPA) as major recalcitrant toxic pollutants. Many biological agents such as bacteria are efficient in degrading those pollutants even when those agents are immobilized on inert matrices. Fixed cells can grow, invade, and focus on large surfaces; this improves their activity. Rhodococcus erythropolis is well known microorganism containing a large set of enzymes that allows carrying out an enormous number of bioconversion and degradation [2.15, 2.16]. Feasibility and performance of recently developed immobilized bacteria on inert support for biodegradation of recalcitrant compounds has attracted considerable and increasing interest since this strategy allows obtaining much more profit from this process. The main advantages in the use of immobilized cells in comparison with suspended ones include the retention in the reactor of higher concentration of microorganisms, easy removal of bacteria after use from the reaction mixture, providing the ability to control reaction time, reuse of cells for many reaction cycles, lowering the total production cost of cells-mediated reactions, provide pure products [2.17, 2.18]

Microbial cells can be immobilized on various polymeric entrapment matrices. The most promising materials and preparation technique for such a purpose are hydrogels and radiation crosslinking, respectively [2.7, 2.20]. Among hydrophilic polymers, poly (vinylpyrrolidone) PVP, poly (vinyl alcohol) PVA, poly (hydroxyethylmetacrylate) PHEMA, poly (ethylene oxide) PEO and others, are the most often used for hydrogel's synthesis [2.21].

In this work PVP was used for the preparation of the immobilization matrix. The objectives of the study are, on one hand, to investigate the immobilization of R. erythropolis B4 pure strain on the PVP matrix crosslinked by gamma radiation, and on the other hand, to evaluate the ability of immobilized cells to degrade PAHs, such as naphthalene and anthracene. After adhesion test, microscopic observation was also performed in order to highlight the strain adhesion. Tests of degradation by immobilized cells of polycyclic aromatic hydrocarbons (PAHs), anthracene and naphthalene, have been carried out. The immobilization effect on the strain degradation effectiveness and re-use tests of the surface matrix contained whole cell system was investigated.

PVP is soluble in water, once crosslinked by irradiation it acquires a permanent three-dimensional network of polymer chains, which render it insoluble gel. The measured values of the gel fraction and the equilibrium swelling rate of the hydrogel were: 86% and 2293%, respectively. These results mean that the irradiation dose delivered to sterilize the hydrogel, at the same time produced a high degree of crosslinking, which render 86% of it insoluble in water. The swelling property of the hydrogel will assure a maximum contact of the fixed bacteria with the PAH contained in water. SEM microscopy observations revealed the bacterium adhesion and growth on the hydrogel surface. PAH degradation by free cells reached 99% after an incubation time of 5 days with a naphthalene concentration of 1 g/l, while it was of 82.02% with a naphthalene concentration of 1.5 g/l.

Maximal anthracene degradation (87%) was reached after incubation of 11 days with an anthracene concentration of 0.7 g/l while it was of 69% with an anthracene concentration of 1 g/l. The strain degradation ability seems to be more efficient on naphthalene than on anthracene. For both hydrocarbons the degradation efficiency is concentration dependent.

Through our results, we have put in evidence that R.erythropolis B4 has been fixed onto the PVP matrix. This was verified by its positive growth further to many rinsing of the matrix. The bio adhesion to the matrix was realized and bacteria fixed to the support remained well active. The matrix does not affect the microbial activity, no loss of activity was observed and the so fixed bacteria were able to reactivate even after a period of storage [2.22]. Furthermore, PVP hydrogel seems to be biocompatible with biological systems [2.23].

We observed a high capability of the reused immobilized strain to degrade PAHs. The degradation rates as a function of the PAH concentration and culture time are given in Tables 2.1. and 2.2. The results show that the reused immobilized cells have a better capability to degrade PAHs. The degradation rate obtained with reused cells after 2 days is higher than that obtained even after 10 days with the first use. This has been reported by several studies [2.24–2.26]. This was most likely due to the increase availability of the substrates for the cells and a better interaction between the substrates and the immobilized cells [2.25–2.27]. The prolonged acclimation and proliferation at the expense of the chemicals of concern, also improves degradative activity of microorganisms towards the contaminants[26]. The maximum degradation is observed at the lowest concentration for both PAHs. Further investigation is required to evaluate the degradation performance of immobilized cells for many times repeated use in a bioreactor system.

TABLE 2.1. NAPHTHALENE DEGRADATION RATES (%) BY IMMOBILIZED R. *ERYTHROPOLIS* B4

| Naphthalene 0.1% | | | Naphthalene 0.15% | | |
|---|---|---|---|---|---|
| Fixed cells (5 days) | Fixed cells (10 days) | Reused fixed cells (2 days) | Fixed cells (5 days) | Fixed cells (10 days) | Reused fixed cells (2 days) |
| 58.67 | 70.97 | 82.23 | 42.97 | 53.4 | 67.23 |

TABLE 2.2. ANTHRACENE DEGRADATION RATES (%) BY IMMOBILIZED R. *ERYTHROPOLIS* B4

| Anthracene 0.07% | | | Anthracene 0.1% | | |
|---|---|---|---|---|---|
| Fixed cells (5 days) | Fixed cells (10 days) | Reused fixed cells (2 days) | Fixed cells (5 days) | Fixed cells (10 days) | Reused fixed cells (2 days) |
| 54.67 | 76.65 | 84.77 | 38.43 | 69.7 | 77.72 |

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# 3. OVERVIEW OF RADIATION TECHNOLOGY FOR ENVIRONMENTAL REMEDIATION IN BRAZIL

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## Abstract

The necessity to decrease the environmental contamination caused by toxic flue gases, liquid and solid effluent delivered by industries, have resulted in search of new treatment technologies. The ionizing radiation is efficient on destroying organic compounds delivered in industrial effluents, independent on the physical-chemical characteristics and origin. Experiments had been performed at laboratory and at pilot plant scale using Electron Beam Facility with a 1.5 MeV, Dynamitron from Radiation Dynamics Inc. with actual effluents from different industries such as chemical, petroleum, wastewater treatment plant, and drinking water. The efficiency evaluation for each case was accomplished by the physicochemical, chemical and toxicity analysis, in addition, the economic analysis of the process. Some studies were done combining technologies with the objective of improving the efficiency for high-contaminated effluents and decreasing the required absorbed doses for future implementation to large-scale design. Technical and economic feasibility study for implementation of a mobile unit for treatment of industrial effluents with electron beam was carried out, and nowadays, the main focus of the group is the construction of a mobile electron beam wastewater treatment plant for technology demonstration *in situ*.

## 3.1.OBJECTIVE OF THE RESEARCH

The main objective is to demonstrate the efficiency of ionizing radiation treatment of water and actual wastewater from distinct origin and with different physical chemical characteristics and organic compounds concentration, through the data obtained by the research group from Energy and Nuclear Research Institute, IPEN-CNEN/SP, in the period of 1992 up to 2014.

## 3.2.INTRODUCTION

Radiation Technology Centre at IPEN-CNEN/SP 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 accelerator (EB). This technology has been extensively studied by many research centers in the world but the use of this technology into environmental area has been moved slowly because industry and government is always conservative in adoption of new process, especially when they cannot observe the efficiency and cost effectiveness of a treatment in a full scale facility. The reactive species formed by the water irradiation are the reducing radicals, solvated electron (e-aq) and H. atoms and the oxidizing radical hydroxyl OH. These reactive species will react with organic compounds in the water inducing their decomposition. The use of ionizing radiation has great ecological and technological advantages, especially when compared to physical-chemical and biological methods. It degrades organic compounds, generating substances that are easily biodegraded without the necessity of adding chemical compounds [3.1–3.7].

A lot of experiments were done at laboratory scale and based on these data, a pilot plant for large-scale experiments was set up in the IPEN-CNEN/SP EB facility[8], 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 microorganisms in wastewater, industrial effluents and sludge. The economic feasibility study and the results of the performed tests could be used to scale up for a demonstration plant on a commercial basis.

The IPEN-CNEN/SP´s pilot plant can process a stream at a flow rate of 0.5 $m^3$ per hour up to 6.0 $m^3$ per hour with an average dose rate of 5 kGy. Two tanks with 1,200 liters 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. A system allows the sample collection just after and before irradiation. The Electron Beam Accelerator is 1.5 MeV from Radiation Dynamics Inc., the beam current range from 1mA up to 25 mA and the electron beam is scanned on a 60 cm length and 4 cm width area, at a frequency of 100Hz [3.8].

The absorbed dose is measured by calorimetric system using a WCOTT Wire Current Output Temperature Transducer, which allows obtaining in real time the average absorbed doses. Two WCOTT are used, one in the influent and the other in the effluent stream and they are connected via an interface to a computer which continuously reads and records temperatures, the absorbed dose is calculated by the conversion of the temperature difference to the equivalent energy transferred to the stream. It's important to note that the irradiation device that was designed by the IPEN-CNEN/SP´s staff has innovative configurations, which reduce the dependence of electron beam voltage acceleration on the efficiency of energy transferred to the stream in order to reduce the costs of the facility including the EB machine and irradiation vault [3.9].

Radiation-initiated degradation of organics helps to transform various pollutants into less harmful substances or reduced to the levels below the permissible concentrations for wastewater reuse in urban irrigation, agriculture, and industry. Radiation processing is an eco-friendly technology and offers the following advantages: no addition of chemical compounds; no heating and easy for automation; in situ generation of the reactive species which are strong reducing and oxidizing agents for efficient decomposition of pollutants; absence of hazardous by-products (no secondary waste generation); converting no-biodegradable pollutants into biodegradable substances from industrial wastewater facilitating the treatment by conventional technology; easy to integrate with the existing systems and has economic advantages in comparison with most of the conventional technologies [3.7].

## 3.3.EXPERIMENTAL

Experiments had been performed at laboratory and at pilot plant scale, for each case study the following analysis were accomplished: physical, chemical, and toxicity of real wastewater before and after irradiation. In addition economic analysis of the process was performed.

### 3.3.1. In partnership with sanitation company SABESP

SABESP is a mixed capital company responsible for providing water and sewage service in 364 municipalities of the State of Sao Paulo, Brazil, and it is considered one of the largest water and sewage service provider companies in the world, based on the number of customers. A population of 27.7 million people is directly and indirectly supplied with water and 21.6 million people have sewage collection. In partnership with SABESP studies were performed on EB application in samples from different origin and different problems as the drinking water treatment plant and wastewater treatment plant.

#### *3.3.1.1. Drinking Water Treatment Plant*

The cyanobacteria, or blue-green algae, owe their name to the presence of photosynthetic pigments. Freshwater cyanobacteria are known to occur throughout the world. The main responsible organic composites for the taste and odor type earth and mould of surface waters used to supply throughout the world are geosmin (GEO) and 2-methylisoborneol (MIB). Geosmin (*trans*-1, 10-dimethyl-*trans*-decalol) is and 2-methylisoborneol is compounding produced by several species of cyanobacteria (blue-green algae) and is extremely difficult to degrade microbiologically. Conventional treatment processes of surface water are not effective in removing or destroying the cyanobacteria toxins. However, certain oxidation procedures as well as activated charcoal were found to be effective [3.10].

#### *3.3.1.2. Wastewater Treatment Plant*

The Suzano Wastewater Treatment Plant (WTP) has a processing capacity of 1.5m$^3$/s, receiving domestic and industrial wastewater from five different cities. About 30% of wastewater in this plant is from chemical, pharmaceutical, textile and dyes industries origin. Five steps of the conventional treatment of the WTP were selected for sampling: Industrial Receiver Unit influent (IRU), Coarse Bar Screens effluent (CBS), Medium Bar Screens effluent (MBS), Primary Sedimentation effluent (PS) and Final Effluent (FE). The IRU and CBS receive exclusively effluent from industrial origin. The samples were collect following the schedule: four sampling each two hours from each step (composed samples), biweekly during 8 months [3.11–3.12].

### 3.3.2. In partnership with Industrial Complex

The effluents were from an industrial complex composed by eight separated production units named: Intermediary Organic Products (IOP), Poly Vinyl Acetate (PVA), Resins (RES), Special Products (SP), Detergents (DET), Sulphonation (SULF), Thiodan (THIO), and Azo dyes (AZO). Each unit delivered its effluent to the small treatment plant, where they were mixed and the pH was neutralized. One effluent sample from each of eight separate industrial units (IOP, PVA, RES, SP, DET, SULF, THIO and AZO) and 5 samples from the mixed effluent (ME1 to ME5), were irradiated at IPENs Pilot Plant [3.13–3.15].

### 3.3.3. In partnership with PETROBRAS/CENPES

PETROBRAS is a publicly traded corporation, the majority stockholder of which is the Government of Brazil, performed as an integrated energy company in the following sectors: exploration and production, refining, marketing, transportation, petrochemicals, oil product distribution, natural gas, electricity, chemical gas, and biofuels. As leader in the Brazilian oil industry, the company has expanded its operations aiming to be among the top five integrated energy companies in the world by 2030 and has a presence in 25 countries. The studies were performed in two distinct areas that are the treatment of effluent from petroleum production and the petroleum and diesel fuel desulfurization enhancement.

#### *3.3.3.1. Effluent from Petroleum Production*

During the offshore oil production large volumes of aqueous waste with high salinity are produced. The produced water originates mainly from the oil-bearing formation but may also include seawater, which has been injected to maintain reservoir pressure. This water is normally separated from oil on the platform generating aqueous effluent with metals, sulfite, ammonium, and organic compounds. The conventional treatment used includes filtration, flotation, ionic change, and adsorption in activated charcoal, but the high salinity of this water decreases the efficiency of those treatments [3.16–3.17].

#### *3.3.3.2. Petroleum desulfurization*

Nowadays sulfuric and high-sulfuric crude oils make up a majority of the world-produced oil. The total sulfur content in these sorts of oil varies in a very wide range from 0.5 up to 10mass%. Composition of the sulfur-containing organic compounds is complicated and multifarious: more than 250 compounds are identified today. The main part of sulfur in oil is represented by such organic compounds as mercaptans RSH, sulfides RSR, disulfides RSSR and cyclic sulfides $CnH_2nS$. The amount of 4 $x10^7$ tons of sulfur is annually burned out together with the oil products. In translation to combustion products, it makes $8x10^7$ tons of sulfur dioxide or $1.2x10^8$ tons of sulfuric acid. Production of these products results in precipitation of acid rains and increase in the sickness rate of the inhabitants [3.18–3.20].

### 3.3.4. In partnership with other companies

The developments carried out with different partnerships using EB on degradation of contaminants were:

- Degradation of pesticides in soil and packaging [3.21–3.26];
- Pharmaceuticals studies: fluoxetine (Prozac®) and mixtures of pharmaceuticals for degradation and toxicity reduction [3.26–3.27];
- Reactive organic dyes and detergents and their effluents in order to improve their treatment by radiation combined process [3.27–3.28];
- Treatment of effluent from industrial automotive and refinish paints for reuse.

### 3.3.5. Radiation Processing

Electron Beam Facility with a 1.5 MeV, type Dynamitron from Radiation Dynamics Inc. was used. The irradiation parameters of EB accelerator were 4.0 mm sample width, scan of 112 cm (94.1%) and stream velocity of 6.72 m/min.

Effluents from industrial chemical complex were irradiated at the IPEN's Electron Beam Pilot Plant that was set up to treat wastewater and industrial effluents. The IPEN-CNEN/SP′s pilot plant can process a stream at a flow rate of 0.5 $m^3$ per hour up to 6.0 $m^3$ per hour with an average dose rate of 5 kGy. Two tanks with 1,200 liters 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. A sample system allows the sample collection just after and before irradiation.

### 3.3.6. Dosimeter system

The absorbed dose was measured by calorimetric system using a temperature transducer type, WCOTT, Wire Current Output temperature transducer, - Intensil, GEAD590, that allows to obtain in real time the average absorbed doses. The sample stream had a medium flow rate of 30 L/min; the electron beam had energy 1.5 MeV and the current was varied from 1.2 mA to 10.6 mA in order to obtain the desired doses [3.4, 3.8].

### 3.3.7. Evaluation of the process efficiency

The irradiation treatment efficiency was evaluated by the chemical and toxicity analysis of the samples before and after irradiation. The organic compounds were analyzed by Gas chromatograph associated to mass spectrometry using Gas Chromatograph associated to Mass Spectrometer Shimadzu model GCMS-QP 5000.

## 3.4.RESULTS AND DISCUSSION

### 3.4.1. Drinking Water Treatment

The results of quantitative analyses of organic compounds GEO and MIB in the three kinds of water samples before and after gamma irradiation with 0.5 kGy, 1.0 kGy, 2.0kGy and 3.0 kGy showed a total removal of GEO and MIB with 0.5 kGy of absorbed dose and the concentrations were near 100 ngL$^{-1}$ in case of sediment water and final water, raw water presented lower reduction. In the case of samples, which concentrations were near to 1000 ngL$^{-1}$, it was necessary higher doses to remove 90% of GEO and MIB. For final and sediment water it was necessary 2.0 kGy to remove 99%. It was not observed acute toxicity in the samples before neither after irradiation. The absence of acute toxicity mainly when 3kGy of absorbed dose was applied is important to verify that no toxic substances were formed after the radiation processing [3.10].

### 3.4.2. Effluent from Wastewater Treatment Plant

Samples from IRU and CBS are mainly of industrial origin, resulting high Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD). In the MBS point occur the reception of domestic wastewater then the organic load increase, resulting in very high Total Organic Carbon; but this organic load represents proteins, carbohydrates, oils and greases but not toxic organic pollutants. The steps that presented more toxic organic compounds were IRU and CBS and the main organic compounds found were dichloroethane, toluene, xylene, methilisobutylketon, and phenol. Samples from the IRU, CBS and MBS steps presented the highest concentrations of organic compounds then it was necessary absorbed doses from 20kGy to 50kGy to remove 90%, while samples from PS needed absorbed doses from 10kGy to 20kGy and FE needed 10 kGy doses. Although the MBS samples presented lower concentrations of organic compounds than IRU and CBS steps, the necessary absorbed dose to remove 90% of the main organic compounds was the same, it may be because the highest organic load concentration that compete to the oxidation by radiation. This can be seen by the yield of Destruction ($G_d$) value obtained for MBS that is lower than $G_d$ value obtained for IRU and CBS in all studied organic compounds (Table 3.1). Phenol presented negative results on removal in the steps IRU, CBS and MBS when irradiated at doses of 10 kGy and 20 kGy, that is because it was observed an increase in its concentration when lower doses were applied. This occurrence suggest a phenol molecule formation when aromatic compounds are oxidized, because this, the $G_d$ of phenol presented lower values than the others studied organic compounds [3.8, 3.6, 3.11, 3.18, 3.23, 3.29].

### 3.4.3. Effluent from Industrial Complex

The physical chemical characterization of these samples showed the complexity and differences of these effluents. The pH ranged from 1.40 (IOP) to 12.80 (AZO), Chemical Oxygen Demand (COD) was from 466 $mgO_2/L$ (THIO) to 29,00 $mgO_2/L$ (DET), sulphates from 70 mg/L (SP) to 22,780 (AZO), oil and greases from 21 mg/L (ME5) to 285 mg/L (DET) and the suspended solids from 58 mg/L (SULF) to 494 mg/L (DET). The most important pollutants found in these effluents were chloroform, dichloroethane, methyl isobutyl ketone, toluene, xylene, and phenol. The necessary dose to remove 90% of these contaminants was presented in Table 3.2 [3.17, 3.19, 3.25–3.26, and 3.30].

TABLE 3.1. ORGANIC COMPOUNDS CONCENTRATION IN WASTEWATER TREATMENT PLANT STEPS AND THEIR REMOVAL AFTER EB IRRADIATION

| **ORGANIC COMPOUNDS** | **IRU** | **CBS** | **MBS** | **PS** | **FE** |
|---|---|---|---|---|---|
| | **Concentration (mg/L)** | | | | |
| Methylisobutyl ketone | 1.00 - 22.30<br>*(20)* | 1.30 - 7.85<br>*(20)* | 0.22 - 3.52<br>*(20)* | 0.98 - 2.69<br>*(10)* | <dl |
| Dichoroethane | 1.30 - 25.70<br>*(20)* | 1.10 - 16.00<br>*(20)* | 1.86 - 5.58<br>*(20)* | 0.98 - 3.69<br>*(10)* | 0.40 - 1.85<br>*(5)* |
| Toluene | 0.80 - 12.00<br>*(50)* | 1.00 - 72.00<br>*(50)* | 0.51 - 2.57<br>*(20)* | 0.85 - 1.60<br>*(10)* | 0.32 - 1.97<br>*(5)* |
| Xylene | 1.50 - 67.00<br>*(50)* | 0.50 - 25.70<br>*(50)* | 1.22 - 3.51<br>*(20)* | 0.96 - 1.82<br>*(10)* | 0.12 - 4.00<br>*(5)* |
| Phenol | 3.20 - 7.80<br>*(50)* | 3.20 - 16.40<br>*(50)* | 0.96 - 2.00<br>*(20)* | 0.86 - 1.60<br>*(10)* | 0.50 - 0.86<br>*(5)* |

dl = detection limit = 0.03 mg/L

Variation = 10%

*() Necessary Absorbed Dose to 90% removal*

### 3.4.4. Effluent from petroleum production

Although originated of the same process, samples from *Production Unit A* and *Production Unit B* showed very different physical-chemical characteristics, such as the higher ammonium concentration and lower sulphite concentration of the samples from *Production Unit A*, and the pH ranged from 9.28 up to 9.88 in *Production Unit A* and from 7.88 up to 8.07 in *Production Unit* B. The most important organic pollutants in both effluent samples were benzene, toluene, ethylbenzene, xylene; and all these pollutants present higher concentration in the samples from *Production Unit A* than *Production Unit B*, Phenol was found in relative low concentration but was considered due to its toxicity and because phenol is formed as first by-product of the degradation of benzene and toluene. From these results the complexity and differences of these effluents can be observed. After radiation processing, the organic

TABLE 3.2. ORGANIC COMPOUNDS CONCENTRATION IN INDUSTRIAL EFFLUENT AND THEIR REMOVAL AFTER EB IRRADIATION

| Sample | Dichloroethane (mg/L) | CHLOROFORM (mg/L) | METHYL ISOBUTHYL KETON (mg/L) | Toluene (mg/L) | XYLENE (mg/L) | *Phenol* (mg/L) |
|---|---|---|---|---|---|---|
| | | | *MIXED EFFLUENT* | | | |
| *ME1* | 87.93 *(20)* | 0.83 *(20)* | na | 6.32 *(20)* | 9.31 *(15)* | 2.81 *(50)* |
| ME2 | 2.65 *(20)* | 0.18 *(20)* | na | 1.10 *(20)* | 1.52 *(20)* | 3.25 *(50)* |
| ME3 | 0.23 *(20)* | <0.010 | na | 1.81 *(20)* | 0.12 *(20)* | 0.04 *(50)* |
| ME4 | 51.32 *(20)* | 0.51 *(20)* | 24.21 *(20)* | 13.08 *(20)* | 24.33 *(30)* | 2.32 *(50)* |
| ME5 | 65.75 *(30)* | 0.83 *(20)* | 33.96 *(20)* | 25.31 *(10)* | 27.21 *(10)* | 1.92 *(50)* |
| | | | Separated units | | | |
| SP | <0.010 | <0.010 | na | <0.10 | <0.10 | 0.62 *(50)* |
| RES | <0.010 | <0.010 | na | 6.22 *(50)* | <0.10 | 1.61 *(50)* |
| PVA | <0.010 | <0.010 | na | 0.30 *(50)* | <0.10 | 1.91 *(50)* |
| DET | <0.010 | <0.010 | na | 0.27 *(50)* | 0.23 *(50)* | 1.11 *(50)* |
| IOP | 28.4 *(50)* | <0.010 | na | <0.10 | <0.10 | 0.62 *(50)* |
| SULF | 0.15 *(50)* | <0.010 | na | <0.10 | <0.10 | <0.10 |
| THIO | 1.85 *(30)* | <0.010 | na | <0.10 | <0.10 | 0.41 *(50)* |
| AZO | 11.38 *(50)* | 0.21 *(20)* | na | <0.10 | 2.14 *(20)* | <0.10 |

na = not analyzed

*( )* = necessary dose (kGy) to 90% removal

Compounds content showed a substantial reduction, but with very high absorbed doses. For samples from *Production Unit A*, a dose of 100kGy was necessary to remove more than 90% of all organic compounds, and in the case of *Production Unit B* a dose of 20kGy was enough to remove 90% of BTEX and phenol in all samples. The exact influence of ammonium concentration is presently not clear enough, but these results would suggest a positive effect in the removal of organic compound after electron beam processing, since the *SA*2 and SA4 with higher ammonium concentration have the higher yield ($G_d$) for BTEX and opposite happened with SA3 (Table 3.2). The degradation yield of the substrate depends on its starting concentration, hence the process was more effective when high number of organic molecules was present, because the reaction among reactive transients produces more radicals and the process continue, but it is not a direct proportion. E.g. in the case of Benzene in samples from PUA has higher concentration than samples from PUB, about three times, but the Gd values was almost the same [3.1, 3.15, 3.16].

TABLE 3.3. ORGANIC COMPOUNDS CONCENTRATION IN PETROLEUM PRODUCTION EFFLUENT AND THEIR REMOVAL AFTER EB IRRADIATION

| *SAMPLE* | BENZENE (mg/L) | Toluene (mg/L) | XYLENE (mg/L) | *Phenol* (mg/L) |
|---|---|---|---|---|
| SA1 | 99.30 (100) | 134.49 (100) | 307.00 (100) | 4.24 (50) |
| SA2 | 146.80 (100) | 218.22 (100) | 585.06 (50) | 3.27 (50) |
| SA3 | 119.79 (100) | 195.36 (100) | 333.44 (100) | 1.47 (50) |
| SA4 | 111.71 (100) | 216.93 (100) | 243.24 (50) | 1.39 (50) |
| *SB1* | 22.46 (20) | 8.53 (20) | 6.61 (20) | 3.73 (20) |
| SB2 | 42.17 (50) | 27.12 (50) | 24.40 (50) | 1.92 (20) |
| SB3 | 35.30 (20) | 20.83 (20) | 12.65 (20) | 1.65 (20) |
| SB4 | 49.05 (20) | 27.33 (20) | 17.70 (20) | 0.98 (20) |

*() Necessary Absorbed Dose (kGy) to 90% removal*

In another experiment the samples were mixture with 0.1, 0.2, 0.5 and 1.0 g/L of $TiO_2$ in powder form, Degussa P-25 catalyst, hybrid mixture of rutile (approx. 70%), and anatase form. The vials were completely filled without headspace. The obtained results of removal efficiency using different absorbed doses and Titanium Oxide concentrations are showed in the Table 3.4. It was expect that $TiO_2$ combined to ionizing radiation would increase the removal of the BTX, but the synergistic effect showed not linear form. The lower concentration of $TiO_2$ (0.1 g/L and 0.2 g/L) increased the BTX removal efficiency for 10 kGy and 20 kGy of absorbed doses, but for higher doses it didn’t make any difference and in higher concentrations (1.0 g/L) the removal efficiency decreased. When higher absorbed doses were applied the removal efficiencies of ionizing radiation alone or combined with $TiO_2$ were almost the same. The presence of $TiO_2$ also increased the discoloration of the industrial effluent, significant reductions occur when 0.1 g/L and 0.2 g/L were added, but with higher concentration the results showed similar [3.22].

TABLE 3.4. ORGANIC COMPOUNDS REMOVAL IN PETROLEUM PRODUCTION EFFLUENT AFTER EB IRRADIATION PLUS TITANIUM DIOXID

| Organic compound | $TiO_2$(g/L) | Removal Efficiency (%) | | | | |
|---|---|---|---|---|---|---|
| | | Absorbed Dose (kGy) | | | | |
| | | 0.0 | 10.0 | 20.0 | 50.0 | 100.0 |
| Benzene | 0.0 | 0.00 | 14.29 | 28.57 | 94.76 | 99.52 |
| | 0.1 | 0.00 | 11.76 | 23.53 | 94.71 | 98.24 |
| | 0.2 | 0.00 | 11.76 | 52.94 | 96.47 | 98.82 |
| | 0.5 | 0.00 | 14.29 | 57.14 | 96.43 | 99.29 |
| | 1.0 | 0.00 | 14.29 | 21.43 | 95.71 | 99.29 |
| Toluene | 0.0 | 0.00 | 26.19 | 44.29 | 66.19 | 96.19 |
| | 0.1 | 0.00 | 27.78 | 33.95 | 59.26 | 95.06 |
| | 0.2 | 0.00 | 20.78 | 56.49 | 66.23 | 98.70 |
| | 0.5 | 0.00 | 19.08 | 55.73 | 79.39 | 99.77 |
| | 1.0 | 0.00 | 17.53 | 12.37 | 49.48 | 99.69 |
| Xylene | 0.0 | 0.00 | 12.50 | 27.08 | 63.19 | 93.06 |
| | 0.1 | 0.00 | 12.00 | 38.00 | 68.00 | 94.00 |
| | 0.2 | 0.00 | 12.33 | 86.30 | 94.52 | 99.59 |
| | 0.5 | 0.00 | 16.67 | 71.67 | 99.50 | 99.50 |
| | 1.0 | 0.00 | 13.33 | 66.67 | 99.00 | 99.00 |

## 3.5.FINAL CONSIDERATIONS

The electron beam processing has shown high effectiveness on removal organic compounds in complex effluents. In terms of yield *Gd* values, the process showed more effectiveness when high organic molecules number are present, because the reaction among reactive transients produces more radicals continuing the process [3.13–3.15]. As described earlier, in partnership with various industrial partners, studies were performed on EB application in samples from different origin and different problems as the drinking water treatment plant and wastewater treatment plants [3.31-3.36].

Besides the high necessary absorbed doses, it is a promising process for future field implementation because, the high complexity of the effluent become its treatment by others technologies, very expensive and not so efficient. Ionizing radiation from EB accelerator is an alternative in the treatment of water and wastewater and for desulfurization enhancement in petroleum and diesel fuel, as it works on the basis of electricity and, according to the purpose, small machines can be built for easy handling and transport for use in different locations, and can be used in combination with other techniques. Homogeneous dose distribution in the irradiated layer has been solved with the development of appropriate irradiation system.

Another point to be considered is the water reuse, that is becoming increasingly important in large industrial centers, where water scarcity represents high operational costs for impounding and distribution, e.g. in Brazil, Sao Paulo water utility charges about 3.80 USD/m$^3$ for water and additionally industries paying the equivalent value for effluent disposal in water bodies, totaling to about 8.34 USD/m$^3$, whereas the price of recycled water is about 0.90 USD per cubic meter.

It's important to point out the following considerations about the radiation processing technology using EB accelerator to treat contaminated effluents:

- Technology can be used: the chosen process can be an alternative for treatment of industrial effluent, the rational for this conclusion is precisely in compliance with Brazilian Decree N. 8468 of 1976;
- Processing speed: compared with traditional wastewater treatment process, this technology proved to be much faster;
- Contribution to sustainability: the wastewater treatment using EB accelerator is a simple process and does not use other chemical products;
- Non-selective process: there is no way to select which product will be degraded, the technology acts uniformly;
- Cost reduction: technology does not require raw materials or other supporting product to eliminate the hazard or minimize the environmental impacts;
- Temperature: electron beam irradiation does not depend on the temperature, since the processing is carried out at room temperature;
- By-product: no sludge production, when compared with traditional processes;
- Disinfection: this type of treatment can be very well used to act as a disinfectant and microorganism eliminator simultaneously to chemical degradation;
- Reactions of organic compounds with reactive species: studies show that this type of processing is very fast, allowing the establishment of projects in irradiation system with good process flexibility;
- Reduction of environmental impacts: it is a safe alternative technique to minimize environmental impacts and contribute to environmental sustainability;
- Possible use of treated effluent as water reuse: a major advantage of this technological process is that it is possible to use water from treated effluent and reuse water for washing streets, garden and industrial processes;
- Association with traditional system: it is even possible to use this technology together with conventional treatment system of industrial effluents;
- Technical feasibility: occurs mainly in wastewater system where there is not a specific and efficient treatment technology and

- Accessibility: there is the possibility to use a mobile unit using electron accelerator for wastewater treatment, which can move up to companies to treat theirs effluents and demonstrate the technology.

## 3.6.CONCLUSION

The possibility of applying this technique in SABESP and PETROBRAS has the advantage of minimizing potential environmental impacts, such as pollution of air, soil and bodies of water, minimizing possible damage to humans, increasing the useful life of treatment systems, the possibility of reducing cost, likely due to the reuse of water treatment, as reused water, and the possibility of industrial water consumption economy. Studies have shown a technological, environmental, economic, social, and competitive advantage for the country.

This technology has been extensively studied by many research centers in the world but the use of this technology into environmental area has been moved slowly because industry and government is always conservative in adoption of new process, especially when they cannot observe the efficiency and cost effectiveness of a treatment in a full scale facility. Nowadays, the main focus of the group is the construction of the mobile unit for demonstration the technology *in situ.*

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# 4. EFFECT OF ELECTRON BEAM IRRADIATION ON THE BIODEGRADABILITY OF REAL TEXTILE AND DYEING WASTEWATER

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**Abstract**

A textile and dyeing wastewater treatment plant is going to be upgraded due to the string discharge standards in Jiangsu province, China. In order to investigate the effects of electron beam (EB) irradiation on the biodegradability of real industrial wastewater, the values of chemical oxygen demand (COD), biochemical oxygen demand ($BOD_5$), hence the ratio of $BOD_5$ and COD ($BOD_5$/COD), were compared before and after EB irradiation. During this process, color indices and absorbance at 254 nm wavelength ($UV_{254)}$ of wastewater were also presented. The results showed that EB irradiation cannot improve the biodegradability of raw textile and dyeing wastewater, which contains a large amount of biodegradable organic matters. In contrast, for the final effluent from the existing biological treatment process, EB irradiation may improve the biodegradability to 224%. These results suggested that the most promising way to apply EB irradiation is after the existing biological process.

## 4.1.OBJECTIVE OF THE RESEARCH

Due to the string discharge standards in Jiangsu province, China, a textile and dyeing wastewater treatment plant is going to be upgraded. The present paper is devoted to investigate the effect of electron beam (EB) irradiation on the biodegradability of real textile and dyeing wastewater. In order to confirm these results, chemical oxygen demand (COD), biochemical oxygen demand ($BOD_5$) of wastewater, hence the ratio of $BOD_5$ and COD ($BOD_5$/COD), were compared before and after EB irradiation. During this process, color indices and absorbance at 254 nm wavelength ($UV_{254}$) of wastewater were also presented.

## 4.2.INTRODUCTION

The textile and dyeing wastewater is one of the largest pollution sources in Jiangsu Province, China. It was estimated that about 400,000 $m^3$/year industrial wastewater dumped into the receiving rivers and lakes. The effluents from this industry may cause scum formation, thermal impacts, color problems, and loss of aesthetic beauty in the environment. Figure 4.1 showed the existing treatment train for the textile and dyeing wastewater in Wujiang sewage wastewater treatment plant. Throughout the primary and secondary sedimentation (in combination with coagulation) and the following biological processes, the COD concentration of initial raw wastewater decreased from 330 mg/L to 60 mg/L in the final effluent. However, a more stringent discharge standards would be put into effect since January, 2015, in which COD and color indices would be ordered less than 30 mg/L and 20 times, respectively. Therefore, a more advanced treatment process is needed.

For this reason, activated carbon adsorption, chemical oxidation and membrane filtration are proposed as possible alternatives to purify the textile and dyeing wastewater. Advanced oxidation processes (AOPs), including ozonation, Fenton reaction, photolysis, sonolysis, have been widely studied for various type of wastewater treatment [4.1–4.3]. The ionizing radiation process also belongs to the AOPs family. A number of researches have been conducted at bench-scale and pilot-scale municipal or industrial wastewater treatment [4.4–4.8].

However, few researches had investigated the effect of ionizing radiation on the biodegradability of real industrial wastewater [4.9–4.11]. The mechanics in this aspect still maintains unclear.

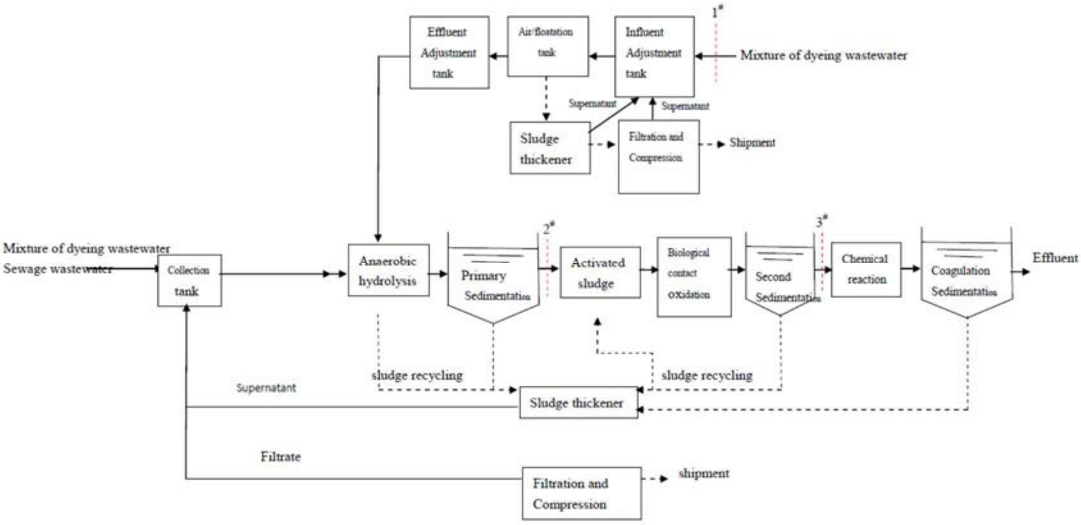

FIG. 4.1. The existing processing for textile and dyeing wastewater treatment

## 4.3.MATERIALS AND METHODS

### 4.3.1. Electron beam irradiation facility

Electron beam irradiation was conducted on a Rhodotron TT200 accelerator (energy 10 MeV, beam current 10 mA, beam power 100 kW). This accelerator was equipped with a track transport system to deliver the wastewater samples to the irradiation room. The absorbed dose was calibrated by GEX B3 dosimeter. All experiments were carried out at ambient temperature.

### 4.3.2. Wastewater samples

As shown in Fig. 4.1, in order to develop the most efficient combined electron beam method for the tertiary purification of textile and dyeing wastewater, the experiments were conducted with three various samples: initial raw wastewater(first sample), wastewater after the primary sedimentation (second sample) and wastewater after the second sedimentation (third sample).

### 4.3.3. Analysis methods

The values of chemical oxygen demand (COD) and biochemical oxygen demand ($BOD_5$) were measured according to Standard methods 5220C and 5210B, respectively[12]. The color indices were determined by dilute times. Additionally, optical absorption spectra of the wastewater were recorded by PerkinElmer instrument (Lambda 25).

## 4.4.RESULTS AND DISCUSSION

### 4.4.1. The effect of EB irradiation on the biodegradability of first wastewater sample

In the view of biological treatment of wastewater, the $BOD_5$ to COD ratio is generally regarded as biodegradability index. A threshold value above 0.3-0.4 is used to classify the stream as easily biodegradable[13]. As can be seen in Fig. 4.2, the COD and $BOD_5$ concentration in the initial raw wastewater is 316 mg/L and 245 mg/L, respectively. Therefore, the $BOD_5$/COD ratio is calculated at 0.77. This indicates that the first wastewater sample is easily biodegradable under the assay conditions. After electron beam exposure (dose between 3-9 kGy), the COD decrease slightly while $BOD_5$ reduce obviously. For example, at the dose of 3 kGy, COD go down 5% in the meanwhile $BOD_5$ reduce 19%. When the dose increases to 6 kGy, COD and $BOD_5$ reduce 2% and 36%, respectively. At the dose of 9 kGy, COD reduces 1% while $BOD_5$ reduces 42%.

Due to the $BOD_5$ decline and COD almost maintain, the ratio of $BOD_5$/COD reduced (in Fig. 4.3). For example, at the dose of 3 kGy, the ratio of $BOD_5$/COD decreases 16%. At the dose of 6 kGy, the ratio of $BOD_5$/COD decreases 35 %. At the dose of 9 kGy, the ratio of $BOD_5$/COD decreases 42%. This result indicates that the easily biodegradable component in the wastewater can be converted to less or non-biodegradable matters and some acidic by-products are formed during EB irradiation[11]. According to the other reports, a small increase of $BOD_5$ was observed at dose<1 kGy[14]. Unfortunately, this observation was not found in present experiment.

### 4.4.2. The effect of EB irradiation on the biodegradability of second wastewater sample

The COD and BOD5 concentration in the second wastewater sample is 310 mg/L and 217 mg/L, respectively. In other words, the BOD5/COD ratio is 0.70, indicating that the second sample also belongs to the easily biodegradable wastewater. After electron beam exposure (in Fig. 4.4), the COD increase while BOD reduce. For example, at the dose of 3 kGy, COD

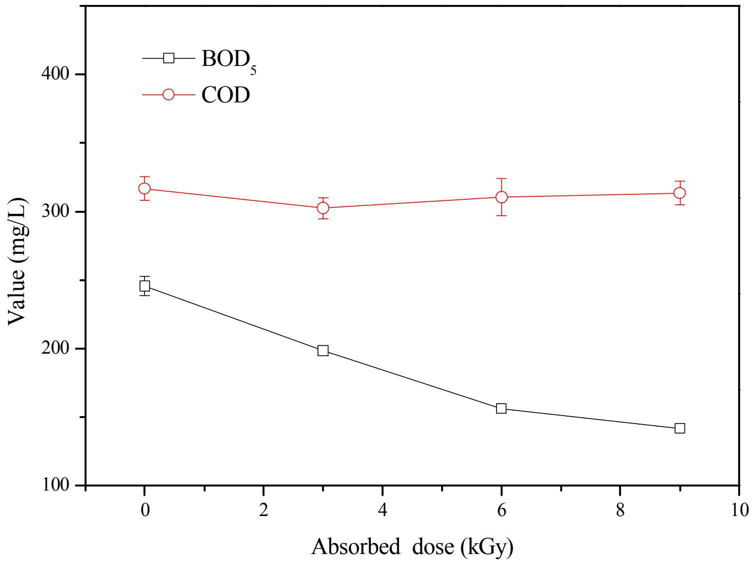

*FIG. 4.2 COD and $BOD_5$ of first sample during EB irradiation*

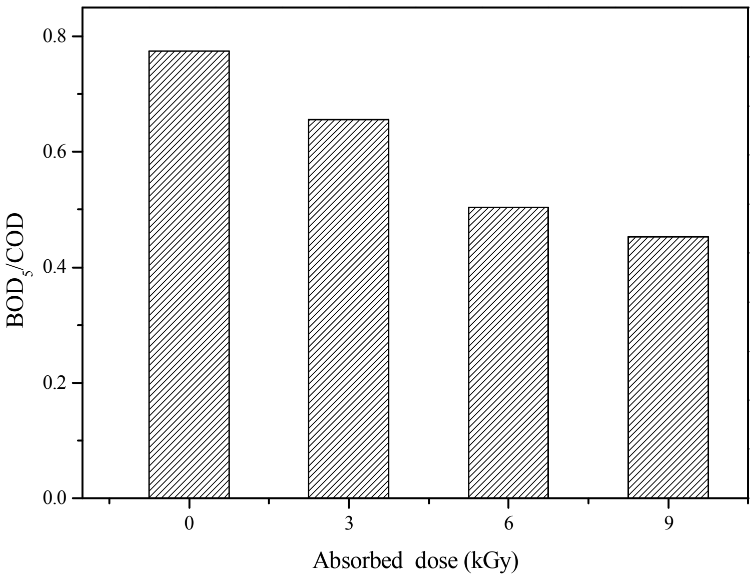

*FIG.4.3. The biodegradability of first wastewater sample during EB irradiation*

Increases 17% in the meanwhile BOD reduces 16%. When the dose increases to 6 kGy, COD increases 4% and $BOD_5$ reduces 38%. At the dose of 9 kGy, COD increases 16% while $BOD_5$ reduces 27%.

Due to the $BOD_5$ decline and COD increase, the ratio of $BOD_5$/COD reduced (in Fig. 4.5). For example, at the dose of 3 kGy, the ratio of $BOD_5$/COD reduces 29%. At the dose of 6 kGy, the ratio of $BOD_5$/COD reduces 41 %. At the dose of 9 kGy, the ratio of $BOD_5$/COD reduces 46%. The above results confirm that by-products formed during EB irradiation are even less biodegradable.

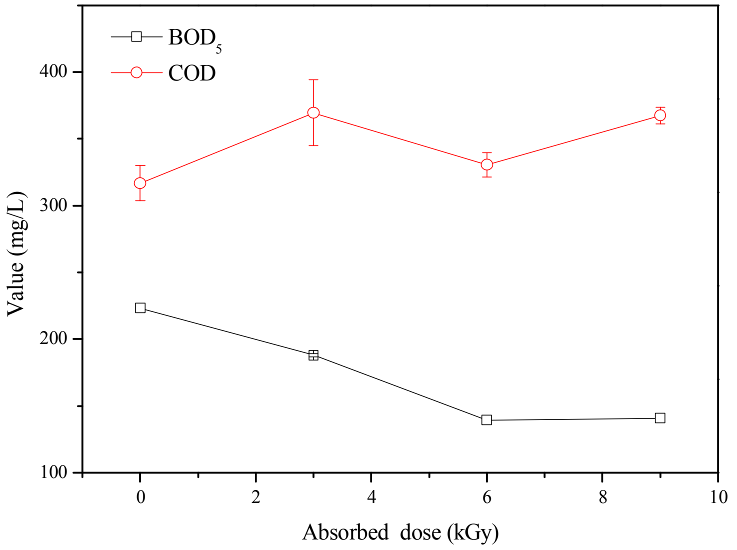

*FIG. 4.4. COD and $BOD_5$ of the second sample during EB irradiation*

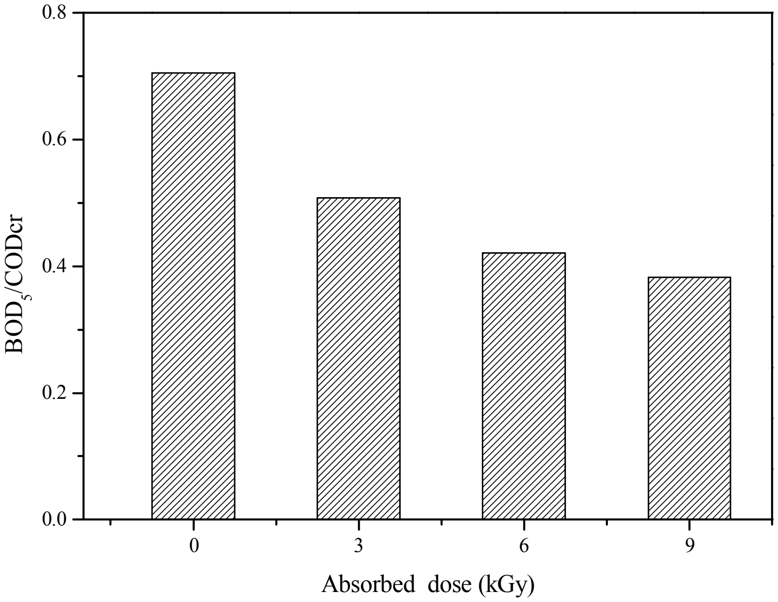

*FIG. 4.5. The biodegradability of the second wastewater sample during EB irradiation*

### 4.4.3. The effect of EB irradiation on the biodegradability of third wastewater sample

The COD and $BOD_5$ concentration in the third wastewater sample is 56 mg/L and 2.9 mg/L, respectively. Hence, the $BOD_5/COD$ ratio is 0.05, indicating that the third wastewater sample is poorly biodegradable after the existing biological treatment process. After electron beam exposure (in Fig. 4.6), the COD decrease while $BOD_5$ increase. For example, at the dose 1 kGy, COD decreases 5% while $BOD_5$ increases 80%. When the dose increases to 3 kGy, COD decrease 45% and $BOD_5$ increase 80%.

Due to the $BOD_5$ increase and COD decline, the ratio of $BOD_5/COD$ was improved to certain extent (in Fig. 4.7). For example, at the dose of 1 kGy, the ratio of $BOD_5/COD$ increases 88%. At the dose of 3 kGy, the ratio of $BOD_5/COD$ increases 224%. This means EB irradiated sample may be considered as partial biodegradable wastewater [4.15].

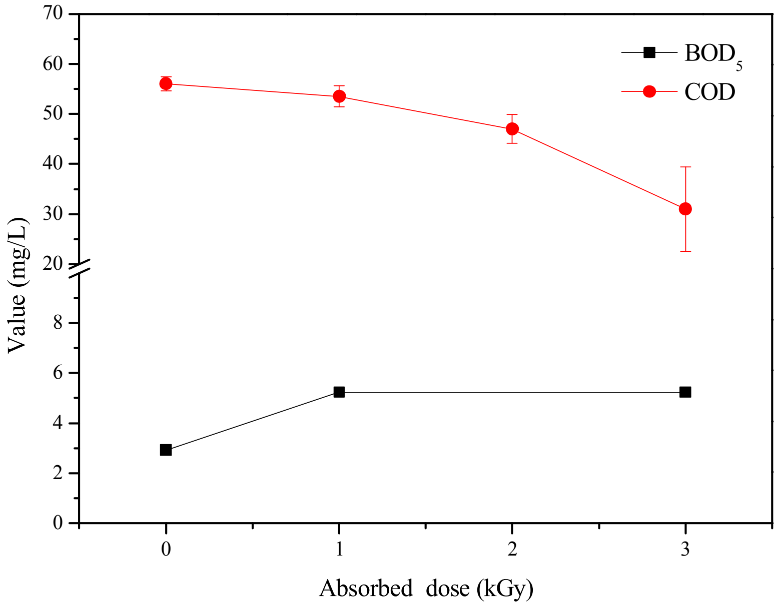

*FIG. 4.6. COD and BOD$_5$of the third sample during EB irradiation*

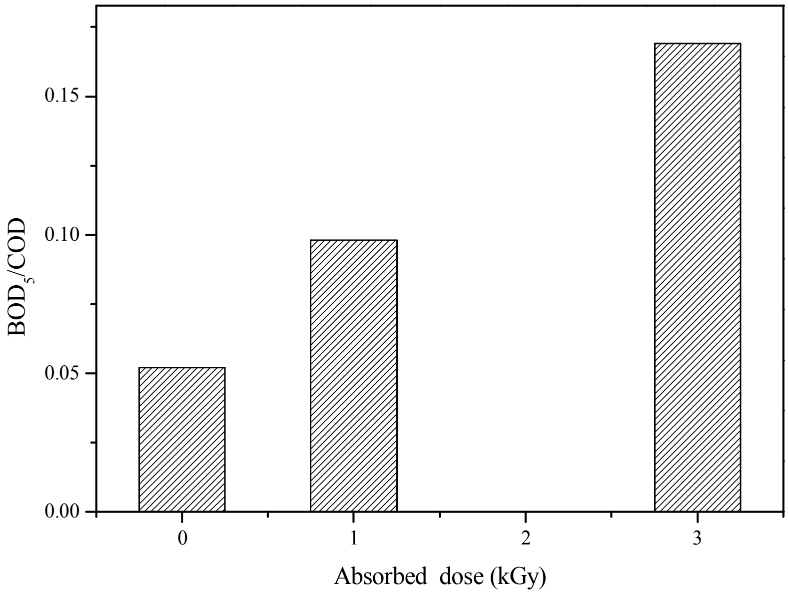

*FIG. 4.7. The biodegradability of third wastewater sample during EB irradiation*

### 4.4.4. The combination of EB and coagulation for the third wastewater sample treatment

From the economical point of view, absorbed dose for the third wastewater sample was determined as 1kGy. For coagulation, the mixtures of $Al_2 (SO_4)_3$ + $Fe_2(SO_4)_3$ solutions (mole ration 1:1, concentration: 50 mg/L) were used. This experiment started from 25 August, 2012 to 19 June, 2013. The results were depicted in the following Fig. 4.8, 4.9 and 4.10. The combination of EB and coagulation can largely remove the organic matters from the third wastewater sample. In author's opinion, this is mainly due to the enhancement of coagulation by EB irradiation.

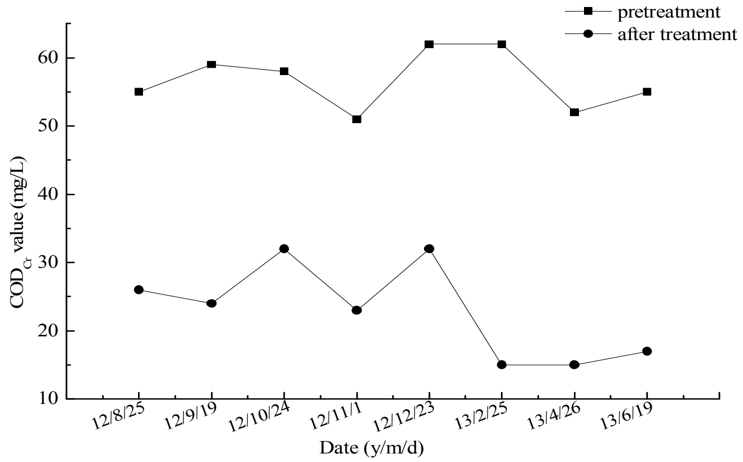

*FIG. 4.8. COD elimination by means of EB irradiation and coagulation*

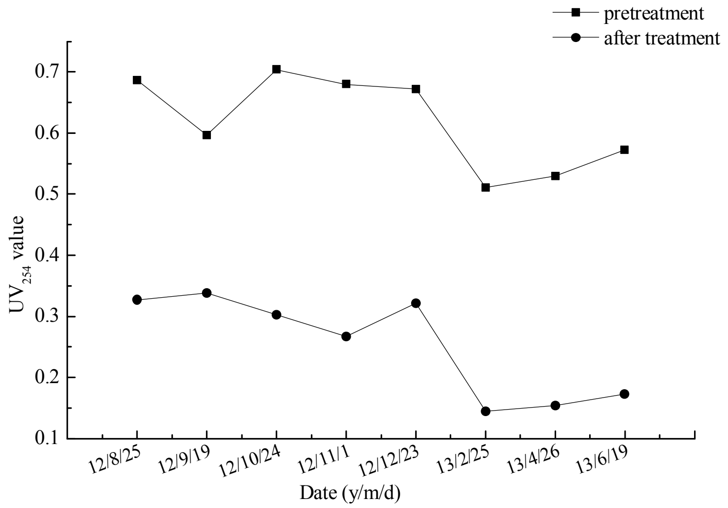

*FIG. 4.9. $UV_{254}$ elimination by means of EB irradiation and coagulation*

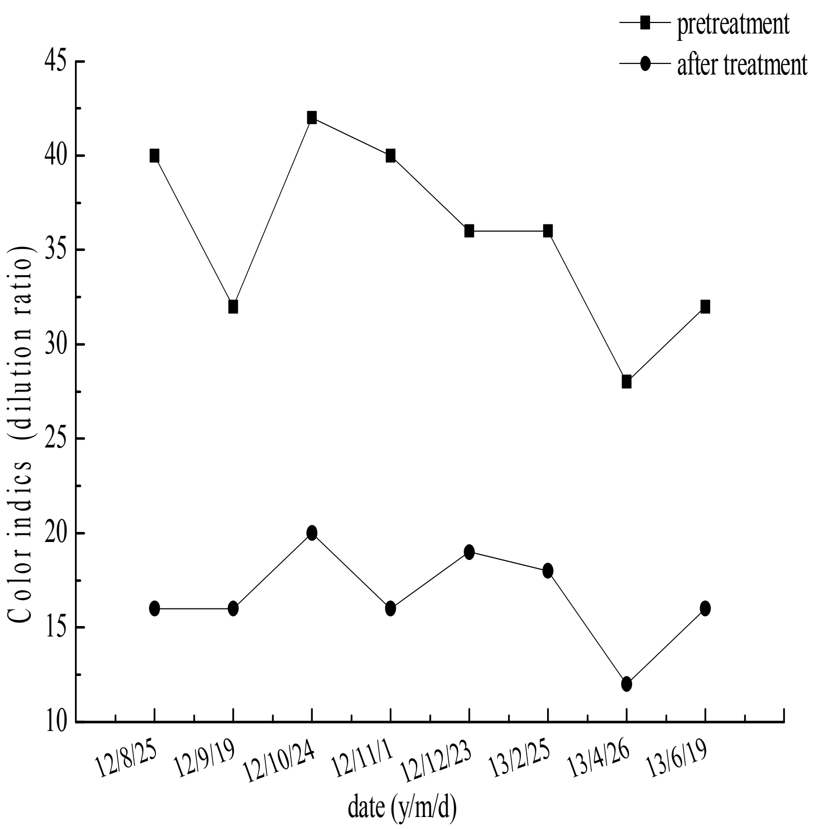

*FIG. 4.10. Color elimination by means of EB irradiation and coagulation*

## 4.5.CONCLUSIONS

The present paper investigated the effects of electron beam (EB) irradiation on the biodegradability of real textile and dyeing wastewater. The results showed that EB irradiation cannot improve the biodegradability of raw textile and dyeing wastewater, which contains a large amount of biodegradable organic matters. On the other side, EB irradiation was found to improve the biodegradability of the final effluent to 224%. In this way, EB irradiation was suggested to use after the existing biological process. The combination of EB irradiation and coagulation was optimized to treat the final effluent of the existing wastewater treatment plant.

## ACKNOWLEDGEMENTS

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# 5. RADIATION PROCESSING OF NATURAL POLYMERS FOR POSSIBLE INDUSTRIAL AND AGRICULTURAL APPLICATIONS

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**Abstract**

Radiation induced degradation technology is a new and promising application of ionizing radiation to develop viscose, pulp, paper, food preservation, pharmaceutical production, and natural bioactive agents industries. Controlling the degree of degradation, uniform molecular weight distribution, saving achieved in the chemicals (used in conventional methods) on a cost basis, and environmentally friendly process are the beneficial effects of using radiation technology in these industries. However, for some development countries such technology is not economic. Therefore, a great effort should be done to reduce the cost required for such technologies. One of the principle factors for reducing the cost is achieving the degradation at low irradiation doses. The addition of some additives such as potassium per-sulphate (KPS), ammonium per-sulphate (APS), or $H_2O_2$ to natural polymers (carboxy-methylcellulose (CMC), chitosan, carrageenan and Na-alginate) during irradiation process accelerates their degradation. The end product of irradiated CMC, chitosan, carrageenan and Na-alginate may be used as food additive or benefited in agricultural purposes. On the other hand, radiation crosslinking of PAAm or PNIPAAm is affected by the presence of natural polymer like CMC-Na and carrageenan due to their degradability which could be controlled according to its concentration in the bulk medium and irradiation dose. The swelling of the prepared copolymer hydrogels was investigated for its possible use in personal care articles particularly diapers or as carriers for drug delivery systems. The prepared cross-linked copolymers possessed high and fast swelling properties in simulated urine media and the swelling ratios of CMC-Na /PAAm gels in urine are acceptable for diaper application.

## 5.1. INTRODUCTION

Interest in radiation degradation chemistry of natural and synthetic polymers has increased tremendously as the potential was recognized for using radiation to improve industrial process such as pulping, viscose, cosmetics and food preservation and new natural active agents. Possibilities for using radiation in degradation include; Natural polysaccharides with high molecular weight like alginate and chitosan, which are found in seaweed and crustaceans and are widely utilized in food, pharmaceutical and bioengineering industries.

Polysaccharides and their derivatives exposed to ionizing radiation had been long recognized as degradable type of polymers [5.1, 5.2]. First event observed during the irradiation of polysaccharides leads to breakdown of the ordered system of intermolecular as well as intramolecular hydrogen bonds. Consequently, the rigidity of chains is influenced by intramolecular hydrogen bonding and the degree of crystallinity of the material decreases. Polysaccharides irradiated in solid state and in diluted aqueous solutions suffer scission of acetal linkages in main chains. Radiation chemistry of cellulose, and its derivatives, has long been investigated with special attention. Random cleavage of glycoside bonds in the main chain, initialized by radicals placed on macromolecules was found to be a leading reaction [5.3, 5.4].

This report presents the effect of ionizing radiations on the crosslinking and degradation of some natural polymers. Trials were made to control and reduce the irradiation dose required for the degradation of natural polymers by the addition of some additives and controlling the irradiation conditions. The possibility to crosslink natural polymers with PAAm blends using electron beam irradiation to obtain good adsorbent materials of unique properties for possible practical uses was also investigated.

5.2.RESULTS AND DISCUSSION

### 5.2.1. Effect of Ionizing Radiations on Crosslinking and Degradation of Natural Polymers:

Several studies revealed that in the case of cellulose derivatives, as CMC, Nitrocellulose Chitosan and Alginate significant part of the free radicals are generated at the substituted side chains. Thus, these free radicals were reported to be responsible for such reactions as grafting or intermolecular crosslinking [5.5, 5.6].

In this sense; radiation effect on CMC, using high energy radiation, was investigated under different conditions. The irradiation process of CMC was taken place in a solid state or in a water-soluble form of different concentrations. The effect of some additive, such as $H_2O_2$, on the degradation process during irradiation was also discussed. To elucidate the effect of irradiation on CMC; an aqueous solutions of different concentrations of CMC were exposed to electron beam irradiation. It was found that, the irradiation underwent degradation at high and low concentrations, however, the crosslinking of these polymer occurs when the polymer irradiated at concentrations ranged between (40-70 wt.%) as shown in Figure 5.1.

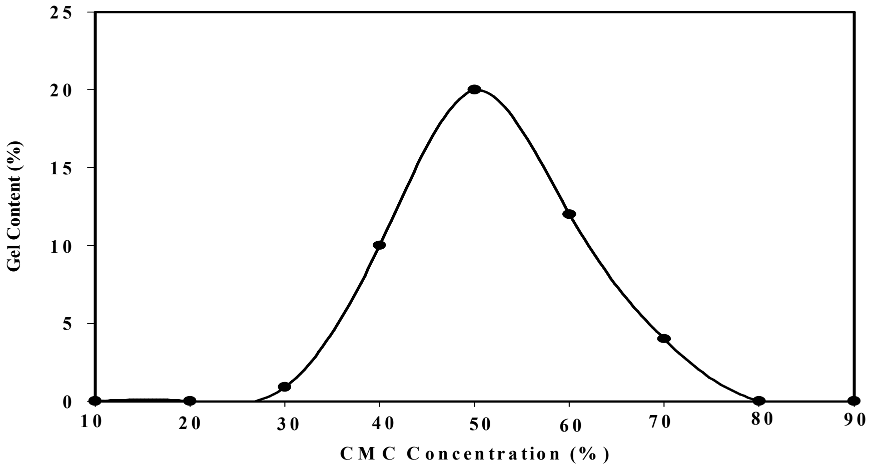

*FIG 5.1. Effect of different CMC concentrations on gel content at 20 kGy EB irradiation in air*

It can be assumed that, water contributes in the crosslinking process of CMC in two ways. First, it enhances the mobility of the rigid molecules of CMC, allowing the diffusion of macro radicals to close the distance between each other's and consequently allow their recombination. Second, it induces an increase of radical concentration such as, hydrogen atoms and hydroxyl radicals, which resulted from water radiolysis. These radicals can create CMC macro radicals by abstracting H-atom from the polymer chain. Hence, the presence of water enhances the yield of macro radicals; crosslinking of CMC was achieved from a direct effect of irradiation when radiation interacts directly with polymer chains and from an indirect effect when it interacts with the products of water radiolysis.

### 5.2.2. Radiation Degradation of CMC in Solid State:

Dry CMC was irradiated at different doses (Fig. 5.2). It can be seen that there is an extreme reduction in intrinsic viscosity at the early doses and thereafter, a gradual decrease is observed with increasing the dose. The viscosity sharply decreased from 17 to 2 when CMC was irradiated at 20kGy. Thereafter, as the irradiation dose increased, the intrinsic viscosity gradually decreased. Meanwhile, as shown in Fig. 5.3, the addition of 10% water enhanced the degradation process at 20 kGy. The intrinsic viscosity of dry CMC is higher than that of moistened CMC at low irradiation doses. However, at 50 kGy irradiation, the intrinsic viscosity of moistened CMC is higher than that of dry CMC. In the presence of water, beside the CMC chain scission, the CMC have the ability to crosslink at high doses. Generally CMC degrade by scission of the glycoside bond.

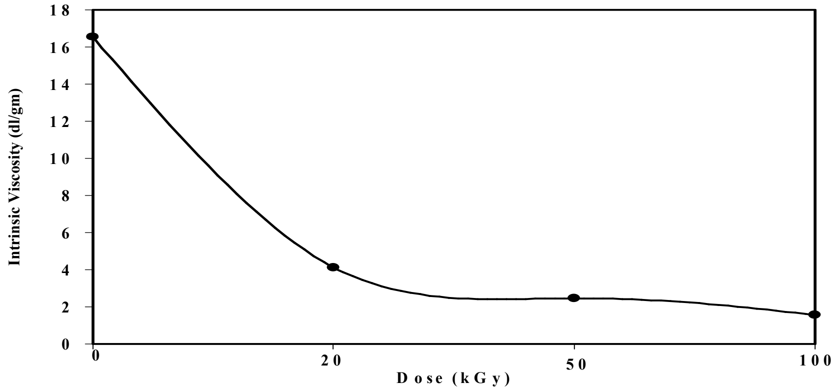

*FIG. 5.2. Effect of irradiation dose on intrinsic viscosity of dry CMC-Na; in 0.01M NaCl, measured in 0.01M NaCl.*

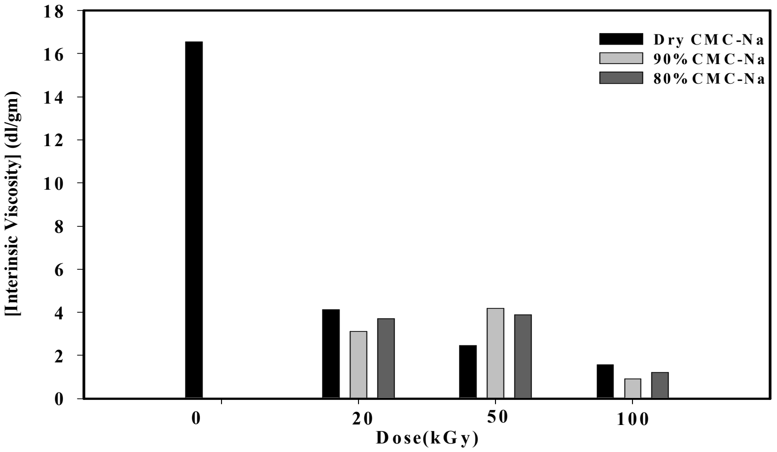

*FIG. 5.3. Effect Of Irradiation Dose On The Degradation Processes Of Different Aqueous Cmc-Na Concentrations In Terms Of Intrinsic Viscosity, Measured In 0.01m NaCl.*

The effects of moistened CMC-Na concentration and salt additive on the **i**ntrinsic viscosity at 20 kGy irradiation dose are shown in Fig. 5.4. It was found that the intrinsic viscosity decreases as the water content increases compared with that irradiated in dry form. However, in the presence of 1% KCl, the intrinsic viscosity is higher than that of moistened CMC, it enhances the crosslinking process and controlling the degradation effects during radiation processing.

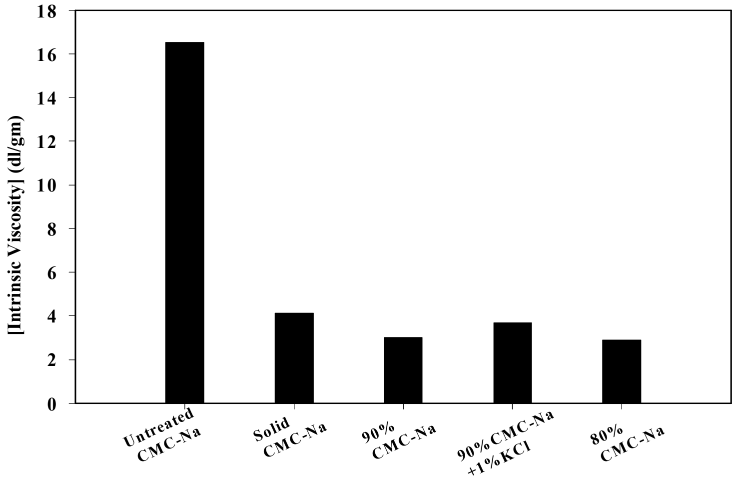

*FIG. 5.4. Effect of different CMC-Na concentrations on the intrinsic viscosity; measured in 0.01M NaCl and irradiated at 20kGy.*

### 5.2.3. Synergistic Effect of Combining Ionizing Radiation and Oxidizing Agents on Controlling Degradation of Some Natural Products:

Studying the effect of hydrogen peroxide and/or Gamma irradiation on the degradation process of Na-alginate was investigated and shown in Figure 5.5 It was found that the molecular weight of the polymer decreases by using gamma radiation or $H_2O_2$. However, combining both gamma radiation and $H_2O_2$ accelerates the degradation rate of alginate and reduces the dose required to degrading the alginate.

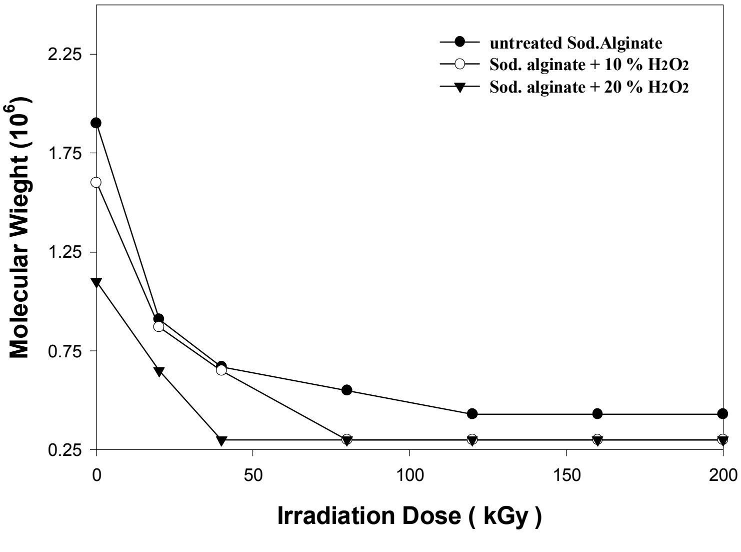

*FIG 5.5. Effect of $H_2O_2$ % and different irradiation dose on molecular weight of Na- alginate.*

The dose required to reduce the molecular weight of Na-alginate from $1.9 \times 10^6$ to about $3\text{-}4 \times 10^5$ is 120 kGy. Meanwhile, the higher the $H_2O_2$ concentration the more pronounced the degradation of Na- alginate. Similar behavior is observed for Chitosan and CMC-Na as shown in Figs. 5.6. and 5.7., respectively.

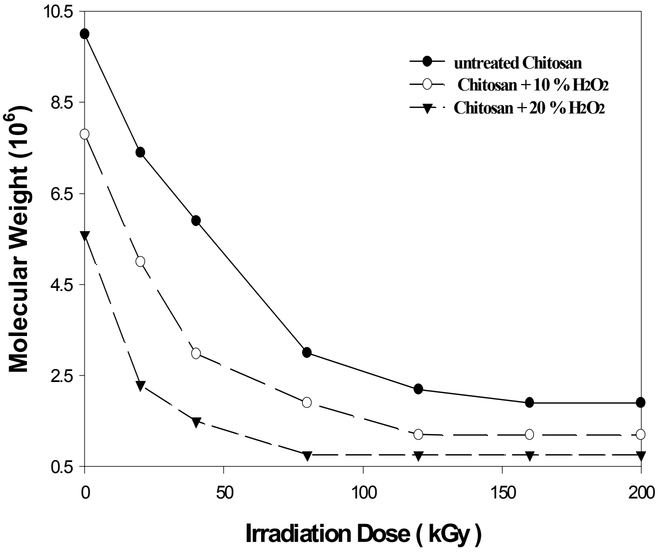

*FIG 5.6. Effect of irradiation dose on the change in molecular weight of chitosan (high molecular weight) in* $H_2O_2$.

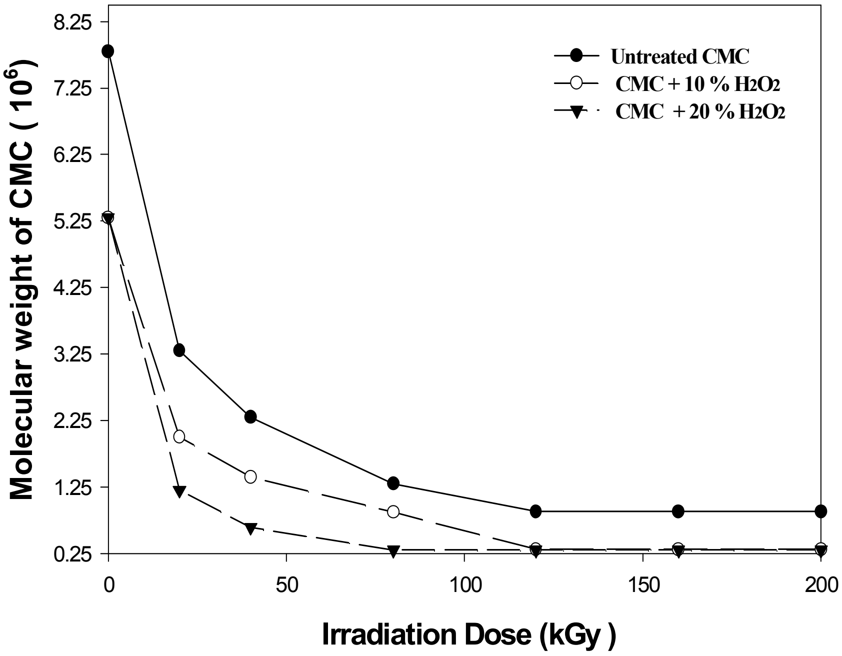

*FIG 5.7. Effect of irradiation dose on the change in molecular weight of CMC in H2O2.*

### 5.2.4. Effect of Gamma Irradiation and Salt Addition on Controlling of Degradation Process of Some Natural Polymers:

Chitosan in a solid form (pure) and that one mixed with different additives (w/w); 10% $H_2O_2$ and 10% potassium per-sulphate KPS or10 % ammonium per-sulphate APS that soluble in 1ml water were subjected to gamma irradiation at different doses that ranged from 20 up to 200 kGy. The molecular weights of irradiated chitosan, Na-alginate and CMC were determined using Mark-Houwnik equation by using the viscometer method in 0.3 M Acetic acid and 0.2 M sod. acetate as a solvent. Figures (5.8–5.10) show the effect of different irradiation doses on the Mw weights of pure chitosan Na-alginate and those mixed with different additives, respectively. It is observed that the addition of additives to the chitosan during the irradiation process accelerates the degradation of chitosan. Meanwhile, as the irradiation dose increases the degradation process of chitosan increases. The degradation rate of chitosan depends on the type of additives used. The highest degradation rate of chitosan is obtained when APS is used and the lower one in pure chitosan. Using 40 kGy irradiation dose reduces the Mw of chitosan from $1x10^7$ to $5.9x10^6$. The irradiation of chitosan at 40 kGy in the presence of APS is enough to reduce the Mw of chitosan from $1\ x10^7$ to $4x10^5$**.** Results also showed that the behavior of Na-alginate and CMC degradation is similar to that obtained for chitosan (Figs. 5.9. and 5.10., respectively). Therefore, the presence of such additives accelerates the degradation processes of such natural polymers resulting in reducing the irradiation dose, which is of economic value to reduce the cost.

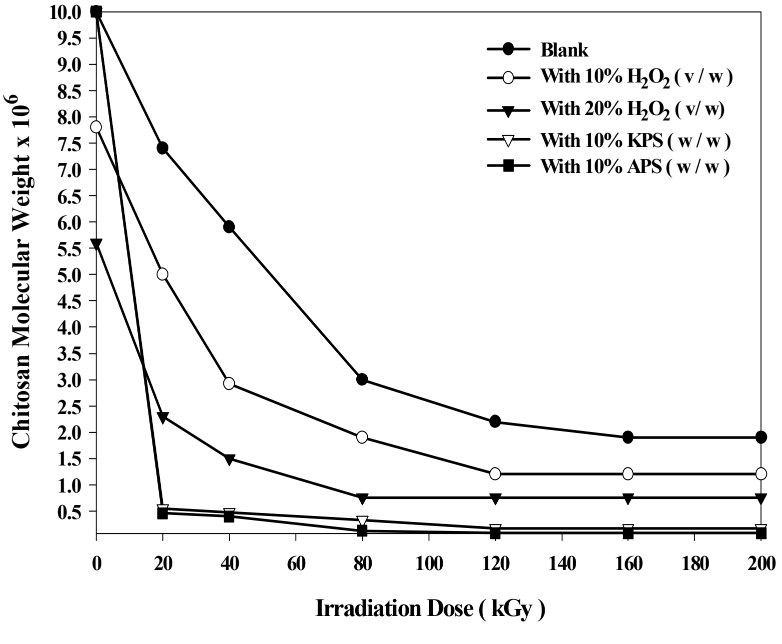

*FIG 5.8. Effect of irradiation dose on the degradation of chitosan in the presence and absence of different additives.*

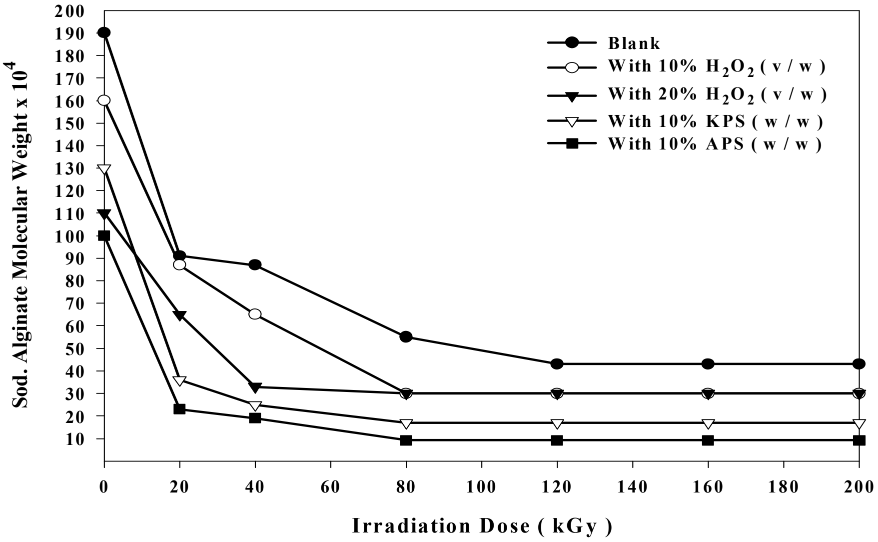

*FIG 5.9. Effect of irradiation dos on degradation of Na-Alginate in the presence and absence of different additives.*

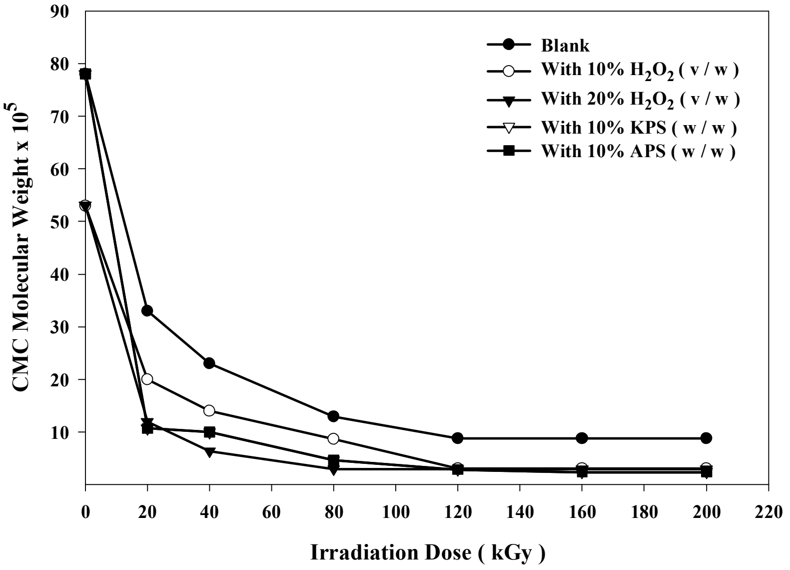

*FIG 5.10. Effect of irradiation dose on degradation of CMC in the presence and absence of different additives.*

### 5.2.5. Applications of Degraded Natural Polymers in Agricultural Field as a Growth Promotion

Degraded Na-alginate could be used as additives during radiation crosslinking of PAAm for the use as soil conditioner in agriculture purposes. The growth and other responses of bean plant cultivated in the soil that treated with PAAm and PAAm /Na-alginate copolymer were investigated. The test field results showed that the mixing of small quantities of PAAm or PAAm /Na-alginate copolymer with sandy soil results in increasing its ability to water retention. The growth of the bean plant cultivated in the soil treated with PAAm/ Na- alginate is better than that one in PAAm alone (see attached photo). The most significant difference between the PAAm and PAAm- Na-alginate copolymer is that the latter is partially undergoing radiolytic and microbial degradation to produce oligo-alginate, which acts as plant growth promoter. The increase in bean plant performance by using PAAm/Na-alginate copolymer suggested its possible use in agriculture uses as a soil conditioner providing the plant with water as well as oligo-alginate growth promoter.

The growth and other responses of zea maze plant that treated with irradiated Na-alginate or chitosan of different Mw were investigated. The test field results showed that the treatment of the zea plant with the irradiated Na-alginate at doses 120, 160, and 200 kGy in the presence of APS results in increasing in plant growth. Meanwhile, the results of the test field showed that the treatment of the zea plant with irradiated chitosan at similar doses and additive enhances not only the plant growth but also the productivity. The increase in plant performance by using degraded alginate or chitosan suggested its possible use in agriculture purposes as growth promoter.

*Photo: Bean plant cultivated in soil after 9 weeks: Left: Untreated (control), Centre: Treated with PAAm and Right: Treated with PAAm/Na-alginate.*

### *The Use of Controlled Degraded CMC Incorporated with PAAm in Diaper Industry:*

The radiation crosslinking of PAAm is affected by the presence of CMC-Na due to the degradability of the latter one which could be controlled according to its concentration in the bulk medium and irradiation dose. Accordingly, the gel content and swelling properties of PAAm-Na-CMC could be controlled. Figure 5.11. shows that the degree of swelling increases with dose and showing a maximum swelling at 30 kGy and thereafter it deceases at higher dose (40 kGy). This is due to the degradation processes at relatively medium doses up to 30 kGy and the partial crosslinking may occur at 40 kGy. So, this is a matter of degradation/ crosslinking ratio depending on the dose and concentration of CMC-Na in the mixture.

The swelling of the prepared hydrogel was investigated for its possible use in personal care articles particularly diapers. Thus, its degree of swelling was measured in simulating urine solution, and compared with commercial super-porous hydrogels based on acrylate polymers, Figure 5.12. It is clear that there is a slight difference between the swelling of the prepared CMC-Na /PAAm hydrogel and the commercialized one in the simulated urine solution. The prepared cross-linked copolymers possess high and fast swelling properties in simulated urine media. An acceptable swelling capacity for super-absorbent is approximately 20-40g of urine per gram of hydrogel. Therefore, the swelling ratios of CMC-Na /PAAm gels in urine are acceptable for diaper application.

### *5.2.5.1. Modification of LCST of PNIPAAm Based Natural Polymers By Controlling The Degradation During Radiation Copolymerization.*

LCST of P NIPAAm (thermo responsive polymer) is around 32°C. To modify the LCST of the PNIPAAm, the hydrophilic / hydrophobic balance between PNIPAAm chains, it is necessary to change its characteristic properties mixing with different polymers of different properties. In this connection, NIPAAm monomer was mixed with different types of natural polymers such as polysaccharides. Thereafter, the mixtures exposed to ionizing radiation at different doses to obtain copolymer with different molecular weights by controlling the degradation of natural polymers. In this regards, the following investigations and applicability of the obtained copolymers are presented.

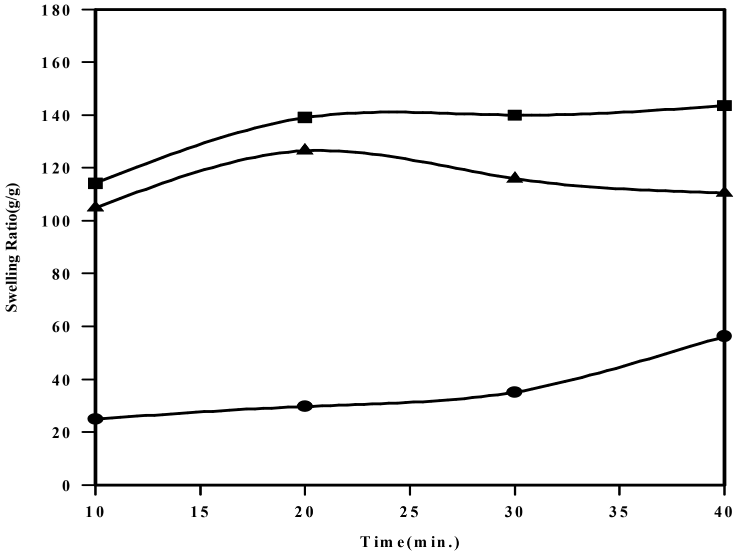

*FIG 5.11. The swelling ratio for CMC-Na in distilled water, irradiation dose; (■) 30kGy, (▼) 40kGy and (●) 20kGy.*

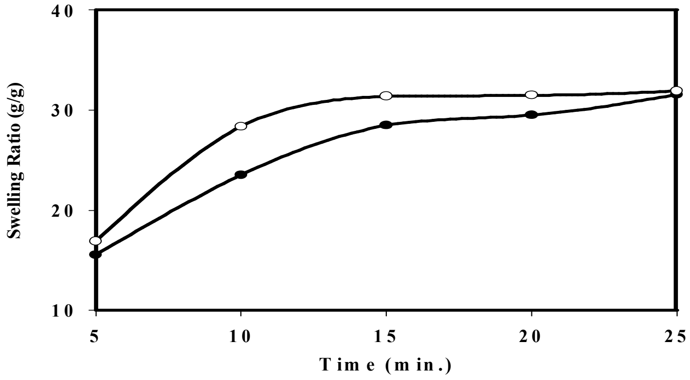

*FIG 5.12. The swelling ratio of (●) CMC-Na /PAAm super-absorbent hydrogel, (o) commercial diaper; in simulated urine solution.*

### 5.2.6. Equilibrium swelling of PNIPAAm/ Natural Polymer Hydrogels:

Temperature sensitivity of NIPAAm-natural polymer hydrogels was investigated by determining the swelling behavior of the prepared hydrogels as a function of temperature as shown in Fig. (5.13). It can be seen that the prepared PNIPAAm/ natural polymer hydrogels possess discontinuous phase transitions. The position and width of such phase transition are dependent on the nature of the natural polymer. The PNIPAAm hydrogel containing CMC- or Carrageenan showed the highest phase transition whereas NIPAAm/ agar showed the lowest phase transition.

From these results, it can be seen an inverse relation between the temperature sensitivity and the gelation degree of the prepared copolymer, i.e. CMC and Carrageenan which possessed the lowest gelation degrees showed the highest phase transition. Meanwhile, agar and Na-alginate PNIPAAm copolymers which possessed higher gelation showed lower phase transition. Such interesting observation may confirm and reveal the importance of the crosslinking density on the degree of phase transition. The low gelation of carrageenan or CMC/PNIPAAm hydrogel would produce a network structure of low crosslinking density which is of large for spaces swelling and do not retard the de-swelling process resulted from the collapse of PNIPAAm moieties.

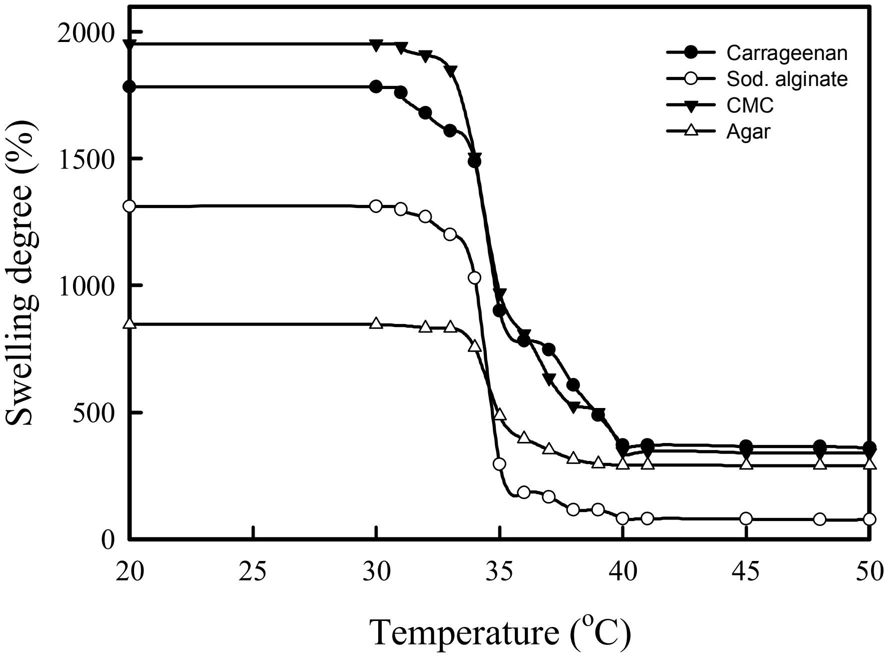

*FIG. 5.13. Temperature dependent swelling behavior of PNIPAAm containing different natural polymeric materials.*

Whereas, the gelling and binding properties of agar and Na-alginate, respectively would increase the crosslinking density which reduces the free spaces available for swelling. In addition such properties would retard the chain relaxation which also restricts the collapse of NIPAAm moieties.

### 5.2.7. Effect of Absorbed Dose on the LCST of NIPAAm/Natural Polymer Hydrogels:

To confirm the relation between LCST and crosslinking density, the effect of irradiation dose on the temperature sensitivity of PNIPAAm/ carrageenan hydrogel was investigated (Fig. 5.14). It shows clearly a direct relation between crosslinking density and the degree of phase transition expressed as a function of swelling degree. The PNIPAAm/Carrageenan hydrogel prepared at low irradiation doses showed higher phase transition. Whereas, the prepared one at high doses showed lower phase transition character leads to the reduction in the swelling degree.

### 5.2.8. Application of PNIPAAm Grafted with Some Natural Polymers:

The prepared thermo-sensitive based natural polymer hydrogels may be used as pH-stimuli responsive for drug delivery systems. Therefore, a trial was made to evaluate its possibility for the use in such purposes for drug delivery under control release depending on the type of based natural polymer. Figure 5.15 shows the time dependent cumulative release of ketoprofen from PNIPAAm based natural polymer formulations at buffer solutions of pH 1 and pH 7. It can be seen that at pH 1, almost 5% of ketoprofen was released within 3h. On the other hand, as soon as the PNIPAAm based natural polymer formulations moved to the dissolution medium of pH 7, immediate release of ketoprofen began. The rate of its release from PNIPAAm-agar hydrogel is much higher than that from other PNIPAAm based natural hydrogels. In general such based natural polymers hydrogels showed pronounced pH-stimuli responsive and the content of released drug is very dependent on the type of natural polymer in the PNIPAAm hydrogel. Such characteristic properties may make them acceptable for drug delivery systems under control release to specific sites such as colon without side effect on the stomach.

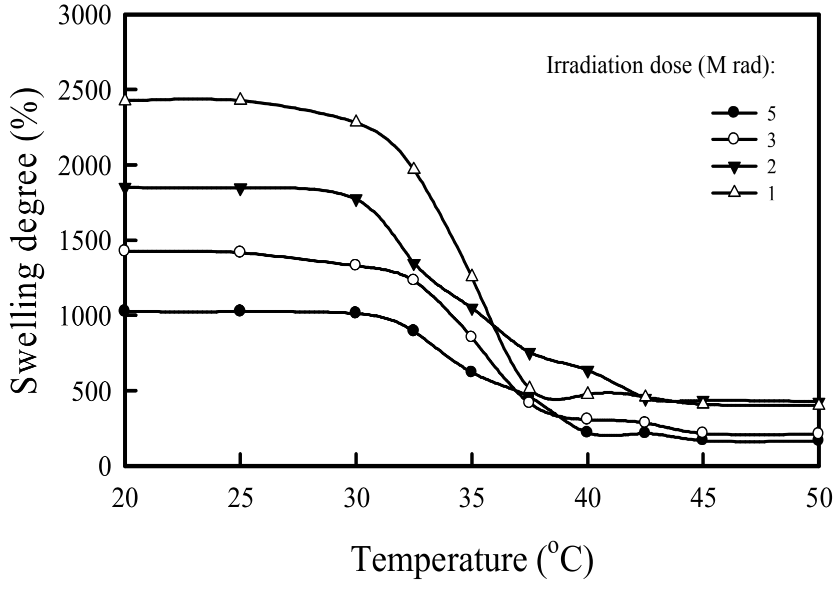

*FIG 5.14. Effect of temperature on the swelling percent for PNIPAAm/natural polymer hydrogels prepared at different irradiation doses.*

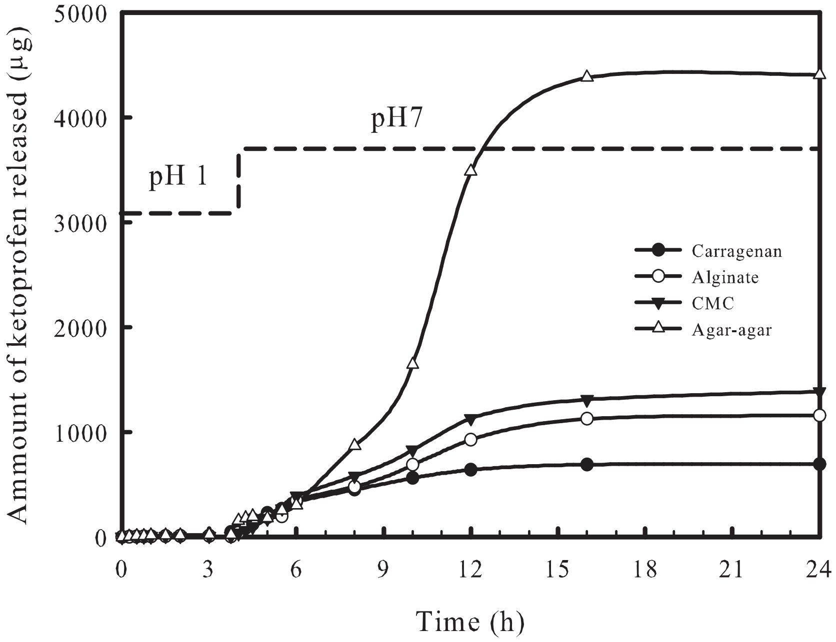

*FIG 5.15. Effect of natural polymer on the release of ketoprofen from its corresponding copolymer with PNIPAAm at different interval times and pH's.*

## 5.3.CONCLUSION

It can be concluded that radiation is a very effective tool for controlling the degradation and cross-linking of natural occurring polymers and the synthesis of relative economic, environmentally friendly super-absorbent hydrogels, which may potentially be used in personal care products industry and in agricultural purposes. One of the principle factors for reducing the cost is achieving the degradation at low irradiation doses. This not only reduces the cost of radiation but also improve the quality of the end use products. The end product of irradiated natural products such as carboxy-methylcellulose, chitosan and Na-alginate may be used as food additive or benefited in agricultural purposes. The test field results showed that the treatment of the zea plant with irradiated Na-alginate or chitosan, enhanced the plant growth and increases its productivity. Radiation crosslinking of PAAm or PNIPAAm is affected by the presence of natural polymer like CMC-Na and carrageenan due to the degradability of the latter ones which could be controlled according to its concentration in the bulk medium and irradiation dose. Accordingly, the gel content, thermo-sensitivity (LCST) and swelling properties of polymer based natural polymers could be controlled. The swelling of the prepared hydrogel was investigated for its possible use in personal care articles particularly diapers or as carriers for drug delivery systems. The prepared cross-linked copolymers possessed high and fast swelling properties in simulated urine media and the swelling ratios of CMC-Na /PAAm gels in urine are acceptable for diaper application. Degraded Na-alginate and chitosan could be used as growth promoter for plants in agriculture purposes.

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# 6. WATER, WASTEWATER AND SEWAGE SLUDGE TREATMENT USING RADIATION TECHNOLOGY

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**Abstract**

When irradiated in aqueous solutions at a concentration of 0.1 mmol dm$^{-3}$ the reactions of sulfamethoxazole, a worldwide used anti-infective sulfonamide antibiotic, were mainly induced by hydroxyl radicals. Complete degradation of aromatic system was obtained with 5 kGy. The sulfur of the molecule was entirely transformed to $SO_4^{2-}$, while $NO_3^-$ and $NH_4^+$ were formed from the nitrogen content. The chemical oxygen demand and total organic carbon values indicated complete mineralization during irradiation. In the toxicity tests, the observed increase in mortality of *Vibrio fischeri* bacteria was mainly due to $H_2O_2$ formed during the radiolytic procedure. The results showed that the degradation was effective; therefore, the irradiation technology can be recommended for treatment of wastewater containing sulfamethoxazole.

## 6.1.OBJECTIVE OF THE RESEARCH

Toxic organic compounds e.g. pharmaceuticals are detected worldwide in the aquatic environment, mainly through the effluents of sewage treatment plants; therefore, it is important to find methods for their decomposition. High-energy radiation (electron beam, EB) treatment is a very effective method for this purpose.

Our objective focused on the ionizing radiation induced decomposition of sulfamethoxazole (SMX). The degradation products were identified and the change in toxicity during irradiation was followed. The effect of $H_2O_2$ formed during the radiolytic procedure on the toxicity of the solution was also discussed.

## 6.2.INTRODUCTION

Wastewater treatment using high-energy ionizing radiation is an important application of radiation technology for environmental remediation. Recent reports have indicated that increasing concentration of recalcitrant pollutants like pesticides, pharmaceuticals and personal care products (PPCP) are entering the aquatic environment and may cause environmental hazard [6.1]. The concentration of these substances may vary from traces to environmentally relevant amounts [6.2]. A large variety of techniques, with a common name advanced oxidation processes (AOP) have been developed to degrade harmful, badly biodegradable organic contaminants in water. Most of these processes were applied only in laboratory experiments, a few of them were tested also on larger scale. Radiation technology was used under real industrial conditions [6.3] at the level of 10 000 m$^3$/day.

The application of radiation technology may be considered for various purposes:

I. Biosolids (sludge) treatment (disinfection, odour control, dewatering, enhanced biogas production)

II. Wastewater treatment

a. High flow, high concentration (wastewater influent, before biological treatment)

b. Low flow, high concentration (process wastewater)

c. High flow, low concentration (sewage treatment plant effluent)

*Sludge treatment*

Sludge treatment by ionizing radiation (using Co-60 gamma source) is a procedure which is perfectly working for a long time on large scale and proved to be economical. Irradiated sludge could be disposed after drying in a landfill or used as manure [6.3, 6.4]. The aim of radiation treatment in this case is disinfection, odor control, and dewatering.

Sewage treatment plants usually produce biogas in the anaerobic digestion step. Biogas can be used for producing electric energy. As energy prices are increasing the importance of producing energy from biogas is increasing as well. According to our preliminary results the efficiency of biogas production can be highly improved by irradiating a part of the bio sludge. Therefore, this may be considered as one of the important deployments of clean (green) radiation technologies for environmental remediation in the future.

*Wastewater treatment*

Radiation treatment usually highly improves the biodegradability of the toxic organic water pollutants. Therefore, it seems to be reasonable to apply radiation treatment as a first step at the sewage plant, before the biological step. However, the majority of the high organic solute content (having chemical oxygen demand (COD) around 400–600 mg $dm^{-3}$) of the influent is biodegradable. Therefore, the majority of the energy of the irradiation is absorbed by the non-toxic components and high doses are needed to decompose all the pollutants including the toxic, non-biodegradable compounds. Due to its high dose requirement case II.a does not seem to be an economical process.

Wastewaters containing organic pollutants in very high concentrations (COD values of several hundreds of thousands) are produced in some chemical factories e.g. in pharmaceutical factories in relatively small volumes (some thousands of tons per months). Due to the high COD values the application of radiation technology for the treatment of these kinds of wastewaters is not economical either. The combination of various methods (chemical treatment, wet air oxidation, irradiation and biological treatment) may be considered in these cases. They usually contain organic solvents; rectification may be suggested to remove them. This procedure may decrease COD to a reasonable value so that radiation treatment with an economical dose (below 10 kGy) will be enough to remove the toxicity and convert non-biodegradable components to biodegradable ones. The applicability of radiation treatment for case II.b. should always be determined by case studies.

Due to the low biodegradability of emerging organic contaminants (EC) sewage treatment plants emit to the surface waters high volumes of effluents containing toxic organic pollutants in low (usually ng $dm^{-3}$–μg $dm^{-3}$) concentrations. This is a very sensitive environmental issue and needs further considerations. In cases when the receiving waters are lakes and the same lakes are the sources of drinking water as well, the problem requires urgent solution. For instance Lake Geneva provides drinking water more than half million inhabitants in Western Switzerland and France, at the same time it is a final receiver of treated wastewater effluents [6.2]. Among the 32 micro pollutants detected in the lake 28 were pharmaceuticals. In laboratory scale 97% removal of the micro pollutants was achieved by using Photo-Fenton treatment. However, it is a question if this method is applicable for the effluent of a wastewater plant treating water 180,000 inhabitants. Processes based on high-energy ionizing radiation are most possibly more economical and effective than other AOP techniques [6.5]. The usefulness and efficiency of radiation technology for treatment of different organic pollutants has been adequately demonstrated at various scales of operation. However, lack of comparative techno-commercial data in pilot scale studies using radiation technique (alone or in combination with other methods) has remained a major issue in further utilization of this method for wastewater treatment. Further mechanistic studies are also needed to facilitate practical application.

In our laboratory the ionizing radiation induced degradation of a wide variety of toxic organic contaminants including pharmaceuticals, pesticides and textile dyes were studied. Mechanism for their degradation was suggested and a correlation between chemical structure and effectiveness of degradation was described. Here we summarize our results on the degradation of sulfamethoxazole (4-amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide, SMX). SMX is a widely used anti-infective sulfonamide antibiotic for both human and animal therapies [6.6, 6.7]. The degradation of SMX was followed in dilute aqueous solutions, the degradation efficiency was determined, changes in toxicity were investigated and reaction products were identified. These results may provide a more complex picture of the whole decomposition process and an opportunity to approach and qualify it from different aspects.

## 6.3.MATERIALS AND METHODS

### 6.3.1. Chemicals, materials and irradiation procedure

The gases were purchased from linde ($N_2O$) and messer ($N_2$), while all the chemicals, except acetonitrile and $H_2O_2$ test kit (Fischer Chemical and Merck), from Sigma-Aldrich. The irradiation was performed with a dose rate of 6 kgy $h^{-1}$ at room temperature by a $^{60}$Co (1.85 PBq) SSl-01 panoramic type source. Prior to analyses the solutions were filtered through 0.2 μm pore sized regenerated cellulose (RC) membranes.

### 6.3.2. Analyses and sample preparation

The UV-Vis absorbance spectra of the samples were taken between 190 nm and 400 nm by a JASCO 550 spectrophotometer in 1 cm cells. Since the yield of the intermediates is pH dependent and SMX is an amphoteric molecule, the measurements were done at pH 4 (set by NaOH and HCl) and at natural pH (5.8). The 0.1 mmol $dm^{-3}$ concentration samples were bubbled with appropriate gases and straightaway sealed airtight.

The degradation products were separated by an Agilent 1200 liquid chromatograph (LC) equipped with a 5 mm × 100 mm Phenomenex Kinetex XB-C18 capillary column. Separations were done under isocratic condition with 80% aqueous formic acid (0.1%) and 20% pure acetonitrile. LC-separations were made at 25 °C at a flow rate of 0.2 $cm^3$ $min^{-1}$. The compounds were detected and identified with on-line mass spectrometry (MS). MS experiments were performed at positive or negative ionization mode using an Agilent 6410 triple quadrupole tandem mass spectrometer (MS/MS) with electrospray ionization (ESI).

Air saturated solutions were irradiated for COD, TOC and toxicity measurements. The COD values were measured according to ISO 6060:1989 by a Behrotest TRS 200 COD system, while the TOC values by a non-dispersive infrared (NDIR) sensor equipped Shimadzu TOC-VCSN instrument. TN was measured by a total nitrogen measuring unit (TNM-L) of a TOC-L total organic carbon analyzer.

The changes of acute toxicity caused by the irradiation were followed by Microtox® tests carried out with LANGE LUMIStox 300 equipment using liquid-dried Vibrio fischeri bacteria. During experiments the natural light emission of microorganisms was measured. The inhibition of the light emission in the presence of samples was determined against a non-toxic control (distilled water). Alteration in light output was evaluated after 30 minutes of exposure to irradiated SMX solutions adjusted to pH 7 ± 0.2.

The concentration of $H_2O_2$ was evaluated with $H_2O_2$ test kit. The test is based on a redox reaction between $H_2O_2$ and Cu(II) ions in the presence of phenanthroline. The reaction leads to formation of a yellow or orange complex that was determined spectrophotometrically at 454 nm [6.8]. In some experiments the $H_2O_2$ was removed from the solutions with catalase enzyme set to pH 7 with phosphate buffer. The toxicity measurements were made on 0.1 mmol $dm^{-3}$ SMX samples.

$NO_3^-$, $NO_2^-$, $SO_3^{2-}$ and $SO_4^{2-}$ were identified and quantified with a Metrohm 861 Advanced Compact IC system using a Metrosep A Supp 4-250/4.0 column with 1.8 mmol $dm^{-3}$ $Na_2CO_3$ and 1.7 mmol $dm^{-3}$ $NaHCO_3$ buffer solution eluent, while the determination of $NH^{4+}$ was performed by a Metrosep C3 column using 5.0 mmol $dm^{-3}$ $HNO_3$ buffer solution. Cation and anion detections were performed at 40 °C and 30 °C, respectively, at a flow rate of 1 $cm^3$ $min^{-1}$.

The ICP-MS measurements were performed on a high resolution, double focusing magnetic sector field inductively coupled plasma mass spectrometer. The samples were introduced through a conical nebulizer system with an uptake rate of 1 $cm^3$ $min^{-1}$. The flow rates of nebulizer, auxiliary and cooling gases were 0.95 $dm^3$ $min^{-1}$, 1.13 $dm^3$ $min^{-1}$ and 15.4 $dm^3$ $min^{-1}$, respectively.

## 6.4.RESULTS AND DISCUSSION

### 6.4.1. Reactions of intermediates and identification of products

In the course of $^{\bullet}OH$ and $O_2^{-\bullet}/HO_2^{\bullet}$ reactions, the 266.5 nm band, which belongs to the aromatic π-π* transition, decreased as a function of dose (Fig. 6.1). This abatement refers to the destruction of aromatic structure that was practically complete at 5 kGy dose. In the 280 - 300 nm region an increasing absorbance revealed the presence of at least one decomposition product. Changes in pH resulted in only a slight dislocation of the 266.5 nm band (Fig. 6.1). The phenomenon is related to the protonation of SMX products and it occurred under all experimental conditions used.

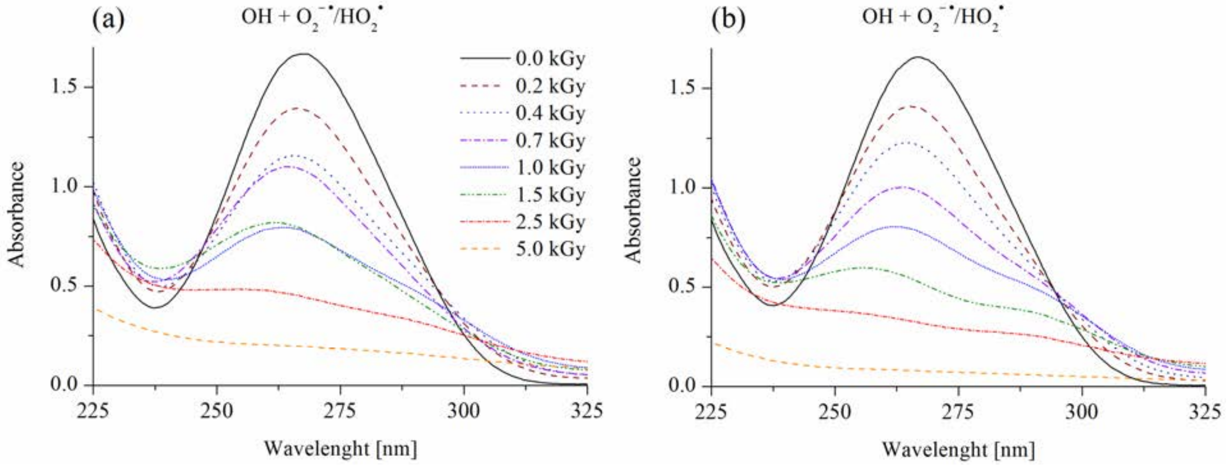

*FIG. 6.1. Absorption spectra of air saturated 0.1 mmol* $dm^{-3}$ *SMX solutions irradiated with different doses at* pH 4 (a) and pH 5.8 (b).

In $^{\bullet}$OH reactions (Fig. 6.2a), the spectra were very similar to those observed in $^{\bullet}$OH and $O_2^{-\bullet}/HO_2^{\bullet}$ reactions (Fig. 6.1a). Substantial difference showed up in experiments with $^{\bullet}$OH and $e_{aq}^{-}$ combination, a less intense decrease of the aromatic absorption band was noticeable (Fig. 6.2b). This refers to lower degradation efficiency. However, it also suggests that the degradation was mainly due to $^{\bullet}$OH reactions. To examine the $e_{aq}^{-}$ reactions 5% *t*-BuOH was added to $N_2$ saturated solutions (Reaction (5)). Thus, beside $e_{aq}^{-}$, *t*-BuOH radical was also present in the samples. As Fig. 6.2c shows, the absorbance was decreasing continuously, similarly to the previous cases. However, at longer wavelengths increase in absorbance was not observable.

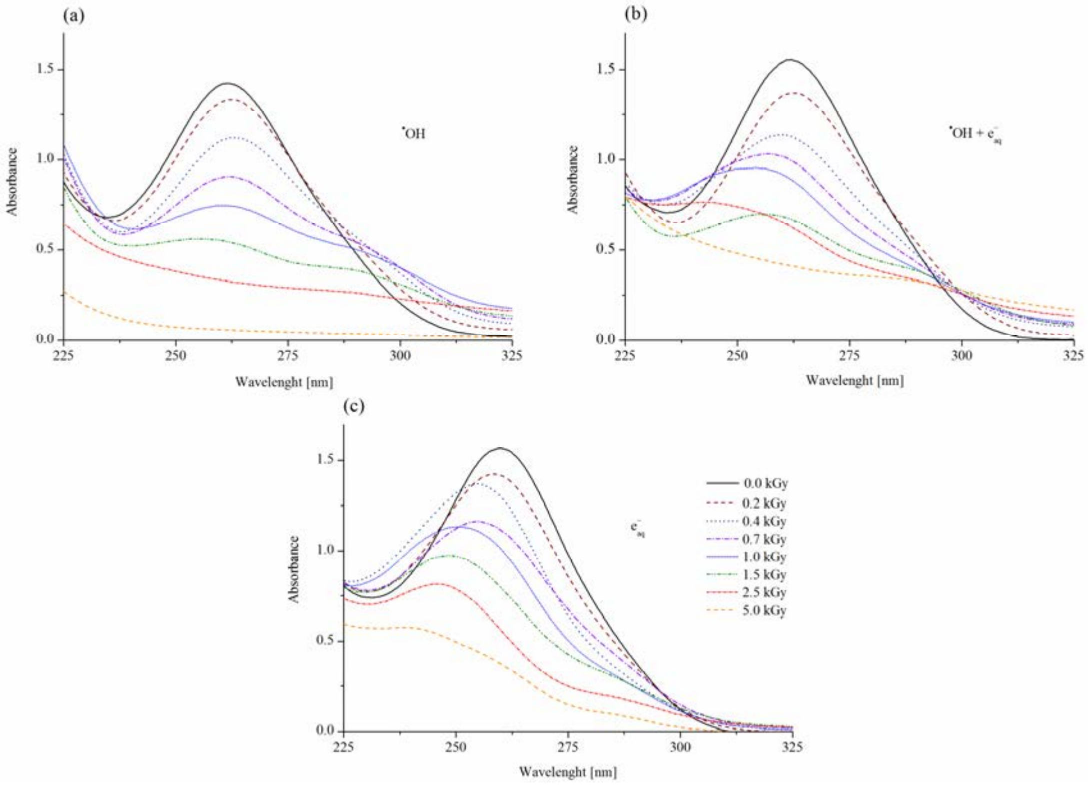

*FIG. 6.2. Absorption spectra of $N_2O$ (a), $N_2$ (b) and $N_2$ + 5% t-BuOH (c) saturated 0.1 mmol $dm^{-3}$ SMX solutions irradiated with various doses at pH 5.8.*

In order to separate the products of SMX the LC-MS method was used. Chromatograms and retention times ($t_R$) are shown in Fig. 6.3 and in Fig. 6.5. In data evaluation only the results of positive ionization mode were used because of much higher signal intensities. The molecular ion generated from SMX had a mass ($[MW+H]^+$) of 254 Da. In the course of fragmentation with different collision energies several fragmentation sites of SMX were found (Fig. 6.4). These results agree with the general fragmentation patterns of sulfonamides [6.9]. The obtained fragment masses were as follows: $F_1^+$=MW–LG =92, $F_2^+$=MW–LG=156 and $F_3^+$=MW–LG+2, where LG means leaving group.

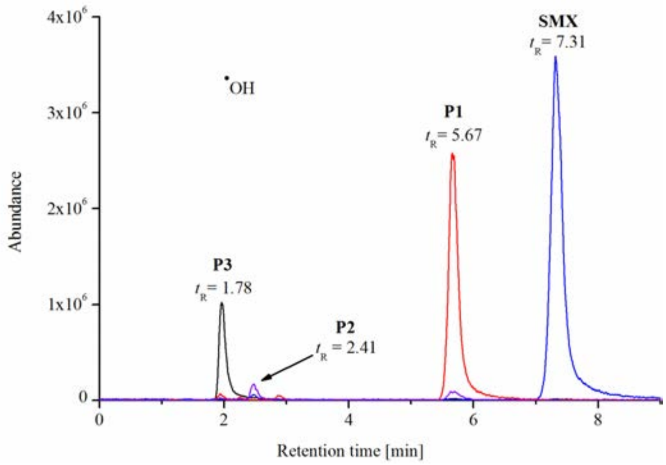

*FIG. 6.3. Chromatogram of 0.5 kGy irradiated $N_2O$ saturated 0.1 mmol $dm^{-3}$ SMX solution at pH 5.8.*

When $^{\bullet}OH$ was the only reactant, the most intense peak on the chromatograms was *P1* ($[MW(P1)+H]^+=270$) (Fig. 6.3) that is attributed to a mono-hydroxylated product of SMX. The hydroxyl group is likely to be on the aromatic ring (proved by the appearance of $F_1^+ + 16 = 108$ and $F_2^+ + 16 = 172$ fragments). *P2* ($[MW(P2)+H]^+=272$) is probably also a hydroxylated product. However, it is suggested that the hydroxyl group is added to one of the double bonds of the isoxazole ring. During hydroxylation the isoxazole ring becomes partially saturated (Fig. 6.4). Fragments of *P2* and SMX are very similar. There are only two informative fragments of *P2* present, $[MW(P2)+H-H_2O]^+ = 254$ and $[MW(P2)+H-2H_2O]^+=236$. *P2* can easily lose two water molecules during the fragmentation process, which has not been observed in the case of other degradation products. Loss of these water molecules is only feasible from the five-membered ring with altered structure. The chromatographic peak of *P2* has low intensity and was observed in case when $^{\bullet}OH$ was the only reactant. Based on the diode array measurements carried out simultaneously, changes in absorbance of UV-Vis spectra around 280 - 300 nm are due to the presence of hydroxylated forms of SMX (as it was mentioned in connection with Fig. 6.1). *P3* forms from bond splitting between the 7-S and the neighboring 8-N atom comprising the isoxazol ring (Fig. 6.4). The corresponding peak was observed under all irradiation circumstances.

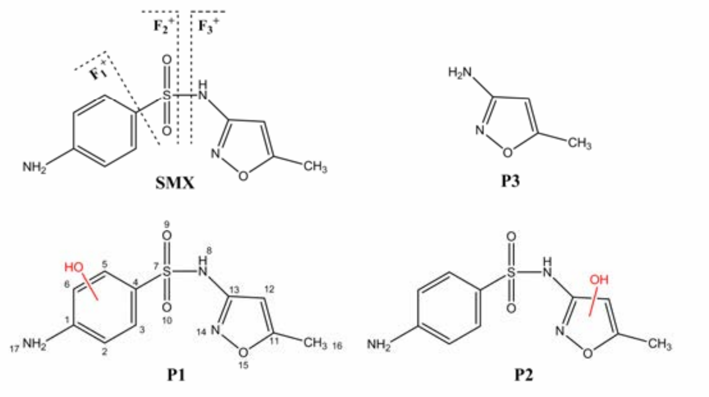

*FIG. 6.4. The structural formula of SMX with important fragmentation sites and its main decomposition products generated from $^{\bullet}$OH reaction.*

In combined reactions of $^{\bullet}$OH and $O_2^{-\bullet}/HO_2^{\bullet}$, the main products were also *P1* and *P3* (Fig. 6.5). However, two new chromatographic peaks, *P4* and *P5* appeared ($[MW(P4)]^+=[MW(P4)]^+=286$). Based on their fragments ($F_1^+{+}32=124$ and $F_2^+{+}32=188$) both products are probably doubly hydroxylated isomers of SMX. Both in *P4* and *P5* all of the substituent is bonded to the aromatic ring.

When both $^{\bullet}$OH and $e_{aq}^-$ reacted with SMX, the peaks obtained were similar to those measured in case of $^{\bullet}$OH and $O_2^{-\bullet}/HO_2^{\bullet}$ reactions, with the difference that only one doubly hydroxylated isomer, *P4* was detected (Fig. 6.5). Products due to $e_{aq}^-$ reactions were not found. Possible intermediates formed during $e_{aq}^-$ reactions may transform back to the starting molecule in reaction with intermediate formed in $^{\bullet}$OH reactions.

When the irradiation was made in $N_2$ atmosphere in the presence of *t*BuOH, interactions of $e_{aq}^-$ and •*t*BuOH with SMX entailed appearance of numerous products, not detected in other cases (Fig. 6.5). Since many products possess substantially higher molecular mass than the parent molecule (*P11*, *P12*, *P13*), we assume that they primarily originate from the reactions of SMX and $^{\bullet}$*t*BuOH. Products with lower masses are probably secondary and tertiary reaction products of SMX and $^{\bullet}$*t*BuOH (*P6*, *P7*, *P8*, *P9*, *P10*). Products indicating reactions of $e_{aq}^-$ were not found in this case, either. However, the *P3* was present with high yield, like in the previous experiments. It is a difficult task to identify the decomposition products of SMX in these solutions because $^{\bullet}$*t*BuOH is expected to react with the isoxazole ring. During the reactions the ring opens, giving rise to internal rearrangement processes. The products mentioned were more or less identified also in other AOP [6.10].

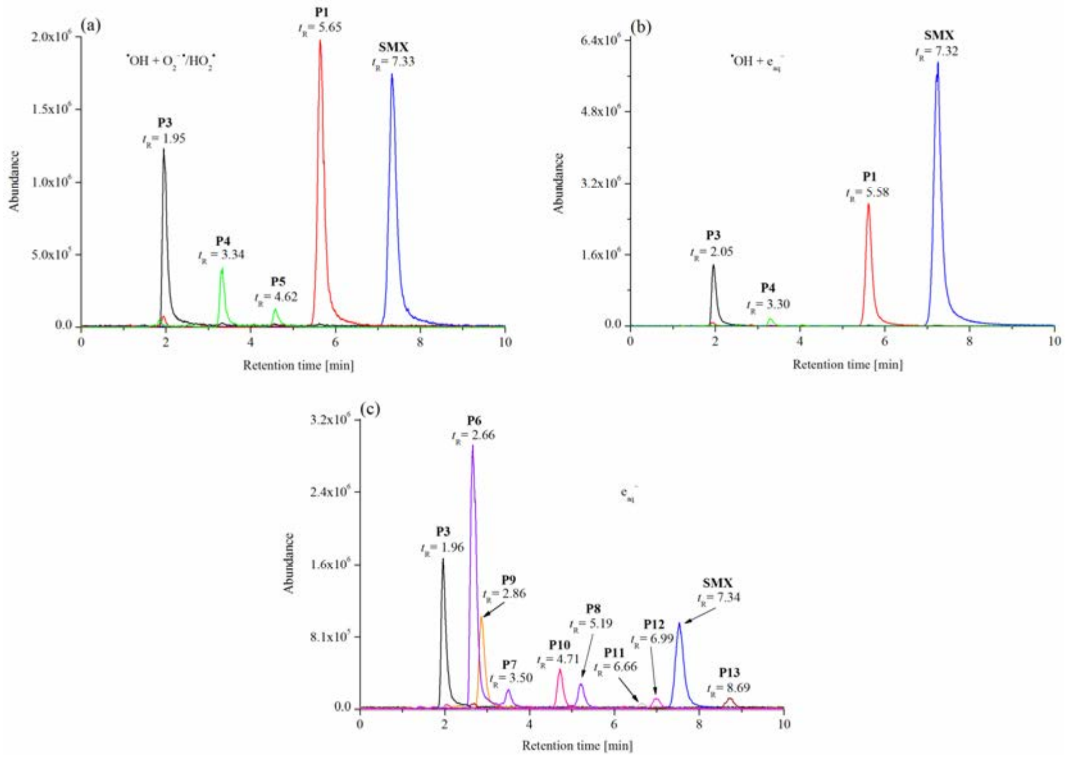

*FIG. 6.5. Chromatograms of irradiated 0.1 mmol dm$^{-3}$ pH 5.8 SMX solutions: air saturated at 1.0 kGy (a), $N_2$ saturated at 0.5 kGy (b) and $N_2$ saturated + tBuOH at 1.5 kGy (c).*

### 6.4.2. Faith of the S and N content during degradation of parent molecules

SMX contains S and N heteroatom in 1 and 3 equivalents, respectively. The quantitative analyses of S and N with ion chromatography and ICP-MS methods allow quantitative comparison of S and N in the products and in the starting molecule. The only S-containing ion in the solution was $SO_4^{2-}$. $SO_3^{2-}$ was not present in detectable quantity. The results indicate total conversion of the organic sulfur to inorganic $SO_4^{2-}$ (Fig. 6a).

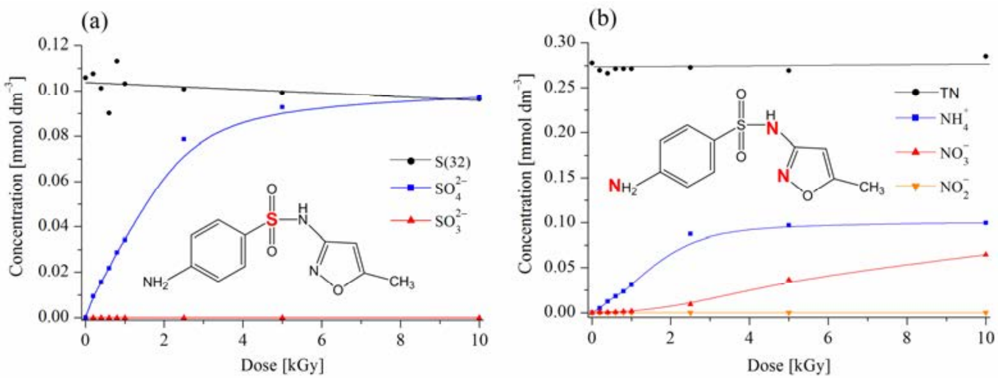

*FIG. 6.6. Formation of inorganic ions containing S (a) and N (b) atoms during irradiation of 0.1 mmol dm$^{-3}$ air saturated SMX solutions.*

Concerning the nitrogen content, formation of $NO_2^-$, $NO_3^-$ and $NH_4^+$ were expected (Fig. 6.6b). The amount of $NH_4^+$ equals 1 equivalent at high doses. These ions presumably form from the terminal amino-group. Half equivalent of $NO_3^-$ was detected. $NO_2^-$ was not observable at all, similarly to the results of Goncalves et al [6.11]. It was found by TN experiments that the nitrogen is almost completely present in the irradiated samples. Results refer to incomplete mineralization of inter-chain nitrogen. The residue is probably in form of simple nitrogen containing organic acids.

### 6.4.3. Evaluation of degradation efficiency

To evaluate the degradation efficiency of SMX, TOC and COD measurements were carried out (Fig. 6.7a) with 1.0 mmol dm$^{-3}$ solutions. The COD values showed a linear dependence on the dose from 0 kGy up to 35 kGy. In this region the formation of hydroxylated products is characteristic (3.1 paragraph) and the reaction rate constant of the $^{\bullet}OH$ is about the same in case of the products and the parent molecule. COD decreased by more than 70% from the initial 347 mg dm$^{-3}$ to100 mg dm$^{-3}$ in this phase. This linearity ceased around 35 kGy, when SMX was almost completely degraded. The larger molecules probably disintegrated to smaller molecular acids. These smaller fragments are known to degrade very slowly in AOP [6.12], as shown by the decreasing trend above 35 kGy. With doses higher than 75 kGy, complete mineralization was achieved.

TOC values only a slight decrease of the 120 mg dm$^{-3}$ starting value was observable at the initial part of the curve. As it was discussed in paragraph 3.1, the first products are hydroxylated derivatives of SMX, so the initial molecules and these products contain the same number of carbon atoms. Therefore, as expected, similar TOC values were measured. (This is also supported by measurements done on 0.1 mmol dm$^{-3}$ solutions (Fig. 6.7b).) From 35 kGy to 50 kGy the degradation rate accelerated (Fig. 6.7a) because of $CO_2$ formation caused by the ring opening reactions. In this region the concentration of organically bound carbon dropped from 88 mg dm$^{-3}$ to 43 mg dm$^{-3}$.

This corresponds to a reduction higher than 50%. Above 50 kGy the values decreased very slowly again, due to the slow degradation of carboxylic acids mentioned previously, in case of COD.

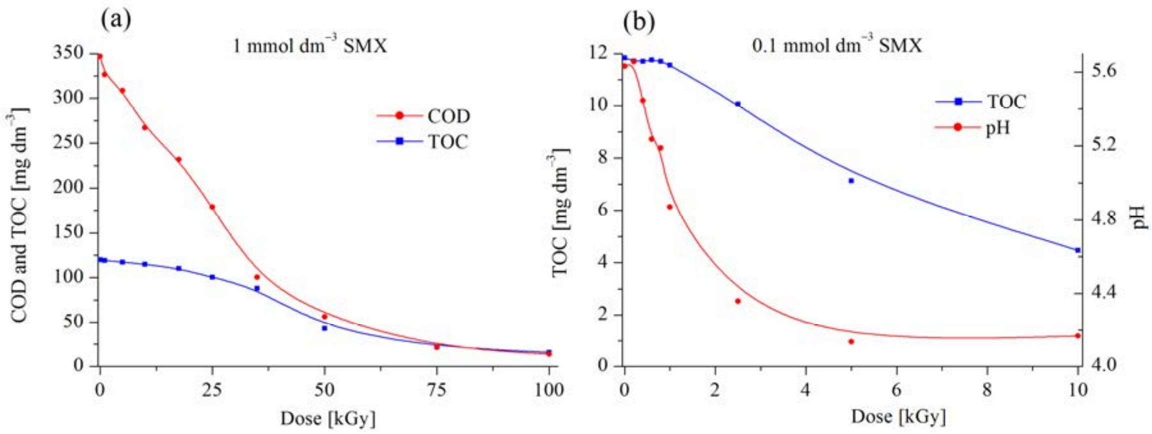

*FIG. 6.7. COD and TOC values measured during the mineralization of SMX in air saturated 1.0 mmol dm$^{-3}$ solutions (a) and changes in pH during TOC measurements on 0.1 mmol dm$^{-3}$ air saturated solutions (b).*

The 1 mmol dm$^{-3}$ concentration used in previous measurements is relatively high; it is very unlikely in municipal wastewater. Changes in pH provide an opportunity to estimate the degree of mineralization in concentrations standing closer to reality. During irradiation of air saturated 0.1 mmol dm$^{-3}$ SMX solutions (pH = 5.8), the pH decreased continuously and this change became slow above 5 kGy absorbed dose. Presumably, the mineralization occurs around this value, because further formation of acidic products was not noticeable (Fig. 6.7b).

### 4.4 Bioassay experiments

The *Vibrio fisheri* luminescence inhibition of the 0.1 mmol dm$^{-3}$ non-irradiated SMX solution was 10%. The toxicity increased during prolonged irradiation and started to decrease above 5 kGy (Fig. 6.8), when almost all organics were degraded as indicated by TOC and COD measurements. At 5 kGy absorbed dose, the toxicity was eight and a half times higher, than the initial. These results suggest formation of inorganic radiolytic products causing high toxicity. During radiolysis considerable amount of $H_2O_2$ is also generated. $H_2O_2$ is highly toxic to the test organisms.

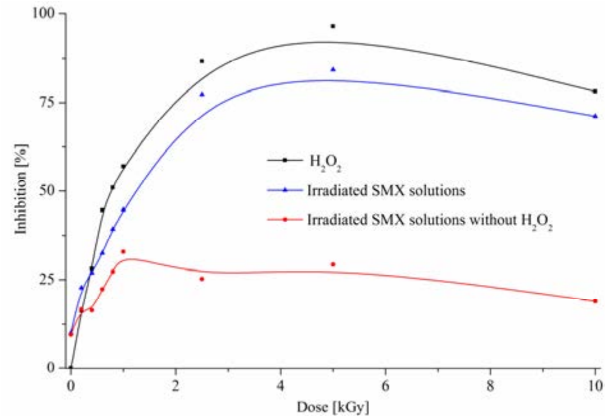

*FIG. 6.8. Luminescence inhibition values measured during the degradation of air saturated 0.1 mmol dm*$^{-3}$ *SMX solutions at pH = 5.8. The toxicity of* $H_2O_2$ *was calculated from the concentration measured in irradiated SMX solutions and the results gained from* $H_2O_2$ *inhibition curve.* $H_2O_2$ *was removed by catalase enzyme.*

In order to separate and evaluate the toxicity related to $H_2O_2$, the inhibition was determined in non-irradiated solutions containing only $H_2O_2$ from 0.05 mmol dm$^{-3}$ up to 2 mmol dm$^{-3}$ concentration (Fig. 6.9a). The results showed that already 0.3 mmol dm$^{-3}$ $H_2O_2$ leads to 50 % decrease in luminescence, while concentrations above 1 mmol dm$^{-3}$ proved to be lethal to the whole bacteria population. With the equation gained from the fitted curve and the known $H_2O_2$ concentrations in irradiated samples, the toxicity linked to the $H_2O_2$ present in the irradiated solutions can be estimated. $H_2O_2$ in irradiated samples was determined with $H_2O_2$ test kit (Fig. 6.9b). It is obvious from Fig. 6.9 that the characteristics of the $H_2O_2$ and SMX toxicity curves are very similar.

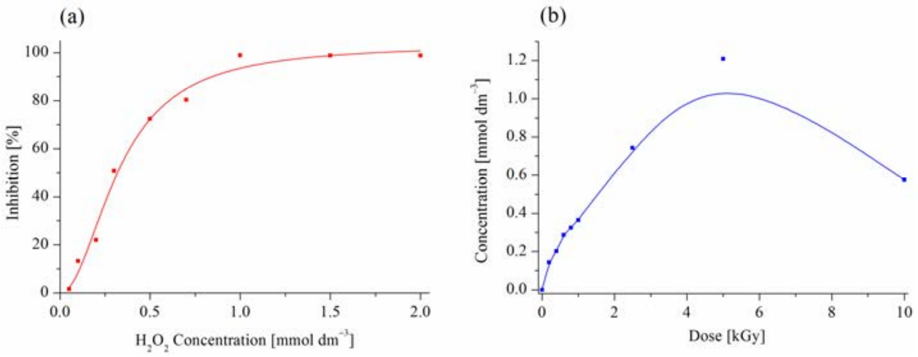

*FIG. 6.9. Toxicity of* $H_2O_2$ *in aqueous solutions (a) and concentration of* $H_2O_2$ *in irradiated 0.1 mmol dm*$^{-3}$ *aerated SMX solutions at pH = 5.8 (b).*

To find out the toxicity caused only by the degradation products and SMX, in a series of experiments $H_2O_2$ was removed from the irradiated solutions by catalase enzyme. In this case, the inhibition values were significantly lower (Fig. 6.8). However, the toxicity was higher than the initial.

To get a more complex picture, the results should be also considered from the aspects of the wastewater treatment technology. Namely, $H_2O_2$ can be utilized as a disinfectant, when irradiation is applied as a post-treatment after the secondary sedimentation. Hydrogen peroxide does not produce residues or gasses and decomposes relatively quickly in natural matrices at low concentrations. From this aspect, the formation of $H_2O_2$ can be considered as a benefit.

## ACKNOWLEDGEMENT

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# 7. RADIATION HYGIENIZATION OF MUNICIPAL SEWAGE SLUDGE – DRY OR WET OPTION?

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## 7.1.INTRODUCTION:

Wastewater discharged from domestic premises consists of human waste and typically contains about 99.9% water and 0.1% solids. The typical water demand in an Indian urban city is estimated as 180 liter per capita per day of which about 80% results in the sewage. The solid waste present in the sewage, which is predominantly organic in nature, is broken down to simple compounds in sewage treatment plants (STP) and results in sewage sludge. The sludge produced is a rich source of many macro and micro nutrients, but carries a heavy microbiological load making its disposal a challenge. The various options for dealing with the sewage sludge namely incineration, land fill, sea disposal and application to the agricultural land, have their own limitations. Disposal into the sea is a site specific option, incineration is highly energy intensive process and expensive, and land filling involves transporting the sludge to faraway places as availability of land in the urban areas is shrinking. In different countries, a mix of these methods is applied for disposal of the sludge. Bacterial counts generally observed in sludge can vary between $10^5$ to $10^9$ per gram. Restricting presence of E.Coli (an indicator organism) in the sludge to less than 1000 per gram is intended.

Department of Atomic Energy (DAE) had set up a Co-60 based demonstration type Sludge Hygienization Research Irradiator (SHRI) at Vadodara in 1992. Vadodara has three waste treatment plants one of which is attached to the radiation facility. The sewage is taken to the settling tanks and thick sludge from the bottom is circulated in the irradiator for a predetermined time to deliver the required radiation dose so as to reduce the microbiological load to acceptable limit. The schematic of the plant is shown in Fig. 7.1. [7.1]

The sewage which is taken up for radiation processing contains 96% water and 4% solid contents. Treated sewage is spread on open drying beds where water evaporates leaving behind hygienized dry cake. In a city like Vadodara with two million of population about 90 tons of sludge is generated per day. This facility at 500 kCi can produce 4.5 tons/day hygienized sludge at a dose of 3 kGy. For the entire sludge of Vadodara City, it would require 10 million curie Co-60 plant.

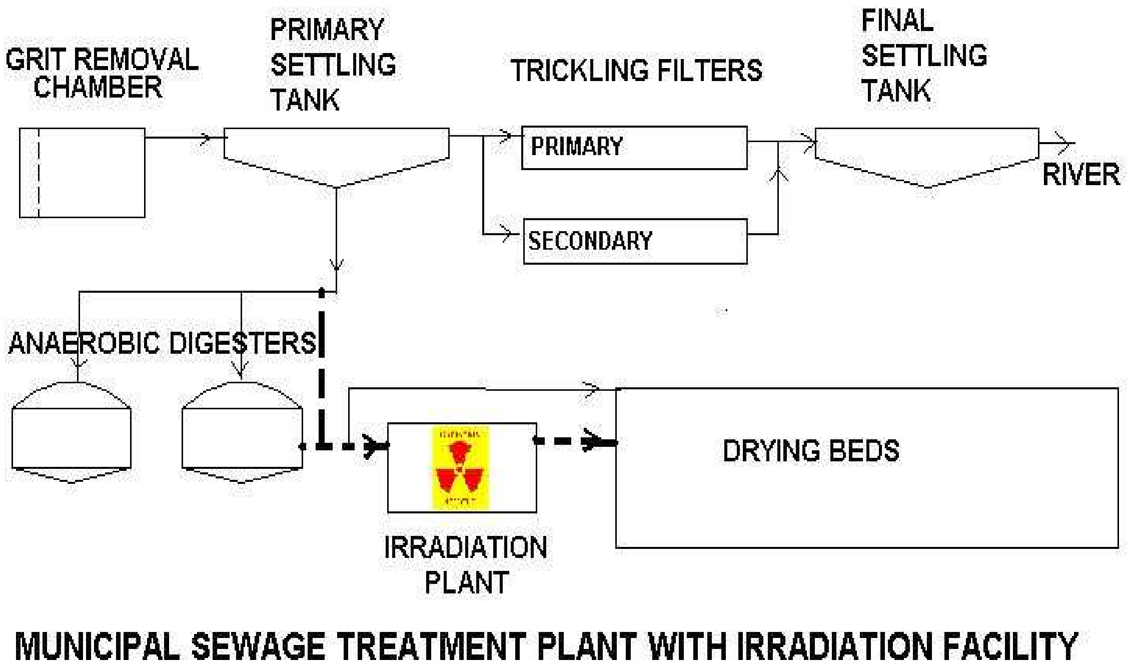

*FIG. 7.1. Municipal sewage treatment plant with irradiation facility*

## 7.2.BENEFITS OF SEWAGE SLUDGE IRRADIATION:

The radiation treated sludge, being free from pathogenic microbes greatly reduces health related risks. Use of sludge can improve soil condition by providing micronutrients and carbon to the depleted agricultural land increasing productivity. Additionally, organic pollutants and odors get significantly reduced. A typical concentration of important nutrients in sludge for agricultural use is given in Table 7.1.

TABLE 7.1. TYPICAL CONCENTRATION OF IMPORTANT NUTRIENTS IN SLUDGE.

| CHARACTERISTIC | SEWAGE SLUDGE |
|---|---|
| pH (1:2.5) | 6.60 |
| Nitrogen (%) | 1.77 |
| $P_2O_5$ (%) | 0.20 |
| $K_2O$ (%) | 0.17 |
| Organic Matter (%) | 36.70 |

The practice of disposing sewage sludge in landfills etc. at many places in the world increases the pathogenic microbiological load on the environment and increases the risk of illness associated with such micro-organisms. So, use of hygienized sludge as manure is very attractive solution if it can be applied in cost effective manner.

## 7.3.EXPERIENCE SO FAR:

In spite of established efficacy of the process and, usefulness of sludge as manure, the technology has not got popular so far. A few research irradiators were made in Germany, Brazil and USA for this. There is one operational electron beam facility for hygienization of sludge in Israel. In some places, public resistance against use of radiation process also is experienced. In India, the situation is different as indicated by increasing number of Gamma Radiation Sterilization/processing plants (18 nos. in 2014) and quite a few more are there in the pipeline. People are realizing its benefits and business potential of such facilities. However, in spite of this, more plants have not come up.

Concern to presence of heavy metals in sludge has been expressed for its use as manure [7.2] .There are no clear norms for disposal of sewage sludge in India. Table 7.2. below shows the heavy metal ion concentrations in dry sludge as measured in Vadodara sludge. The concentrations of heavy metals are much lower than the permitted limits in the US Environmental Protection Agency guidelines for agricultural use in the USA.

TABLE 7.2. CEILING CONCENTRATION OF HEAVY METAL POLLUTANTS IN SEWAGE SLUDGE FOR AGRICULTURAL USE.

| Metal | Typical Conc. In Vadodara sludge<br>Conc. /ppm (dry basis, mg/kg) |
|---|---|
| Cadmium | 10 |
| Copper | 190 |
| Lead | 125 |
| Mercury | nd |
| Nickel | 65 |
| Zinc | 620 |

From the above table it is quite clear that, presence of heavy metals is not a concern and it may not be a concern at many places where municipal waste is not getting mixed with industrial waste and can be usefully employed.

One of the major reasons which appear to be coming in the way of making the radiation hygienization is the costs involved in setting up such facilities and very little compensation which results due to sale of the irradiated sludge as manure. Keeping the above in view, an exercise was taken up to investigate the alternative method of radiation hygienization viz. dry sludge hygienization. [7.3]

## 7.4.WET OR DRY OPTION:

Economics remains a key factor in successful implementation. The capital cost of radiation facility for radiation hygienization of wet sewage is high due to large volumes of sludge involved and the fact that the major product being produced is water rather than the actual sludge. Vadodara has a population of two million which generates about 90 tons of sludge per day. The facility at Vadodara at 500 kCi can process sewage and produce hygienized sludge @4.5 tons/day at a dose of 3 kGy. This means that to treat entire sludge of Vadodara City, it would require 10 million curie plant.

In wet sewage sludge irradiation which may contain only 4% of solids, the size of plant required will be large one. A typical standardized 1000 kci Co-60 radiation facility in India costs around US$ 2 million with running expenditure of US$ 0.2 million including Co-60 decay. For a city like Vadodara, 10 such facilities will be needed.

To meet the requirement of entire city, the current economics of wet sludge treatment due to very large radiation source requirement is coming in the way for its promotion.

The other option of first allowing the sludge to first to dry out in the sun to enable water to evaporate will reduce the available quantity of sludge to be irradiated.

Experiments done on dry sludge have shown that hygienization of dry sludge cake which is about 1/20th in weight of wet sludge can be achieved at a minimum of 6 kGy instead of 3 kGy for wet sludge. It also has comparable or better properties for inoculation purpose for making bio-fertilizers. Therefore, if solid sludge with 80% solid content is treated at 6 kGy, a 1.0 MCi Co-60 plant would be enough to treat the entire sludge being treated by Vadodara Municipal Corporation. This in turn would bring down the treatment cost to about 1/10th of the present cost and would be much more economical.

## 7.5.DISCUSSIONS AND RECOMMENDATIONS:

There is no doubt about efficacy of radiation hygienization of sewage sludge and its benefits. To further promote use of this technology, the following need to be addressed by:

(a) Reduction in cost of the processing control of heavy metal ions in the sludge and soil
(b) Awareness and its use in agricultural practices as supplement and not as replacement for fertilizers.

World over sludge contains heavy metals. Study done in India shows that the sludge generated at Vadodara plant is well within international permitted levels. Sludge which can be taken up radiation processing should be well characterized before using it on agricultural applications for its suitability with regard to presence of heavy metals so that it can be safely used in agricultural fields. It can be targeted to be used as a supplement and not as a replacement for chemical fertilizers. Possibility of converting sludge to bio-fertilizers makes it a value added product and can be exploited commercially.

Considering the above facts, particularly much improved economics of dry sludge processing; it is recommended that establishing a dry sludge irradiator of a well characterized wet sludge would enhance utilization of this technology for societal benefits in India. This would be a much more practical approach to handle the sewage sludge disposal problem and its utilization in agricultural practices. The process will consist of drying the treated sludge breaking into granules and packaging into sacks for radiation processing. The granules can be sprinkled directly over the soil or can be mixed with other diluents like gypsum, saw dust, humous etc. for use.

## REFERENCES TO CHAPTER 7

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# 8. RADIATION TECHNOLOGY APPLICATIONS TO DEVELOP CLEAN INDUSTRIAL PROCESSES IN INDONESIA

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**Abstract**

The environmental problems such as the increasing contamination on the environment and land degradation are one of the major environmental issues in the 21st century due to an effect on food security and environmental quality. Some methods, including ionizing radiation can be used to degrade organic pollutants. Furthermore, natural polymers such as polysaccharides can be used for removal of toxic metal as well as organic contaminants in limited capacity, therefore ionizing radiation can be used for improving natural polymers to enhance physicochemical properties. The natural polymers modified by ionizing radiation so that can be used as adsorbent better than before modified. In addition, the use of ionizing radiation to graft monomers onto starch can produce biodegradable plastics in the environment. This paper describes the involvement of the use of ionizing radiation to overcome environmental issues in Indonesia.

## 8.1.OBJECTIVE OF THE RESEARCH

The objective of the research was gained the contribution of nuclear science and technology for developing the clean environment in Indonesia.

## 8.2.INTRODUCTION

The environment problems such as the increased contamination on the environment and land degradation is one of the major environmental issues in the 21st century due to an effect on food security and environmental quality [8.1–8.4]. Contamination and degradation can reduce the productive capacity of an ecosystem and affect global climate. Increased contamination to the environment with the various industrial waste materials, pesticides, fertilizer in modern agriculture resulted in a strong overloading of water resources [8.1–8.3], while increased land degradation leads to changes of water and energy balances, and biogeochemical cycle of damage that affect the global climate [8.5]. In addition to factors such as natural degradion, increasing land degradation is also associated with human activities such as mining, industrial, agricultural practices that do not pay attention to aspects of land conservation and land use that is not suitable with the carrying capacity of the land[5]. Land degradation process that starts from soil degradation can occur due to physical, chemical and biological degradations[6]. Physical degradation of soil associated with worsening of soil structure that triggers the movement, compaction, surface runoff and accelerating soil erosion. Chemical degradation of soil occurs because many human activities such as the disposal of sludge from the petroleum refining, industrial waste, transportation and storage of petroleum, and pesticides which contribute to hydrocarbon pollution in the environment [8.7–8.8].

Furthermore, it is already well known that plastic is valuable material for human life, it is used in an enormous range of products, due to easy to manufacture, versatility and imperviousness to water. They have already displaced many traditional materials, such as wood, metal, glass, and ceramic, in most of their former uses. About 100 million tons of plastics are produced worldwide every year. Plastics are used for packaging, building materials, and virtually every type of consumer product. Nowadays, the total volume of plastics produced worldwide has surpassed the steel and continues to increase. Without a doubt, we have entered “the Age of Plastics” [8.9–8.10]. It is important to understand the nature of plastics, and the consequences of their production and use. Virtually all plastics are made from nonrenewable resources, such as oil, coal or natural gas, which will eventually deplete. Beside of valuable materials, plastics are durable and degrade very slowly, the molecular bonds that make plastic so durable make it equally resistant to natural processes of degradation. Billion tons of plastic has been discarded and may persist for hundreds or even thousands of years. The plastic waste becomes a serious environmental pollution problem [8.9–8.10]. In many countries, plastic recycling programs were used to reduce the plastic waste problem, but it has been proven difficult. In the other hand, many scientists carried out research on biodegradable plastics that break down with exposure to sunlight, water or dampness, bacteria, enzymes, insect attack, which are also included as forms of biodegradation or environmental degradation. Some researchers have actually genetically engineered bacteria that synthesize a completely biodegradable plastic, but this material is expensive at present [8.10].

In the meantime, contamination by heavy metals from electroplating industry and textile dyeing wastewater which threatens aquatic ecosystem is a critical problem, mainly because metals are not biodegradable and tend to accumulate in the living organism of the environment. Meanwhile the textile dyes usually is recalcitrance substances and carcinogenic. In order to eliminate that problem, it is important to reduce the concentration of heavy metal ions and textile dyeing wastewater in the aquatic ecosystems [8.11–8.15]. Due to the high cost of adsorbents such as activated carbon and some ion-exchange resins used for the treatment of water and wastewater, natural polymers such as polysaccharides that are available in large quantities or industrial waste products can also be improved as new more effective and cheaper adsorbents [8.16].

Recently, a great interest has been made to use radiation-induced graft copolymerization of functional monomer onto polysaccharides, such as chitosan and cellulose back bones. Radiation is a versatile tool to induce graft copolymerization and crosslinking of polymer due to no chemicals or catalysts have to be added to the reaction matrix [8.17–8.18]. However the new functional group which is incorporated with polysaccharides should be able to increase the density of sorption sites.

To overcome those problems, we took part in a way good conducting research using radiation technology directly to degrade the waste, as well as a toll to use radiation to obtain the modified materials that can be used to absorb toxic metals and organic pollutants. The summarized works were described in this paper.

## 8.3.IRRADIATION EFFECT ON INSECTICIDES AS POLLUTANTS MODEL[1]

One of the alternative methods for degrading the organic pollutants is the oxidation using hydroxyl radical. The hydroxyl radical can be produced by UV irradiation that is combined with Fenton reagent ($UV/H_2O_2/Fe^{+2}$ or $UV/H_2O_2/O_3/Fe_{+2}$), UV/semiconductor ($UV/TiO_2$, $UV/ZrTiO_2$), UV/ozone, and ionizing radiation (gamma and electron beam) [8.19]. At the last decades, the studies on the use of the ionization radiation technique for removing the organic pollutants have been conducted [8.1–8.3, 8.19–8.22].

Indonesia is one of the agricultural countries, more than 2,400 trademarks of pesticides are circulating in Indonesia, and it has cost no less than 600 dollars a year. Therefore, the study of irradiation effect on pesticides as pollutants model has been our focus.

Two kinds of organophosphorus insecticides, namely: fenitrothion and prothiofos; and one of pyrethroid insecticide, namely cypermetrin were used as models of organic pollutants. The chemical structures of these pesticides are shown in Fig. 8.1.

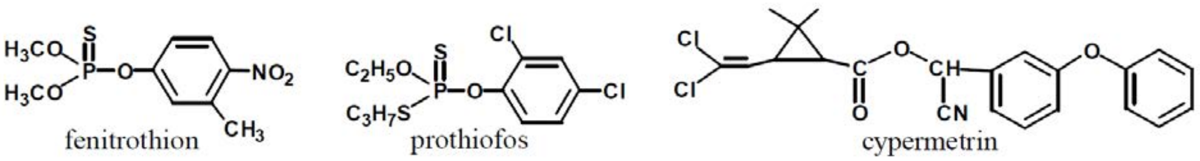

*FIG. 8.1. The chemical structures fenitrothion, prothiofos, and cypermetrin*

Fenitrothion and prothiofos are organophosphorus insecticide, moderately toxic in rats [8.1, 8.34]. Fenitrothion is usually used to control *Spodoptera exigua* on onion plant, *Atherigona sp.* on corn plants and commercially sold in some formulations, whereas prothiofos is general used for protection of fruit from leaf-eating caterpillar *Pseudococus sp.*, cutworms, *etc.* In aqueous solution, prothiofos is hydrolyzed into *O*-ethyl-S-propyl dithiophosphate and 2, 4-dichlorophenol. Gamma irradiation on fenitrothion in aqueous solution with a concentration of 55.5 mg/L and pH 5.6 showed that irradiation without aeration caused the increase of UV absorption at 279 nm (maximum wavelength) (Fig. 8.2). This fact suggested that the additive ingredients reacted to each other or reacted with fenitrothion to form new compounds that cause UV absorption. Irradiation with added $O_2$ caused the increase of the oxidizer species, resulting in more intensive degradation of fenitrothion and additive ingredients. Irradiation of fenitrothion in various pH's showed that irradiation in acid pH's (pH 3 and 5.6) is rather more effective than irradiation in neutral and basic pH's. Determination of fenitrothion by HPLC on reverse-phase column showed that the concentration decreased with increasing irradiation doses. At a dose of 6 kGy, fenitrothion decreased from 55.5 to 1.63 mg/L (> 97%), and the colloidal solution changed to a clear solution. Under the similar condition, prothiofos also underwent degradation in the same manner as degradation of fenitrothion. It suggested that both of them are organophosphorous insecticides with the same backbone [8.1].

Gamma irradiation on cypermetrin by adding 0.05% of $FeCl_3$ and $H_2O_2$ as catalysts at pH 11 exhibited decreasing of UV absorbance compared to the addition of $TiO_2$ or $CuSO_4$ (Fig. 8.2). The hyperchomic effect suggested that this is a result from the reaction of additive agents in insecticide formulation with the primer species of radiolysis products, or the reaction between additive ingredients in the formulation, forming new polymer compounds that would be difficult to degrade. Irradiation at dose of 15 kGy with the addition of 0.05% $FeCl_3$ as a catalyst resulted in the best condition of degradation. At this condition, the UV absorbance of solution decreased to 87%.

The aerated and irradiated cypermethrin solution at the best condition (pH 11 + $FeCl_3$ 0.05%) appeared the organic acids as the degradation products of cypermethrin. The COD value could decrease 78% (from 581 mg/L to 130 mg/L) at irradiation dose of 20 kGy. Organic acids formed, namely formic acid, acetic acid, oxalic acid, and maleic acid are detected by HPLC. These organic acids are unstable, so they are further easily degraded to $H_2O$ and $CO_2$.

The plausible mechanisms of degradation of fenitrothion, prothiofos, and cypermetrin have been described in previous paper [8.1].

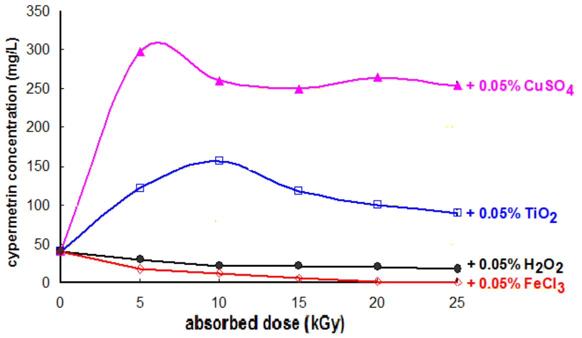

*FIG. 8.2. The effect of irradiation with adding the catalyst on cypermetrin degradation (cypermetrin concentration = 40 mg/L, pH adjusted to 11, catalyst = 0.05 %)*

Subsequently, researches on the use of ionizing radiation to degrade organic pollutants in Indonesia have been started in the end of eighties, even the study of sewage sludge has been started since the early eighties. Together with some stakeholders such as Environmental Management Center – The Ministry of Environment of Indonesia and other institution, the effort for promoting the radiation application to overcome the environmental problems have been done. However, until now there have been no end users who are interested in adopting the technology. Finally, along with the progress of research in the field of polymer grafting and crosslinking, then we are also involved in modifying the natural polymer to produce the better physicochemical properties that can be used to solve an environmental problem.

### 8.3.1. Biodegradable plastics

Starch gel is made by mixing tapioca flour or dried flour of tapioca waste with water, other compound then heated at a certain temperature; then dried starch mixed with a solution of vinyl monomer and other compounds and then irradiated with gamma rays or electron beam at certain dose at room temperature. The irradiated product then dried by the sun or oven by machine at temperature of 40-190 °C, and then chopped and pelletized. Plastic pellet obtained then was tested to be made plastic bag or other products, and then evaluated by testing the tensile strength, elongation at break, and biodegradability. It found that plastic products could be degraded completely by soil burial in less than one year.

### 8.3.2. Microbial inoculants rhizosphere consortia for land remediation

#### *8.3.2.1. Compost-Based Carrier*

As described previously, improvement of the the carrier and optimization of the growth of microorganisms should be approached first in order that survival and activity of microorganisms in the field is assured [8.23–8.25]. Peat has been used as a carrier material standard for most commercial microbial inoculant [8.26]. The use of peat is not recommended in some countries because excessive peat mining will disrupt ecosystem sustainability, therefore other potential materials are necessary [8.27]. Compost is a potential alternative carrier material as the substitute of peat, because it is abundantly available, renewable, and environmentally friendly. Compost-based carrier has a better ability to support the survival of *Azotobacter sp.* compared to peat as presented in Fig. 8.3.

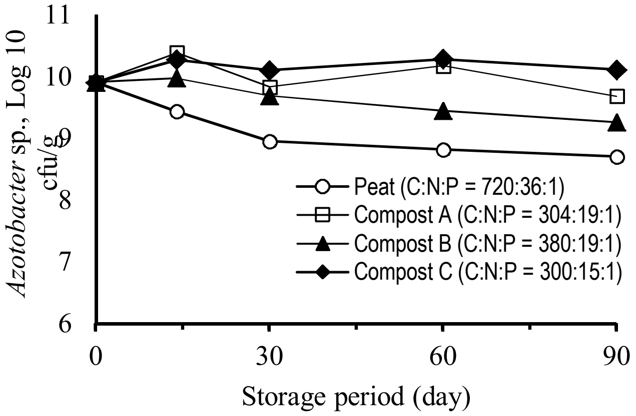

*FIG. 8.3. Compost and peat based-Azotobacter sp. during 90 days storage period*

Liquid cultures of *Azotobacter sp.* (10% v/w) are inoculated into carriers in all kinds of materials that have been sterilized by gamma irradiation at a dose of 40 kGy. After storage for 90 days at about 28 ºC, there is a decrease in the population of *Azotobacter sp.* in peat from 8.0 x $10^9$ to 5.0 x$10^8$ cfu (colony forming units)/g. In all carrier-based compost, *Azotobacter sp.* population remains high, being around $10^9$ - $10^{10}$ cfu/g. These results indicated that the compost-based carrier materials are suitable for use as an alternative instead of peat in the formulation of inoculant of *Azotobacter sp.*

### *8.3.2.2. Sterilization of Compost-Based Carrier*

Sterilization process of carriers is conducted to prevent the competition between microbial targets and other microorganisms in a nutrient-rich environment[25]. Cleaning of indigenous microorganisms in the compost-based carrier can be done by steam sterilization or gamma irradiation as shown in Table 8.1. In the steam sterilization treatment by autoclave at 121 ºC for 30 minutes and gamma irradiation at a dose of 10 kGy, sterile compost-based carrier was not generated. However, sterilization by autoclave at 121 ºC for 60 minutes and gamma irradiation at a dose of 20 kGy and 30 kGy produced sterile compost-based carrier (<101 cfu/g). According to McNamara and co-worker (2003) [8.28], the majority of soil microorganisms including *Actinomycetes* and fungi can be destroyed by gamma irradiation at a dose of 20 kGy. Therefore, the sterilization of compost-based carrier (< $10^1$ cfu/g) can be done with an autoclave at 121 ºC for 60 minutes or gamma irradiation at dose of 20 and 30 kGy.

After 90 days of storage period, the population of *Azotobacter sp.* in the carrier material sterilized by autoclave decreased from 1.2x$10^9$ to 8.6x$10^8$cfu/g. Meanwhile, in the carrier with sterilization by gamma irradiation at doses of 20 and 30 kGy could maintain the *Azotobacter sp.* population remains at $10^9$cfu/g. These results indicated that irradiation sterilization at doses of 20–30 kGy is more appropriate for the survival of *Azotobacter sp.* It was also reported that the gamma irradiation sterilization process does not produce toxic substances to some microbes. In further observation on irradiation dose, it was known that a dose of 25 kGy could produce compost-based carrier with the most appropriate sterility and quality for microbial inoculants. Gamma irradiation at a dose of 25 kGy can clean total aerobic bacteria (5.7x$10^8$ cfu/g) and fungi (1.4x$10^7$ cfu/g) to an undetectable (10 cfu/g). The gamma irradiation sterilization of compost-based carrier can sustain population of *Azotobacter sp., Bacillus circulans,* and *Bacillus stearothermophilus* with high concentrations during the 180 days of storage period. After the storage period, the population of *Azotobacter sp., B. circulans,* and *B. stearothermophilus* were 3.2x$10^{11}$, 1.7x$10^{11}$, and 1.9cfu/g, respectively. These results indicated that carrier-based compost sterilized by gamma irradiation at a dose of 25 kGy has a potential for producing microbial inoculants for plant growth enhancement.

TABLE 8.1. THE EFFECT OF STERILIZATION TREATMENT AGAINST TOTAL CONTENT OF AEROBIC BACTERIA AND FUNGI IN COMPOST-BASED CARRIER

| *No* | *Sterilization treatment* | *Microorganism, cfu/g* | |
|---|---|---|---|
| | | *aerobic bacteria total* | *fungi total* |
| *1* | *Control (without sterilization)* | *5.9x10*$^{8}$ | *6.5x10*$^{6}$ |
| *2* | *Autoclave, 121 °C, 30 min* | *9.0x10*$^{3}$ | *1.3x10*$^{3}$ |
| *3* | *Autoclave, 121 °C, 60 min* | *nd* | *nd* |
| *4* | *Gamma irradiation, 10 kGy* | *6.4x10*$^{4}$ | *5.0x10*$^{3}$ |
| *5* | *Gamma irradiation, 20 kGy* | *nd* | *nd* |
| *6* | *Gamma irradiation, 30 kGy* | *nd* | *nd* |

*Note: cfu = colony forming unit; nd = not detected at 10*$^{1}$ *cfu/g.*

### *8.3.2.3. Low-Dose Gamma Irradiation Effect on Microbial Inoculant*

Study on bioremediation of hydrocarbon contaminants and heavy metals ($Pb^{2+}$, $Cd^{2+}$) in the liquid medium showed that low-dose gamma irradiation treatment can improve the performance of microbial inoculants. Microbial inoculants *T.viridie, T. harzianum* and *A. Niger* are irradiated at doses of 0 (control), 125, 250 and 500 Gy, then the inoculants added into a liquid medium containing hydrocarbon contaminants (27 ppm) and heavy metals [$Pb^{2+}$ (27.1 ppm) and $Cd^{2+}$ (18.8 ppm)], subsequently incubated at room temperature of 28°C with agitation at 150 rpm for 9 days. Compared to control, it showed that the optimum degradation of total petroleum hydrocarbon (TPH) was obtained at inoculation treatment by irradiated *T.viridie, T. harzianum and A. Niger* at a dose of 250 Gy. In this treatment, the ability of *T.viridie, T. harzianum* and *A. Niger* to degrade TPH decreased by 15%, 21%, and 19%, respectively (Fig. 8.4). Gamma irradiation at a dose of 250 Gy also significantly enhances the ability of *T. viridie, T. harzianum*, and *A. Niger* in reducing contamination of $Pb^{2+}$ and $Cd^{2+}$ in a liquid medium. The ability of these fungi in reducing $Pb^{2+}$ increased by 22% (*T. viridie*), 22% (*T. harzianum*), and 20% (*A. Niger*) compared to control as shown in Fig. 8.5, while the ability of these inoculants in reducing $Cd^{2+}$ also increased by 16% (*T. viridie*), 14% (*T. harzianum*), and 12% (*A. Niger*) compared to control (Fig. 8.6). These results indicated that gamma irradiation at a dose of 250 Gy is the optimum dose for increasing their ability of *T.viridie, T. harzianum*, and *A. Niger* in reducing TPH, $Pb^{2+}$, and $Cd^{2+}$ in a liquid medium. The same results also reported by Chakravarty B. and Sen S [8.29] and Afify A.E.M.R. *et al.* [8.30] that low-dose gamma irradiation has effect on the acceleration of enzyme activity by microbes. According to Afify A.E.M.R. *et al.* (2012) [8.30], gamma irradiation at a dose of 250 Gy affects the increase in dry weight of mycelia of *T. harzinum* and *T. viridie* at 23% and 16%, respectively.

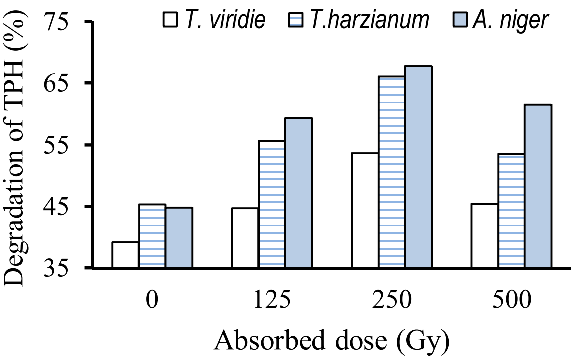

*FIG. 8.4. Effect of low-dose gamma irradiation on the ability of fungi to degrade TPH*

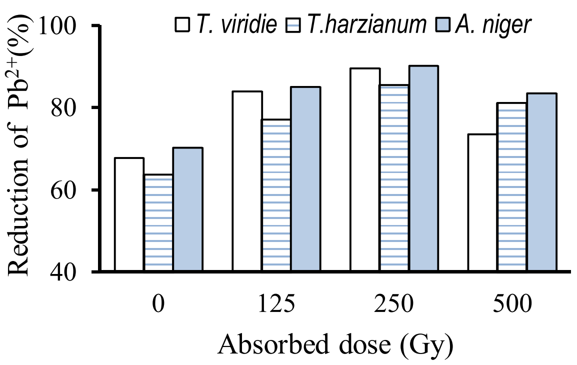

*FIG. 8.5. Effect of low-dose gamma irradiation on the ability of fungi in to reduce Pb*$^{2+}$

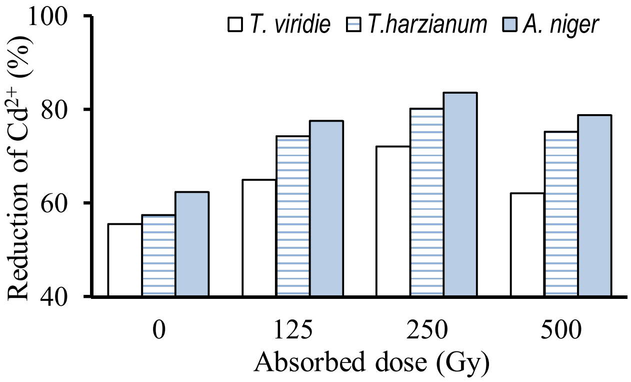

*FIG. 8.6. Effect of low-dose gamma irradiation on the ability of fungi in to reduce Cd*$^{2+}$

### 8.3.2.4. *Application of Irradiated Fungal Inoculant Consortium on Remediation of Degraded Lands in South Tangerang-Banten Province*

Bio-compost made from manure is composted and enriched by microbial consortium inoculants which have function as decomposition of organic substances, biological control, N-fixation, and phosphate solubilizing. A total of 200 g of functional microbial consortium-based compost activated in 4 liter solution of 5% molasses, and then used for producing 80 kg of bio-compost. Before applied to corn plants (*Zea mays* L., P21variety) and soybean (*Glycine max* L., Pearl I variety), firstly bio-compost is incubated at 28 ºC for 5 days. Bio-compost applied on degraded land of ex-sand mining in South Tangerang-Banten Province with the characteristics as shown in Table 8.2.

The study was conducted using a randomized block design (RBD) with 4 treatments and 4 replications in each plot = 10 x 20 m$^2$. The dose of NPK, manure, and bio-compost are 200 kg/ha (100%), 2.5 tons/ha and 500 kg/ha, respectively, with the composition of the treatment as shown in Table 8.3. The addition of NPK at dose from 50 to 100% gave the potential increase in biomass of corn crop, biomass of soybean, and dried soybean seeds. Nevertheless, this treatment did not provide the optimal results such as the addition of bio-compost. The addition of manure (from cow dung) as much as 2.5 tons/ha only gave a significant effect on the increase the productivity of soybean biomass. These result suggested to be related to the low nutrient content in the manure, so the plants are not getting enough nutrients. The use of bio-compost as much as 500 kg/ha is more capable to optimize the yield productivity of corn and soybeans compared to other treatments. Addition of bio-compost could increase the productivity of dried biomass of corn crop about 22% (from 4.62 to 5.64 ton/ha) and dried soybeans biomass about 53% (from 3.16 to 4.82 tons/ha). The use of bio-compost could also increase the productivity of dried corn seeds about 52% (from 3.24 to 4.94 tons/ha) and dried soybean seeds of about 77% (from 1.59 to 2.81 tons/ha).

TABLE 8.2. THE CHARACTERISTIC OF DEGRADED LANDS

| No | Parameter | value | criteria |
|---|---|---|---|
| 1 | pH (1:5 $H_2O$) | 6.01 | Slightly acid |
| 2 | C organic (%) | 0.72 | very low |
| 3 | Total N (%) | 0.05 | very low |
| 4 | C/N ratio | 16.62 | high |
| 5 | $P_2O_5$ (ppm) | 4 | very low |

TABLE 8.3. COMPOSITION OF TREATMENT

| No | Treatment | Composition |
|---|---|---|
| 1 | A | 50% NPK |
| 2 | B | 100% NPK |
| 3 | C | 50% NPK + manure |
| 4 | D | 50% NPK + bio-compost |

### 8.3.2.5. *Remediation Application on Petroleum Oil Sludge-Contaminated Dry Land in Rejuvenation of Teak Tree (Tectona grandis) in Cepu-Central Java*

Dry land contaminated by petroleum oil sludge in traditional oil extraction sites (Cepu) has mild alkaline condition (pH 7.6 - 8.5), very high organic content (C > 5%), low N (0.1 - 0.2), very high C/N ratio (> 25), and very low $P_2O_5$ (P < 4 ppm). This condition gradually requires remediation for improvement of soil quality parameters, degradation of hydrocarbon and its potential toxicity, in order to recover the productive functions of land. The initial stages of the remediation carried out by the method of composting at the target site (*in-situ* composting) and the second stage through the cultivation of non-food crops, namely elephant grass (*Pennisetum pupureum*). *In-situ* composting was done on a plot of 150 $m^2$ with 300 g of hydrocarbon degrading functional microbial inoculants, 60 kg of sawdust and 3.6 kg of NPK fertilizer. The treated soil was divided into six subplots @ 20 $m^2$ with a height of 20 cm, then covered with plastic and composted for 60 days. After composting, stem of elephant grass was planted in subplots with the treatment of A = control, B = treated with plant growth enhancer microbial inoculants. A total of 50 g microbial inoculants activated in 5 L of a solution of 5% molasses for 24 h, then diluted with water to 25 L and spread on the surface of plot B. All of subplots were also given 300 g of NPK fertilizer/plot. Maintenance of elephant grass (*Pennisetum pupureum*) was performed for 90 days. It was shown that application of functional microbial inoculant $50g/20m^2$ (=25kg/ha) significantly affect plant growth enhancement of elephant grass.

After *in-situ* composting for 60 and 120 days without treatment, the content of TPH (total petroleum hydrocarbons) reduced by 58% and 77%, respectively. Moreover, the reduction of TPH could be achieved in 82% when treatment *in-situ* composting followed by stimulated with microbial inoculants consortia. These results indicated that the of microbial inoculant consortia suitable for remediation petroleum oil sludge-contaminated dry land using *in-situ* post-composting.

Improvement of plant growth in petroleum oil sludge-contaminated land after *in-situ* post-composting was suggested by detoxification of hydrocarbon decomposition products by rhizosphere microbial isolates. Rhizosphere microbial isolates in the functional microbial inoculant also suggested capable to N-fixation and dissolved phosphate for the growth of grass plants, even though the height of elephant grass plant did not show significant differences, but other parameters such as the weight of the biomass, N, and P uptake showed a significant increase. The weight of dried biomass increased from 47 to 101g, N uptake increased from 415 to 914mg/plant and P uptake increased from 77 to 178 mg/plant. These results suggested that the microbial consortia containing inoculant bacteria isolates (KDB2, KLB5, BM5, KLBN1) and fungal isolates (KLF6, RK1) suitable for plant growth of elephant grass in petroleum oil sludge-contaminated land after *in-situ* post-composting.

All evaluations showed that consortia of microbial inoculant containing functional hydrocarbon degrading microbial isolates (BMC2, BMC4, BMC6, FMC2, FMC6) from hydrocarbon-contaminated soil has the potential to reduce TPH (total petroleum hydrocarbons), whereas consortia of microbial inoculant containing functional of plant growth enhancers which contain bacterial isolates KDB2, KLB5, BM5, KLBN1 and fungal isolates (KLF6, RK1) have the potential to increase the growth of corn crop (*Zea mays* L. varieties P21) on dry land with very low available of P (P<4 ppm).

### 8.3.3. Improvement of natural polymer properties by radiation grafting of adsorbent

Polysaccharide-based materials are biodegradable and bio-renewable which are suitable for various applications, for example as an adsorbent in wastewater treatment. In this study polysaccharides were chemically modified by radiation grafting. Hydroxymethyl acrylamide or acrylic acid monomers were grafted onto polysaccharides using pre-irradiation graft copolymerization technique. The physicochemical properties were studied then the capability as a toxic metal adsorbent and textile dyes were examined.

#### *8.3.3.1. Metal Ion Adsorption by Cellulose-g-Acrylamide*

Polysaccharide of rice straw cellulose is irradiated in air with a dose up to 40 kGy and a dose rate of 5 kGy/h. The irradiated cellulose is immersed immediately in 5-30% volume of aqueous monomer (acrylamide) solution containing 10% methanol at 40-60 $^{o}$C for 1-3 h (liquor ratio: 0.1g sample/10ml solution). The mixture is then bubbled with $N_2$ for 30 min to deoxygenate the monomer solutions before grafting and it is continued during the whole process. Samples are washed in distilled water at 80 $^{o}$C to remove the homopolymer and dried at 50 °C until the weight remains to get cellulose-g-acrylamide (cellulose-g-AA).

Ion exchange capacity experiment of the cellulose-g-AA showed that it has ion exchange capacity of 3.54 meq/g, higher than pure cellulose (0.56 meq/g), which indicates that grafted carboxylic functional groups can act as ion exchangers. Cellulose has ion exchange capacity of 0.56 meq/g is expected due to the adsorption on the surface of cellulose.

### 8.3.3.2. *Metal Ion Adsorption by BKP-g-N-(Hydroxymethyl) Acrylamide*

Polysaccharide of banana peel powder (BKP) was copolymerized with *N*-(hydroxymethyl) acrylamide by using gamma irradiation for improving the physicochemical properties of BKP as adsorbent. Mixed banana peel powder-*N*-(hydroxymetil) acrylamide was irradiated at doses of 4 kGy, 8 kGy, 16 kGy, and 32 kGy. The results showed an increase in Cu (II) adsorption capacity of adsorbent from irradiated copolymer, which gradually increase by increasing the irradiation dose. While the adsorption of Cr (VI) did not change significantly before and after irradiation at dose of 4 kGy, even gradually decrease by increasing the irradiation dose. An increase in physical strength was indicated by a decrease of BKP-NHMA damage. BKP-NHMA adsorbent can be recycled and can be reused with a decrease of 48% adsorption ability.

### 8.3.3.3. *Metal Adsorption by Chitosan-g-Acrylamide*

The chitosan sample was prepared from chitin (extracted from shrimp shell) as described in previous work [14]. The chitosan-acrylamide solution with the concentration of chitosan 1, 2, and 3% (w/v) solutions were prepared by dissolved 1, 2 and 3 g chitosan in 1.5 g acetic acid glacial respectively, then followed by adding 20 mL of distilled water. Furthermore, 7.5 g acrylamide was added to the each solution and distilled water was poured to get 100 mL solution. The mixed solutions were packed in 5×5 cm plastic bag, sealed and subjected to gamma irradiation with dose of 10 to 40 kGy. The irradiated sample then cut into pieces and dried at 40 °C for further examination. The physicochemical properties namely *gel fraction and the degree of swelling were* determined by gravimetric method. The results showed that chitosan-co-acrylamide hydrogel which irradiated with gamma rays up to 15 kGy was an effective adsorbent for the removal of various metal ions ($Cu^{2+}$, $Cr^{6+}$, $Ni^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Zn^{2+}$) from aqueous solutions. The pH experiment revealed that adsorbent was efficient for the uptake of metal ions at pH over 7. The percentage of metal ions uptake was found to be a function of adsorbent dose and time at a given initial solute concentration. It is increased with time and initial concentration but decreased with adsorbent dose. The order of heavy metal ions uptake on Chi-co-PAAm hydrogel was $Zn^{2+} > Cr^{2+} > Pb^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. Experimental results are in good agreement with Langmuir and Freundlich adsorption isotherm model and have shown a good fitting to the experimental data.

### 8.3.3.4. *Textile Dyestuff Adsorption by Polysaccharide-g-Acrylic Acid*

The aim of this study to determine the ability of polysaccharide of banana peel as an adsorbent of textile dyes (maxilon yellow) before and after the grafting process. The grafting copolymerization process was done by using acrylic acid as monomer, and then irradiated by gamma rays as initiator. Parameters observed were adsorption ability of dye, soaking time with KOH, acrylic acid concentration, irradiation dose and resistance to acids. The results showed the optimum absorption obtained at the time of KOH immersion for 3 hours, the concentration of acrylic acid by 20% and the irradiation dose of 30 kGy. Adsorption percentage of polysaccharide to maxilon yellow after grafting increased by 18.5% compared to before grafting. Resistance to the acid test increased significantly. The results of this study are expected to overcome the problems of waste dyes in the textile industry.

#### *8.3.3.5. Radiation-Induced Degradation of Chitosan*

Oligo chitosan can be produced from marine product waste by combination chemical and radiation processes. Firstly, marine product waste from Crustaceae, such as shrimp and crab shells, *etc.* was deprotinated and demineralized by using aqueous solution of NaOH and HCl, successively. The chitin obtained was then de-acetylated by using NaOH-$H_2O$ to get chitosan. Subsequently, the oligo chitosan could be prepared by irradiation of chitosan by using gamma ray with a dose of 75 to 100 kGy. The field test on the effect of oligo chitosan in 0.5% acetic acid solution as plant growth promoters was examined toward soybean, chili, and other plants. The results showed that oligo chitosan could significantly increase total P-uptake of soybean plant. Combination of oligo chitosan with bio-fertilizer showed more P-uptake of soybean plant. Furthermore, the application of oligo chitosan on chili plants showed the significant results. It was clarified that oligo chitosan with the concentration treatment of 50-100 ppm could increase harvest times from normally 12 times to 20-25 times. Moreover, oligo chitosan also could destroy *Gemini virus* which attacked to chili plant.

## 8.4.CONCLUSION

The use of ionizing radiation to degrade organic pollutants in wastewater directly proved to be very powerful, but the application in the field is still required the big effort to convince the decision makers and end users.

Radiation-induced grafting of vinyl monomer onto starch can produce biodegradable materials which can be used for producing a variety a variety of environmentally friendly plastic products. Furthermore, the use of ionizing radiation to modify natural polymers to produce materials which have better physicochemical properties can be applied for absorbing heavy metals and other pollutants such as textile dyes, pesticides, and others, as a more promising clean/green technology, and can be more easily public-accepted.

The use of ionizing radiation for sterilization of carrier for microbial inoculant and the use of low-dose irradiation on microbes to generate functional microbial inoculants can be applied for remediation of degraded lands.

Moreover, the use of oligo chitosan for plant growth promoter, plant elicitor, and anti-virus, especially for chili plant on a pilot scale proved to give a significant impact, and efforts are being made to commercialization.

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# 9. RADIATION PROCESSING OF POLYMERS FOR ENVIRONMENTAL REMEDIATION

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**Abstract**

Radiation processing is environmentally friendly process since the initiation process needs no chemicals such as initiator and catalyst. Only simple step of high-energy irradiation can initiate the chemical reactions which modify the chemical and physical properties of commercially available polymers. Radiation-induced crosslinking can improve the heat-resistance and gelation properties of biodegradable polymers such as poly (lactic acid) and polysaccharides, respectively. As practical applications of these polymers, environmentally friendly biodegradable dummy lens, super water absorbent, 3D dosimeter, etc. are produced. In the case of chitosan, radiation-induced degradation to certain molecular weight enhances the property of plant grow promoter. Adsorbents for hazardous metals can be synthesized by radiation-induced graft polymerization. The tailored adsorbents can be available for environmental remediation. Industrially, the cleaning chemical agents in semiconductor production process are reused after removal of dissolved metals to decrease the environmental burden. Generally organic solvent used in grating reaction can be replaced by water. This novel emulsion grafting is environmentally friendly technology which has been was transferred as industrial process for the production of fibrous metal adsorbent.

## 9.1.INTRODUCTION

Radiation processing of polymers is initiated by high-energy irradiation toward raw polymers. The generated active radical induces the chemical reactions for the modification for chemical and physical properties of the raw polymers. The advantages of radiation processing for these modifications of the polymers are as follows; Chemical reaction is initiated only by irradiation so that the resulting products do not contain any chemical initiator or catalyst as impurities. There is little thermal damage in the resulting products since chemical reactions are initiated even in room temperature and lower. The initiation of chemical reactions is so quick that irradiation process becomes simple. Even excitation leads the homogeneous reaction in whole part of polymers. These advantages cannot be realized by the chemical process. Accordingly, radiation processing of polymers is superior to present chemical process for material development. The radiation processing is environmentally friendly process as well as useful tool for material development.

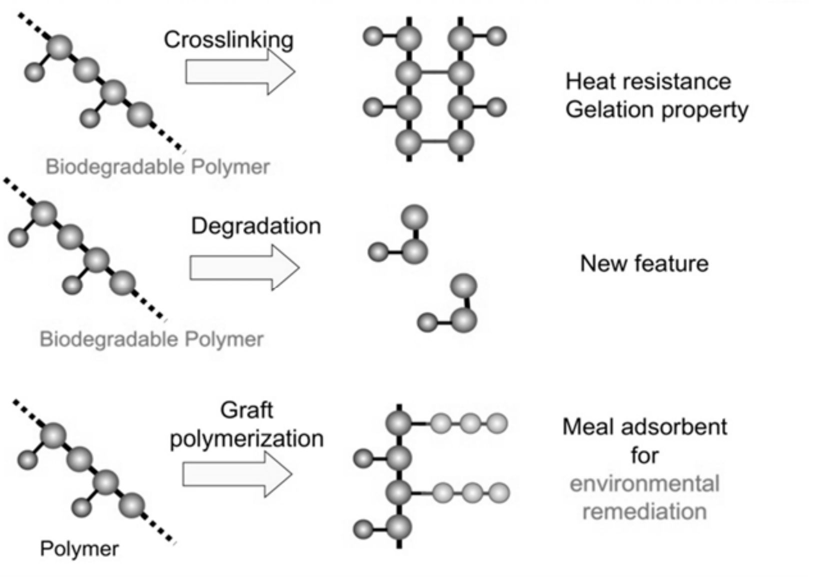


*FIG. 9.1. Three major reactions of crosslinking, degradation, and graft polymerization in radiation processing of polymers and induced modifications.*

There are three major reactions of crosslinking, degradation, and graft polymerization in radiation processing of polymers as shown in FIG. 9.1. Biodegradable polymers were modified by radiation-induced crosslinking to produce environmentally friendly materials so called green products. Practical applications of these materials are biodegradable dummy lens, mechanically strengthened Washi (Japanese traditional paper), etc. by modification of heat resistance and gelation property. Plant growth promoter is produced by radiation-induced degradation of natural polymers. Graft polymerization produces metal adsorbents for environmental remediation. Hence the radiation processing is convenient tool for the development of needs-oriented polymeric materials in practical applications. The details were described in the following two sections of environmentally friendly products and products for environmental remediation.

## 9.2.ENVIRONMENTALLY-FRIENDLY PRODUCTS

Poly (lactic acid), PLA, is synthesized by condensation polymerization of lactic acid obtained by fermentation of starch. Cellulose is originated from woods. Carbon dioxide released by incineration of these materials is reused for growth of plants and woods. The total amount of carbon dioxide is maintained at certain level in our global environment. Uses of these materials do not affect the global warming caused by increasing carbon dioxide. Hence such PLA and cellulose are called green products. Similarly chitosan is chemically extracted from crab shells etc. Chitosan is easily decomposed by microorganism and does not cause environmental burden. This section explains the radiation-induced modification of biodegradable polymers such as PLA, cellulose derivatives, and chitosan for practical applications.

### 9.2.1. Crosslinking to improve thermal deformation of Dummy Lens

PLA is so transparent and hard that the promising applications are thermally molded products such as optical lens, cabinets of electrical applicants, and regeneration medicine which require the property of high thermal stability. However, PLA thermally deforms at temperature higher than its glass transition temperature of 60 °C in spite of high melting point of 175 °C. Crosslinking is a suitable method to improve the heat resistance of PLA. Unfortunately, PLA is not cross-linked by irradiation without a certain cross linker and is degraded by high-energy radiation. It was found that addition of polyfunctional monomers as cross linker, triallyl isocyanurate (TAIC), could induce the crosslinking of PLA. The gel fraction reached 83.3 % for 3 % of TAIC after irradiation of 50 kGy. Without crosslinking the PLA became clouded due to crystallization after heating 100 °C for 1 h. To avoid this white turbid by heating, conditions of 3~5 % TAIC and 50 ~ 100 kGy is optimum for crosslinking. The Crosslinked PLA by radiation processing maintains high transparency so that it can be used as dummy lens of display eyeglass frame [9.1] as shown in FIG. 9.2. Dummy lens are discard after corrective lens was set in the eyeglass frame. They should be biodegradable to reduce the environmental burdens. Popular Japanese eyeglass-frames are used to be exported and are transported by surface. Dummy lens in the eyeglass frames should maintain their shapes in 70 °C of the hatch cargo temperature. Hence, the thermal property must be improved by crosslinking. After crosslinking the enzyme degradability was fortunately still maintained half level of intrinsic PLA. This result revealed that PLA was an environmentally acceptable lens material.

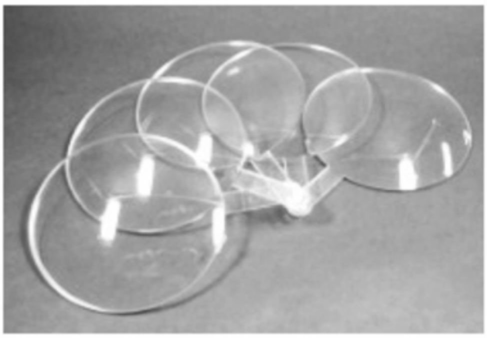


*FIG. 9.2. Dummy lens produced by crosslinking of PLA.*

### 9.2.2. Crosslinking to synthesize hydrogel for Washi improvement and Soil Conditioner

Cellulose derivative, carboxymethyl cellulose (CMC), is a water-soluble polymer and is used for food additives such as viscosity modifier and thickener. Such CMC could be cross-linked when it was irradiated in high concentrated aqua solution called paste-like state without any chemical additives [9.2]. In the CMC concentration is less than 10 % and higher than 80 %, degradation is preceded and little gel fraction was obtained as shown in FIG. 9.3. This result implies the distances among CMC molecules are not enough for crosslinking reaction in the concentration less than 10 %. At concentration higher than 70 %, CMC are not homogenously incorporated with water and some part of CMC behave like solid state. The cross-linked CMC becomes biodegradable hydrogels. When CMC hydrogel was soaked into water, swelling reached equilibrium after soaking of 4 h. The degree of swelling was 400, which is the ratio of weight increment to dry weight of CMC. [9.3]

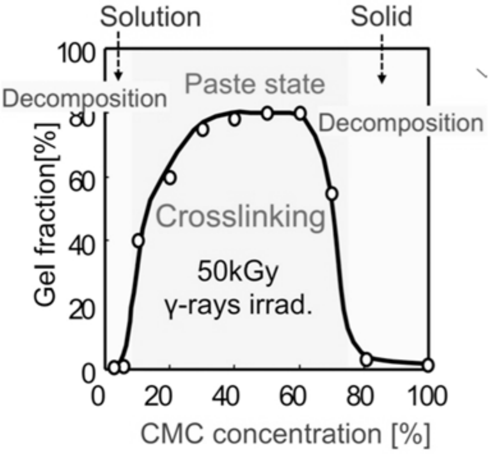


*FIG. 9.3. Effect of CMC concentration on gelation.*

The property of water absorption of CMC hydrogel can be applied as super water absorbent (SWA) for soil conditioner in arid area. Sandy soil in arid area has too low capacity to keep rain water in the soil. When 3 % dry CMC hydrogel was incorporated with sandy soil in arid area, available soil water content increased 2 times in irrigation system of tomato culture as shown in FIG. 9.4. As a result, tomato fresh yield increased from 19 to 31 Mg/ha when fresh yield was normalized by drained water. This application revealed the combination of SWA and drip irrigation system can significantly enhance efficiency of water utilization in tomato culture. Trial of semi-filed test using SWA developed by radiation processing of polymer has been carried out in project of electron accelerator application in Forum for Nuclear Cooperation in Asia (FNCA).

*FIG. 9.4. Tometo culture in combination of SWA and drip irrigation system.*

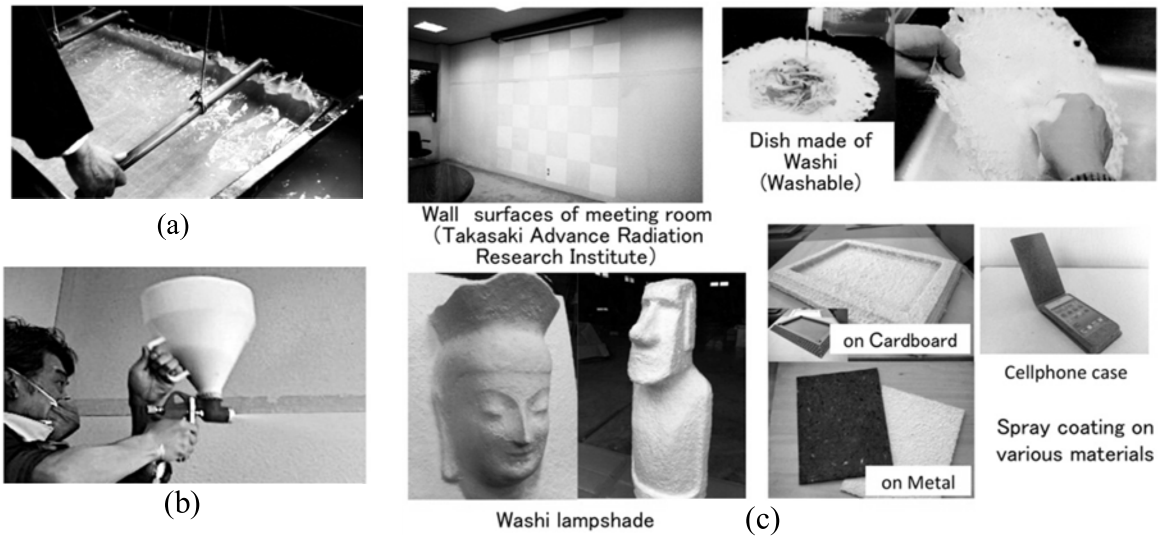


*FIG. 9.5. Applications of crosslinked CMC; (a) Traditional process of Washi fabrication using screen, (b) New precess of Washi preparating by spray coating, (c) Vairous applications of Washi spray coating.*

Washi is traditional paper in Japan and is prepared by spreading plant fibril such paper mulberry etc. from its aqua suspension onto screen as shown in FIG. 9.5(a). Adding of CMC hydrogel into plant fibril aqua suspension is capable of spray coating of Washi in FIG. 9.5(b). The new spray coating of Washi is enabled to be coated on interior wall and 3D structural surface in FIG. 9.5(c). Wall surfaces of the meeting room in Takasaki Advanced Radiation Research Institute were coated by this technique. Other applications of novel plant fibril suspension with CMC hydrogel are lampshade and washable dish. If CMC gel was not added to Washi suspension, sprayed coated lampshade cannot maintain the original shape due to insufficient mechanical strength. Paper dish without CMC hydrogel cannot be used repeatedly after washing with water. These products were commercialized by private company using program of expanding the achievements (patents) in Industrial Collaboration Promotion Department, JAEA.

Similar cellulose derivatives, hydroxypropylcellulose (HPC), in paste-like state can be cross-linked by irradiation. HPC gives highly transparent hydrogel. When dried HPC hydrogel sheet was soaked into solution of irradiation-sensitive monomer, a gel dosimeter is obtained. This transparent gel sheet became cloud around 2 Gy. Degree of white turbidity in the range from 1 to 15 Gy can be controlled by monomer compositions. [9.4]. This range is suitable for quantitative determination of dose for cancer therapy. When HPC gel sheets including monomer, some mm thick, were stacked until certain thickness, 3D dosimeter was assembled.

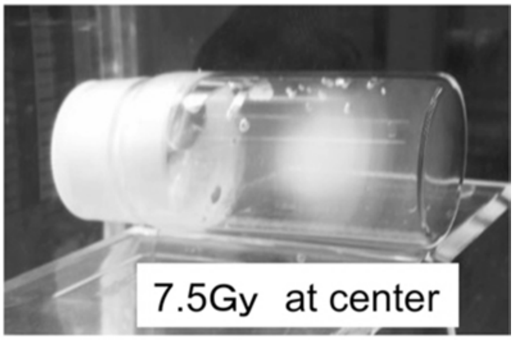
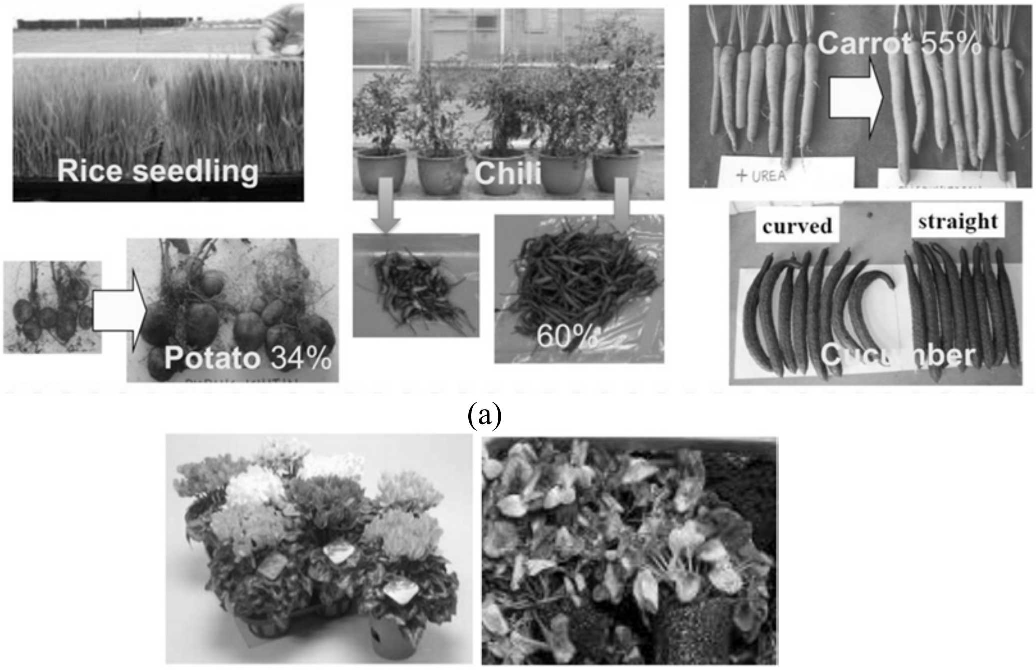


*FIG. 9.6. Detection of dose for cancer therapy using 3D gel dosimeter.*

Fig. 9.6. shows performance of 3D dosimeter for cancer therapy. Visualized irradiated part gives us the 3D image of irradiation for cancer therapy.

### 9.2.3 **Degradation to synthesize Plant Growth Promoter**

Decomposed marine polysaccharides such as chitosan from crab and shrimp shells play role of the plant growth promoter (PGP) in shoot elongation and harvesting yield. Low molecular weight chitosan called oligo chitosan can be degraded by acid hydrolysis and enzymatic reaction. However, the oligo chitosan prepared by radiation-induced degradation shows higher activity than that obtained by acid hydrolysis and enzyme reaction. This is because the oligo chitosan has larger portion of pyranose rings in some thousands of molecular weight by means of the radiation degradation than that prepared by non-irradiation methods. Liquid phase of chitosan is degraded effectively in lower dose than that in solid phase. Addition of hydrogen peroxide accelerates the degradation of chitosan [9.5]. This enhancement was caused by



(a)

(b)

*FIG. 9.7. Performance of PGP and elicitor in various plans; (a) Effect of olligochitosan on plant growth, and (b) cyclamen and infected one.*

hydroxyl radicals produced more in liquid phase with additive. In the field test for crops and vegetables such as rice, chili, potato, carrot, etc., foliar spray of oligochitosan solution induced 30 - 60 % increase of harvesting yield in Asian countries as shown in FIG. 9.7(a). FIG. 9.7(b) shows additional elicitor effect of oligochitosan on serious fungal infection of cyclamen. Electron Accelerator Application Project in FNCA supplies the standard protocol for PGP preparation in "FNCA Guideline on Development of Hydrogel and Oligosaccharides by

Radiation Processing" in http://www.fnca.mext.go.jp/english/eb/eb_guideline_v1_5.pdf. Synergetic effect of oligochitosan on PGP and bio-fertilizer on the increase of nitrogen fixation in soybean was found through collaborative work with FNCA bio-fertilizer project.

## 9.3.PRODUCTS FOR ENVIRONMENTAL REMEDIATION

Radiation-induced graft polymerization can introduce the desired functional groups into the commercially available trunk polymers. When a functional group having strong affinity to specified metal is selected, we can tailor metal adsorbents to respond the demands of environmental problem and the needs of end users. Fibrous adsorbents can be synthesized by using the fibrous polymers as a trunk polymer of graft polymerization. The resulting adsorbent has so large surface area that adsorption rate of metal ions is extremely higher than commercial resin adsorbent. Novel emulsion graft polymerization can enhance grafting yield. In this grafting process, monomer used in grafting is suspended in water. Organic solvent generally used in grating process is substituted by water. Usage of water instead of organic solvent in the grafting reaction considered to be environmentally friendly process.

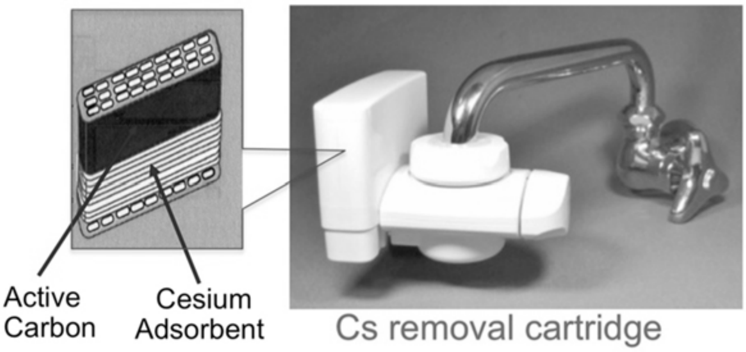


*FIG. 9.8. Prototype cartridge for Cs removal using APM-grafted adsorbent.*

### 9.3.1. Cesium adsorbent for safety of drinking water in Fukushima

Cesium (Cs) adsorbent was synthesized by grafting of acrylonitrile together with ammonium phospho-molybdate (APM) in dimethyl sulfoxide onto polyethylene nonwoven fabric to remediate contaminated areas in Fukushima Prefecture. In the laboratory experiment, 47 mg of the synthesized adsorbent was packed into column, 7 mm in inner diameter and 5 cm high. One ppm of non-radioactive Cs solution at pH 7 was pumped into the column with flow rate of 300 $h^{-1}$ in space velocity. The adsorption capacity was calculated at 54 g-Cs/kg-adsorbent from the breakthrough point of 3000 [9.6]. It was concludes that this adsorption capacity had enough high for removal of Cs. APM-grafted adsorbent can reduce the Cs concentration level to limit of detection (10 Bq/L) when radioactive Cs solution of 88 Bq/L was treated. However, the conventional method, combination of anion and cation ion exchange papers, reduced the Cs concentration to 56 Bq/L and cannot remove it until concentration level to limit of detection. It is confirmed that APM-grafted adsorbent is special material having high performance of Cs removal dissolved in water. Prototype cartridge for Cs removal was assembled by stacking

APM-grafted adsorbent and active carbon as shown in Fig. 9.8**.** The cartridges were distributed to 13 voluntary families for the safe of drinking water though the Cs is not detected in drinking water so far.

### 9.3.2. Environmental-friendly grafting process (Emulsion grafting)

Glycidyl methacrylate (GMA) is a precursor monomer for the synthesis of metal ion adsorbent. After grafting of GMA, the epoxy groups in grafted GMA on the trunk polymer can be chemically modified to various functional groups such as iminodiacetic acid, sulfonic acid, ethylenediamine and glucamine as shown in FIG. 9.9. Grafting of GMA is carried out in organic solvents such as methanol and dimethyl sulfoxide since GMA is not dissolved well in water but organic solvent. It is found that GMA can be grafted on the trunk polymer when it is suspended in water as emulsion using surfactant. The emulsion of 5% GMA in the water was stable for 48 h at 0.5% surfactant of Tween 20 (polyoxyethylene sorbitan monolaurate). Graft polymerization of GMA on polyethylene fiber was carried out in the emulsion state at various pre-irradiation doses. Degree of grafting (Dg) reached 130% for 2 h grafting at 40°C at pre-irradiation of 10 kGy in FIG. 9.10 [9.7]. In the case of dimethyl sulfoxide the Dg of 70 % needed 6 h grafting in 10 % GMA at the irradiation of 200 kGy. Environmentally friendly emulsion grafting can be used in the other monomers. Emulsion grafting of vinyl acetate enhance the monomer consumption rate 100 times [9.8]. Emulsified 4-chloromethylstyrene in water realized enough high Dg for biodiesel catalyst application [9.9].

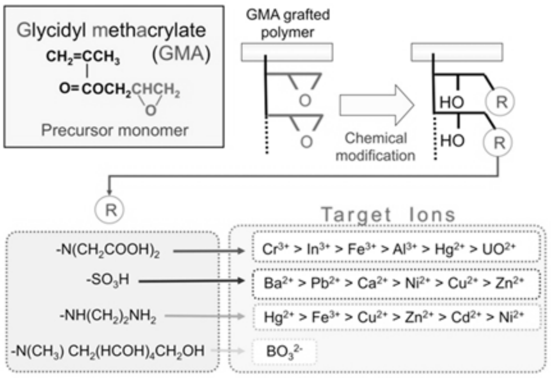


*FIG. 9.9. Chemical straucute of GMA and its chemical mofification to functional groups having affitity against target ions.*

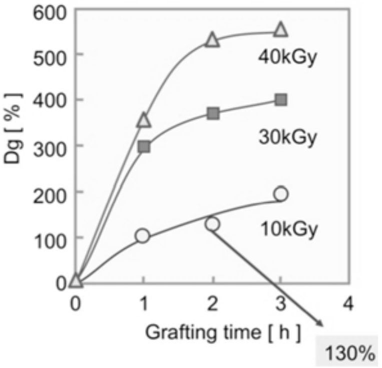


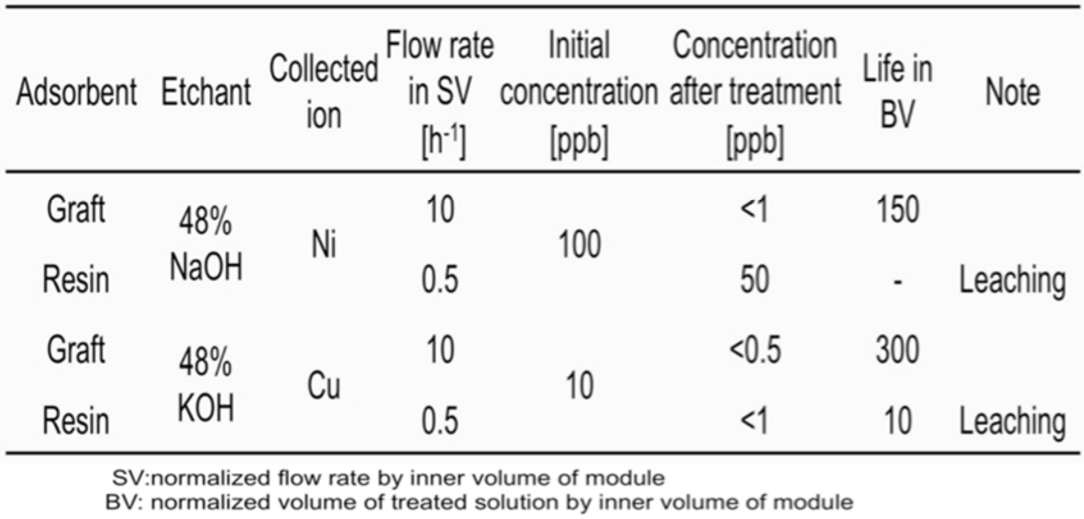
*FIG. 9.10. Reratioship between Dg and grafting time at several irradiation doses.*

### 9.3.3. Purification filter for reuse of wafer washing-agent

High effectiveness of emulsion grafting in terms of preirradiation dose, monomer concentration, grafting time is attractive for industrial grafting process owing to the reduction of production cost. There was a need for high-performance adsorbent which can remove Ni and Cu ions from strong alkaline solution used in the surface etching process of Si wafer. [9.10]. When the wafer washing-agent was contaminated by Ni and Cu ions at the concentration ofsome mg/kg (ppm), these ions diffused into the Si wafer and caused the creation of pits on the surface of the wafer. The removal of Ni and Cu ions in the wafer-washing agent can maintain the high productivity of Si wafers having fine smoothness of surface without any pits. Hence, fibrous adsorbent was synthesized in the bench scale of radiation-induce emulsion graft polymerization onto polyethylene nonwoven fabric and subsequent amination for practical application. The reaction condition was optimized using 30 L reaction vessel and nonwoven fabric, 0.3 m width and 18 m long. The resulting fibrous adsorbent was evaluated by 48 % NaOH and KOH contaminated with Ni and Cu ions, respectively. TABLE 9.1 shows that the concentration levels of Ni and Cu ions were reduced to less than 1 μg/kg (ppb) at the flow rate of 10 $h^{-1}$ in space velocity.

The life of adsorbent was 30 times higher than that of the commercialized resin. This novel adsorbent was commercialized for the metal removal in Si wafer processing since the ability of adsorption is remarkably higher than that of commercial resin.

TABLE 9.1. COMPARISON OF METAL REMOVAL PERFROMANCE USING FINROUS GRAFT ADSORBENT AND COMMECIALLY AVAILABLE RESIN ADSORBENT .



| Adsorbent | Etchant | Collected ion | Flow rate in SV [$h^{-1}$] | Initial concentration [ppb] | Concentration after treatment [ppb] | Life in BV | Note |
|---|---|---|---|---|---|---|---|
| Graft | 48% NaOH | Ni | 10 | 100 | <1 | 150 | |
| Resin | | | 0.5 | | 50 | - | Leaching |
| Graft | 48% KOH | Cu | 10 | 10 | <0.5 | 300 | |
| Resin | | | 0.5 | | <1 | 10 | Leaching |

SV:normalized flow rate by inner volume of module
BV: normalized volume of treated solution by inner volume of module

Irradiation-grafted nonwoven filter media was successfully commercialized, ®" which has metal removal function to reduce the concentration of harmful metal ions dissolving in the liquids. Straw type aqua filter was developed for the purification of water at catastrophic emergency. This filter can remove the hazardous metals such as Cs, As, Cd, Pb, Cr, etc. in streaming water.

## 9.4.CONCLUSION

Environmental remediation was considered from the viewpoint of radiation processing of polymers. Radiation processing can modify various kinds of polymers. The clean and biodegradable polymers such as poly (lactic acid) and natural polysaccharides need the improvement of heat resistance and gelation property, respectively, when they can be used for practical materials. The radiation processing is a clean tool for modification of the biodegradable polymers for practical applications. This is a direct contribution of radiation processing of clean products. Another contribution is to create the products for environmental remediation in terms of removal hazardous metals in contaminated water. Radiation-induced grafting easily synthesized tailored adsorbent for the removal of targeting toxic metals. Radiation processing is a superior tool for the development of polymeric materials. Emulsion graft polymerization realizes environmentally friendly process using water instead of organic solvent. It is expected that many environmental problems will be solved by matching of seeds technology of polymer modification with radiation processing and needs of environmental remediation.

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# 10. APPLICATION OF MOBILE E-BEAM FOR GREEN ENVIRONMENT

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**Abstract**

Due to the necessity of pilot scale test facility for continuous treatment of wastewater and gases on site, a mobile electron beam irradiation system mounted on a trailer has developed in EB TECH Co. Ltd. This mobile electron beam irradiation system is designed for the individual field application with self-shielded structure of steel plate and lead block which will satisfy the required safety figures of ICRP. Shielding of a mobile electron accelerator of 0.7 MeV, 30 mA has been designed and examined by Monte Carlo technique. Based on a 3-D model of electron accelerator shielding which is designed with steel and lead shield, radiation leakage was examined using the MCNP code. Calculations using two different versions (version 4c2 and version 5) of MCNP showed agreements within statistical uncertainties, and the highest leakage expected is $5.5061 \times 10^{-01}$ (1± 0.0454) μSv/h, which is far below the tolerable radiation dose limit of 1mSv/week.

This mobile unit will be used for on-site test of liquid waste and gaseous waste in U.S. by PELE Technology Inc. and EB TECH Co. Ltd. This unit could treat up to 500m$^3$ of liquid waste per day or 10,000 Nm$^3$ of gases per day.

## 10.1. OBJECTIVE OF THE RESEARCH

Radiation technologists have been investigating the use of high-energy radiation for treatment of pollutants such as wastewaters, flue gas, and sewage sludge. The major advantage of radiation technology is that the reactive species are generated in-situ during the radiolysis process without addition of any chemicals. The results of practical applications have confirmed that radiation technology can be easily and effectively utilized for treating large quantities of pollutants [10.5–10.7]. Even the advantages of radiation technology on environmental pollution control, there are very few commercial scale plants in operation since the cost for proving this technology by pilot scale test on site.

Thus, the needs for economical ways applying pilot scale are getting more and more the issues in the field. Due to the necessity of pilot scale test facility for continuous treatment of wastewater and gases on the spot, a mobile electron beam irradiation system mounted on a trailer has developed in EB TECH Co. Ltd.

## 10.2. INTRODUCTION

The problems of environmental damage and degradation of natural resources are receiving increasing attention throughout the world. The increased population, higher living standards, increased urbanization and enhanced industrial activities of humankind are all leading to degradation of the environment. Increasing urbanization has been accompanied by significant water pollution. Industrial activities to produce heat and electrical energy are responsible for emitting a large number and amount of pollutants, such as fly ash, sulphur oxides ($SO_2$ and $SO_3$), nitrogen oxides ($NO_X = NO_2 + NO$) and volatile organic compounds, into the atmosphere.

Electrons interact with gas creating divergent ions and radicals including oxidizing radicals and excited species. These excited species react in a various ways of neutralization reactions and dimerization. Irradiation of flue gas to convert $SO_2$ and $NO_X$ into a dry product containing $(NH_4)_2SO_4$ and $NH_4NO_3$ that was usable as a fertilizer. Two larger scale plants were constructed in Indianapolis, USA [10.2] and Karlsruhe, Germany [10.3]. The engineering design technology for electric utility applications was established at the pilot plant in Kaweczyn, Poland (2×$10^4$ $Nm^3/h$) using two accelerators (5kW, 700keV each) [10.4].

Electron beam processing of wastewater is non-chemical, and uses fast formation of short-lived reactive radicals that can interact with a wide range of pollutants. Such reactive radicals are strong oxidizing or reducing agents that can transform the pollutants in the liquids wastes. The first studies on the radiation treatment of wastes were carried out in the 1950s principally for disinfection. In the 1960s, these studies were extended to the purification of water and wastewater. After some laboratory research on industrial wastewaters and polluted groundwater in 1970s and 1980s, several pilot plants were built for extended research in the 1990s. The first full-scale application was reported for the purification of wastewater at the Voronezh synthetic rubber plant in Russia. Two accelerators (50kW each) were used to convert the non-biodegradable emulsifier, 'nekal', present in the wastewater to a biodegradable form [10.5]. The installation treats up to 2,000 $m^3$ of effluent per day. A pilot plant of 1,000 $m^3/d$ for treating textile-dyeing wastewater has been constructed in Daegu, Korea with 1MeV, 40kW electron accelerator [10.6].

## 10.3. MATERIALS AND METHODS

### 10.3.1. Design of Mobile Electron Accelerator

This mobile electron beam irradiation system is designed for the individual field application with self-shielded structure of steel plate and lead block which will satisfy the required safety figures of ICRP. Design parameters are limited by the allowable total weight and height of the trailer on the road which controlled by National Authorities. Therefore, the output parameter of electron beam is designed for 0.7MeV and 20kW through 600mm window. This mobile unit will be used for on-site test of liquid waste and gaseous waste in U.S. by PELE Technology Inc. and EB TECH Co. Ltd. This unit could treat up to 500$m^3$ of liquid waste per day or 10,000 $Nm^3$ of gases per day.

Shielding of a mobile electron accelerator of 0.6 MeV, 33 mA has been designed and examined by Monte Carlo technique. Based on a 3-D model of electron accelerator shielding which is designed with steel and lead shield, radiation leakage was examined using the MCNP code. Calculations using two different versions (version 4c2 and version 5) of MCNP showed agreements within statistical uncertainties, and the highest leakage expected is 5.5061x$10^{-01}$ (1±0.0454) μSv/h, which is far below the tolerable radiation dose limit of 1mSv/week.

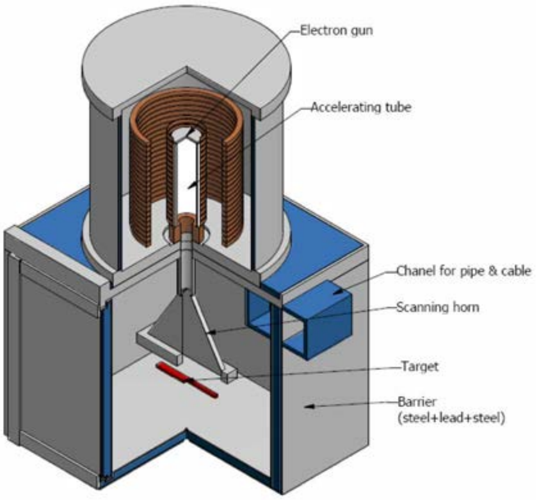
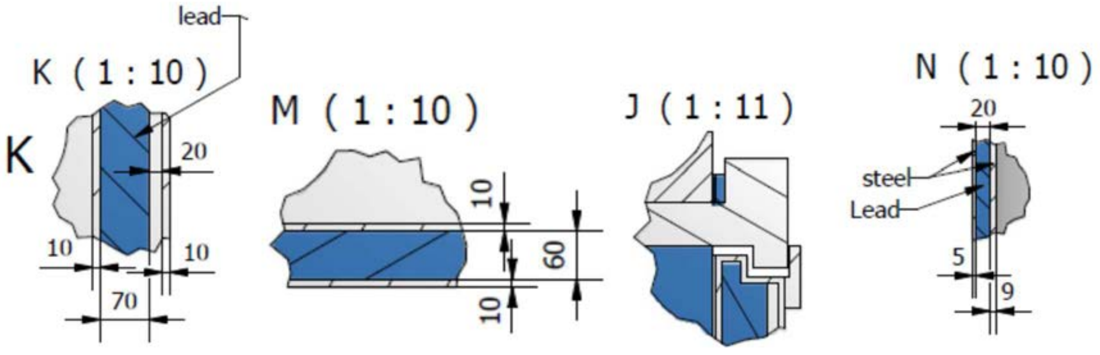


*FIG. 10.1. Section view of Accelerator and primary barrier*



(wall) (bottom) (middle) (vessel)

*FIG. 10.2. Detailed section view of the barrier*

### *10.3.1.1. Material and Thickness for primary barrier*

Section view of Accelerator and primary barrier is showned in Fig. 10.1 while Fig 10.2 provides detailed section view of the barrier.

– Wall: Steel (10mm) + Stiffener gap (20mm) +Lead (70mm) +Steel (10mm)

– Bottom: Steel (10mm) +Lead (60mm) +Steel (10mm)

– Top: Steel (160mm)

– Vessel: Steel (5mm) +lead (20mm) +steel (9mm)

### *10.3.1.2. Material and thickness for secondary Barrier*

- Real value 50mm: Epoxy Glass 5mm +Urethane40mm +EpoxyGlass5mm

(Polyethylene 10mm-assumed for MCNP)

Layout of primary and secondary barrier are presented in Fig. 10.3

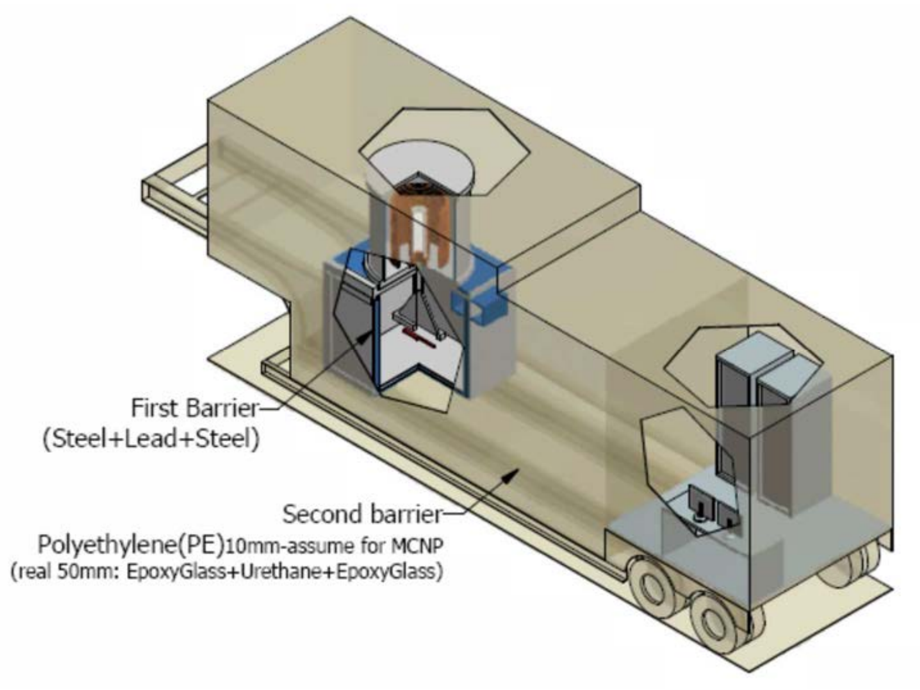


*FIG. 10.3. Layout of primary and secondary barrier*

#### 10.3.1.3. *Statement of operating assumptions on which barrier calculations were based, including workload, use, and occupancy factors.*

- Operating condition of electron accelerator
  - \+ Accelerating energy: max. 0.6 MeV
  - \+ Beam current: max. 33 mA
- Work loads
  - \+ 2,000hours per year (@ 8hours/day*5days/week*50weeks/year)
  - \+ 40hours per week (@ 8hours/day*5days/week)
- Use factors (or beam direction factor)
  - \+ For floor, wall and ceiling (1st radiations and 2nd radiations)
- Occupancy factors for all adjacent Trailer Vehicle (controlled area)
  - \+ 1/16 for the public (uncontrolled area)

### 10.3.2. Calculation of Radiation Leakage

The barrier calculations for radiation shielding are calculated by Monte Carlo N-Particle Transport Code (MCNP). Therefore, we summarize operating assumptions on barrier calculations for radiation shielding by MCNP code as follows; to prepare an input for the MCNP code, the electron beam accelerator including the trailer have been modeled.

- Electron source: 0.6 MeV, 33 mA, mono-directional
- Target: material=stainless steel
- Width=52 cm, depth=5 cm, height=1 cm, z=46.1 cm

Other components including accelerator assembly, scan hood, titanium window, shielding door, shield wall, trailer wall, and the ground have been modeled according to the drawings (Fig. 10.4).
The resulting geometrical models of the mobile accelerator for the MCNP code are illustrated TABLE 10.1, and locations of 20 gamma detectors are listed in Fig. 10.5.

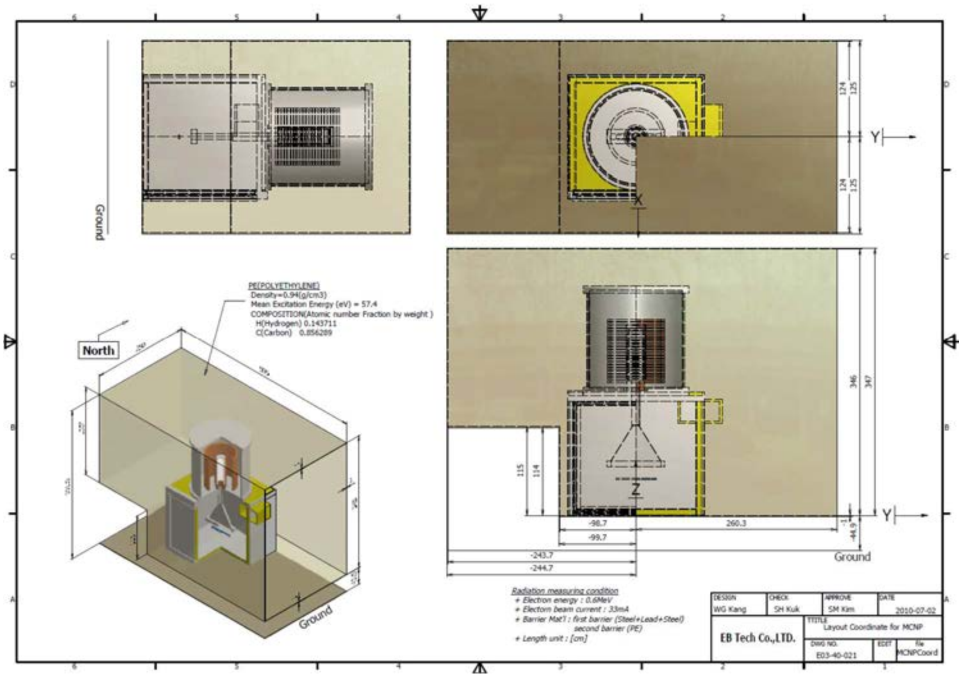


*FIG. 10.4. Layout coordinates and dimensions for MCNP Calculation*

TABLE 10.1 DOSE CALCULATIONS USING MCNP ($100X10^6$ HISTORIES)

| Detector No | Detector Location (x,y,z) | Average Dose MCNP4 $\bar{D} \pm R$ μSv/hr | Average Dose MCNP5 $\bar{D} \pm R$ μSv/hr | Tally No. |
|---|---|---|---|---|
| 1 | (0,-228,-43) | $6.7135x10^{-02}$0.0677 | $5.9359x10^{-02}$0.0680 | 5 |
| 2 | (0,-228,6) | $9.1882x10^{-02}$0.0536 | $8.1185x10^{-02}$0.0529 | 15 |
| 3 | (0,-228,67) | $9.4518x10^{-02}$0.0651 | $8.6097x10^{-02}$0.0694 | 25 |
| 4 | (0,-228,117) | $1.4111x10^{-01}$0.3044 | $1.0392x10^{-01}$0.3738 | 35 |
| 5 | (0,-228,217) | $3.8811x10^{-01}$0.3853 | $3.0133x10^{-01}$0.4695 | 45 |

| | | | | |
|---|---|---|---|---|
| 6 | (0,-228,253) | 8.7883x10$^{-02}$0.3371 | 4.7540x10$^{-02}$0.3056 | 55 |
| 7 | (0,228,67) | 8.9230x10$^{-02}$0.0472 | 8.5501x10$^{-02}$0.0740 | 65 |
| 8 | (0,228,117) | 3.7980x10$^{-02}$0.3191 | 5.6559x10$^{-02}$0.3979 | 75 |
| 9 | (0,228,217) | 2.4626x10$^{-02}$0.6885 | 2.6934x10$^{-02}$0.6683 | 85 |
| 10 | (125,0,-43) | 1.2295x10$^{-01}$0.1045 | 1.0380x10$^{-01}$0.0762 | 95 |
| 11 | (125,0,6) | 2.0328x10$^{-01}$0.0509 | 1.7660x10$^{-01}$0.0395 | 105 |
| 12 | (125,0,67) | 2.1053x10$^{-01}$0.0398 | 1.8794x10$^{-01}$0.0388 | 115 |
| 13 | (125,0,117) | 4.2511x10$^{-03}$0.0424 | 3.7886x10$^{-03}$0.0426 | 125 |
| 14 | (125,0,217) | 1.0983x10$^{-01}$0.0558 | 1.2487x10$^{-01}$0.1710 | 135 |
| 15 | (-125,0,6) | 2.5866x10$^{-01}$0.1802 | 1.9430x10$^{-01}$0.0564 | 145 |
| 16 | (125,0,253) | 5.5061x10$^{-01}$0.0454 | 5.4732x10$^{-01}$0.0386 | 155 |
| 17 | (0,40,357) | 4.3783x10$^{-01}$0.7161 | 4.1760x10$^{-01}$0.7426 | 165 |
| 18 | (0,0,357) | 2.2082x10$^{-01}$0.0330 | 2.1224x10$^{-01}$0.0330 | 175 |
| 19 | (125,206,290) | 8.6008x10$^{-03}$0.1890 | 8.6735x10$^{-03}$0.2143 | 185 |
| 20 | (-125,88,120) | 9.8107x10$^{-04}$0.0508 | 8.5752x10$^{-04}$0.0513 | 195 |

Based on a 3-D model of electron accelerator shielding which is designed with steel and lead shield, radiation leakage was examined using the MCNP code. Calculations using two different versions (version 4c2 and version 5) of MCNP showed agreements within statistical uncertainties, and the highest leakage expected is 5.5061x10-01 (10.0454) μSv/h, which is far below the tolerable radiation dose limit of 1mSv/week [10.8].

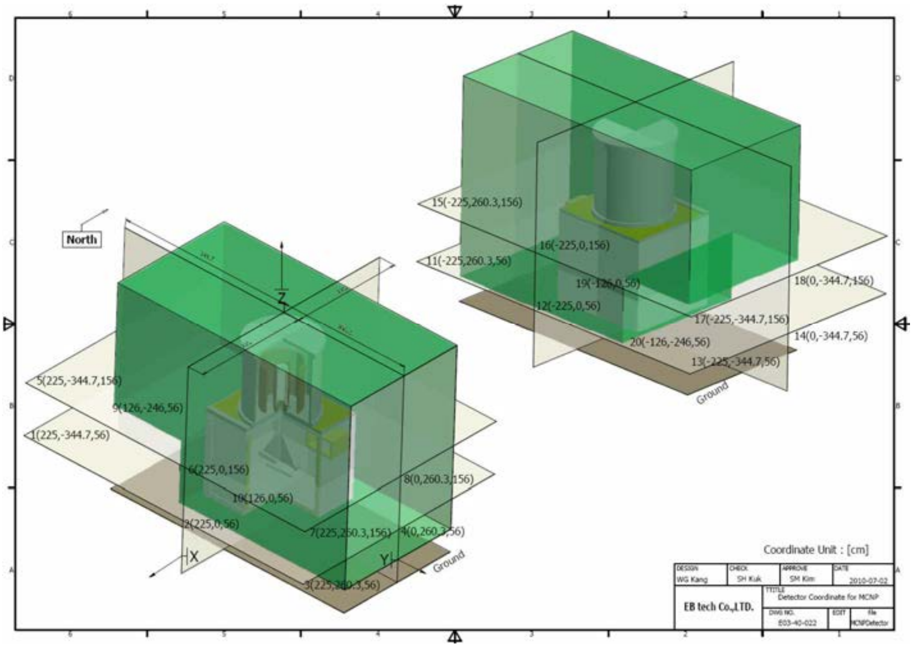


*FIG. 10.5. Detector location in x, y, z coordinates*

## 10.4. ASSEMBLING OF MOBILE ACCELERATOR

Mobile electron accelerator of 0.6 MeV, 33 mA has been mounted on a mobile trailer vehicle (low-bed trailer); a cabinet body installed on the chassis of trailer; an electron accelerator, which generates electron beam for electron beam processing; and an accelerator control box, which controls operation of the accelerator, wherein the electron accelerator is provided in the cabinet body. Since the electron accelerator is provided in the cabinet body of the mobile trailer, it has a small volume with flexible maneuverability, which can be transferred rapidly in a short time. In addition, the mobile accelerator system does not require additional working environment, and does not need any additional construction works. (Additional working environment connotes monitoring, control and waste supply/return systems related to the operation of the mobile accelerator, such as ozone ventilation, air/water cooling system, CCTV, radiation monitoring, etc. – all of which are already equipped in the mobile unit). An actual picture of a mobile electron accelerator with outer shelter, is presented in Fig. 10.6

Moreover, the mobile accelerator system has a high degree of automation assembly with easy operations and safety. Please note: Pele Technology does not expect to move the mobile unit more than once a quarter.

*A. Specification of radiation types*
- Electron Beam (0.6MeV x 33mA)

*B. Specification of Radiation Machine*
- Electron beam accelerator (ELV-0.6M)
- Accelerating energy 0.6 MeV
- Electron beam power max. 20 kW
- Beam current max. 33 mA
- Extraction window dimensions 640×75 mm

- Model: ELV-0.6M will be housed as a mobile unit.
- Type of trailer : semi-trailer(without truck-tractor)
- Dimension : 99 inches(Width)*156 inches(Height )
- *442 inches(Length)

FIG. 10.6. Mobile electron accelerator with outer shelter

Besides this, the mobile unit is equipted with a control system to treat waste water, the schematic of the system is showed in Fig. 10.7.

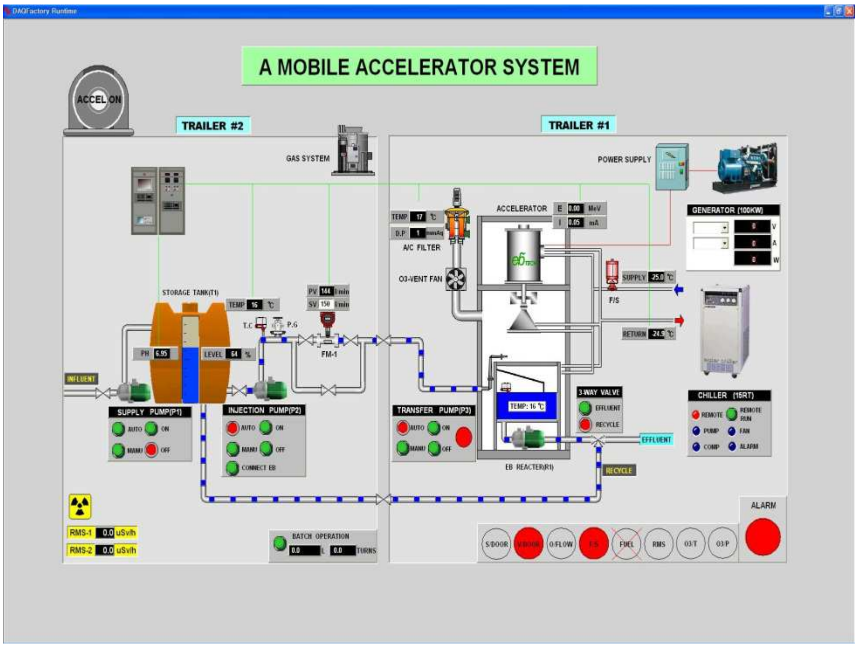


FIG. 10.7. Wastewater control system in Mobile elctron accelerator

## 10.5. CONCLUSION

1. A mobile electron beam irradiation system mounted on a trailer has developed in EB TECH Co. Ltd. This mobile electron beam irradiation system is designed for the individual field application with self-shielded structure of steel plate and lead block.

2. Shielding of a mobile electron accelerator of 0.7 MeV, 30 mA has been designed and examined by Monte Carlo technique, leakage was examined using the MCNP code.

3. Calculations using two different versions (version 4c2 and version 5) of MCNP showed agreements within statistical uncertainties.

4. This mobile unit will be used for on-site test of liquid waste and gaseous waste in U.S. by PELE Technology Inc. and EB TECH Co. Ltd. This unit could treat up to 500m$^3$ of liquid waste per day or 10,000 Nm$^3$ of gases per day.

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# 11. NEW DEVEELOPMENTS IN TREATMENT OF POLLUTANTS BY RADIATION TECHNOLOGIES

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Korea

**Abstract**

Four kinds of researches using radiation treatment technology for the environmental conservation were carried out in this study. In the study on treatment of PCBs, decomposition of PCBs in commercially used transformer oil used for more than 30 years has been carried out at normal temperature and pressure without any additives using an electron beam accelerator. The electron beam irradiation seemed to transform large molecular weight compounds into lower ones, but the impact was considered too small on the physical properties of oil. Residual concentrations of PCBs after irradiation depend on the absorption dose of the electron beam energy, but aliphatic chloride compounds were produced at higher doses of irradiation. As the results from FT-NMR, chloride ions decomposed from the PCBs are likely to react with aliphatic hydro carbon compounds rather than existing as free radical ions in the transformer oil. In the study on the sewage sludge treatment, electron beam irradiated sewage sludge mixed with a starfish was evaluated in order for it to be used as a fertilizer for soil. The most of PAHs were destructed completely by low irradiation of absorption dose. Disinfection of a coli form and a bacillus was completed by less than 3 kGy absorbed dose. Toxicity on ecological system from antibiotics was also detoxified by electron beam treatment. Superiority on fertilizer was evaluated from the comparison of plant growth with and without one. In the study on groundwater remediation, synthetic groundwater contaminated by TCE and PCE was irradiated. Higher removal efficiency on TCE and PCE could be obtained by irradiation. TCE and PCE were removed at an irradiation dose of 300 Gy in the presence of $O_3$ and $TiO_2$, where $TiO_2$ showed explicit enhancement of decomposition. The catalytic activity of $TiO_2$ was characterized by EPR spectroscopy and spin-trapping method. The EPR signal of $TiO_2$ was increased up to 15 % after gamma-irradiation and these results in the increase of hydroxyl radical production by 5 %. Regarding on field demonstration study for sewage effluent, decomposition of antibiotics and endocrine disruptors contained in sewage effluent by MEB (Mobile Electron Beam accelerator) was conducted. The field study was carried out over four seasons in order to observe the effect of seasonal temperature changes on decomposition of chemicals contained in effluent of sewage. The major antibiotics and endocrine disruptors with initial concentration of 0.5 mg/l were decomposed completely by the irradiation dose less than 1.5 kGy, and coli form and microorganisms were also sterilized under the same irradiation dose. Toxicity arising by antibiotics on algae was reduced according to irradiation dose. The results obtained from field study played an important role in acquiring a certification on advanced treatment of sewage effluent by radiation, NET (New Environmental Technology), which is issued by Korea ministry of environment.

## 11.1. PART 1: DECOMPOSITION OF PCBS IN WASTE TRANSFORMER OIL

### 11.1.1. Introduction

Polychlorinated biphenyls (PCBs) are chemically stable and resist microbial, photochemical, chemical, and thermal degradation. The public, legal, and scientific concerns regarding PCBs arose from research indicating that they are environmental contaminants that have the potential to adversely impact the environment, and therefore, became undesirable as commercial products. Eventually, most producers reduced or stopped their production of PCBs in the 1970s.

Previous studies to degrade the concentration of PCBs have been performed in a diluted solution such as water and/or alcohol. This may prevent the treated oil from recycling or converting to other purpose even though after detoxification. This study focused on the decomposition of transformer oil containing PCBs, which was commercially used for more than 30 years in Korea, without any additives using an electron beam accelerator.

### 11.1.2. Experimental

Commercially used transformer oil contaminated with 10-900 ppm of PCBs was used as a sample material for decomposition. Sources of PCBs in Korea are known to be mixtures of Aroclors 1242, 1248, 1254, and 1260.

For a pilot scale treatment, we newly designed an irradiation reactor having a declined stainless steel plane to flow the oil into the irradiation area of the electron beam accelerator. The irradiation reactor was consistently cooled by water during the irradiation to prevent a rise in temperature. The irradiation dose for one passage of oil on the declined plane was measured as 15 kGy at a fixed electron beam power of 50 kW. The absorbed dose was measured with a dichromate solution.

The electron beam was generated with an ELV-4 (EB-tech Co., LTD, Daejeon, Korea) with energy of 1.5 MeV, a 50 mA current, and 75 kW power of a commercial scale accelerator. All experiments were performed at room temperature and ambient pressure without any additives.

The concentration of PCBs was measured by both a GC/ECD and a HRGC/MS. The molecular structure and chemical element were determined by FT-NMR.

### 11.1.3. Results and Discussion

#### *11.1.3.1. Molecular weight changes*

To observe the molecular weight changes between pre- and post-irradiation, the transformer oil was irradiated with 200 kGy. Comparing the data in Fig. 11.1. between the pre- and post-irradiation, the peak intensity of the C17 compound was increased by 5% against pre-irradiation, but the C19 and C22 carbon compounds were decreased as much as 5%. Based on this, electron beam irradiation seems to transform large molecular weight compounds into lower ones. In this experiment, the magnitude of molecular weight transformation was less than 5%, which was considered too small to impact the physical properties of the oil.

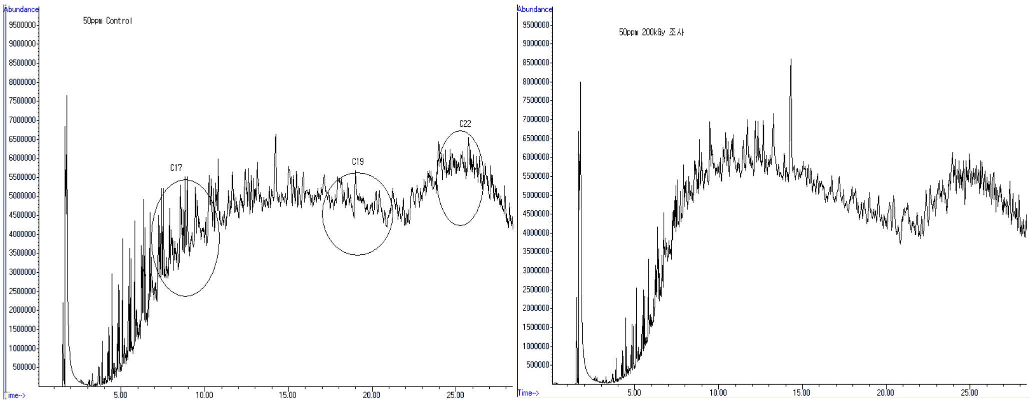


*FIG. 11.1. Molecular weight before (left) and after irradiation (right) of transformer oil (50ppm of PCBs)*

#### *11.1.3.2. Physical and electrical property changes*

Table 11.1 shows that the physical and electrical property changes both pre- and post-irradiation being considered important characteristics for transformer oil. Kinematic viscosity was increased a little; this seems that molecular weight is transformed into lower ones by electron beam irradiation. The increase of the dielectric breakdown voltage related to the concentrations of the impurities, and the total acid number related to the amount of moisture in the oil, seem to be due to the fact that the oil was used for more than several tens of years and held outside for a long time. No other properties were changed remarkably.

A decrease of the dielectric breakdown voltage can be protected by preventing oxidation of impurities during irradiation.

TABLE 11.1. PHYSICAL AND ELECTRICAL PROPERTIES OF TRANSFORMER OIL BEFORE AND AFTER IRRADIATION.

| Property | Before irradiation | After irradiation |
|---|---|---|
| Kinematic viscosity at 40℃, $mm^2/s$ | 10.82 | 11.86 |
| Kinematic viscosity at 100℃, $mm^2/s$ | 2.589 | 2.763 |
| Sludgy (%), Oxidation stability at 120℃ for 75h | 0.01 | 0.01 |
| Total acid number (mg·KOH/g), Oxidation stability at 120℃ for 75h | 0.38 | 0.55 |
| Dielectric breakdown voltage, kV, 2.5mm | 28.61 | 16.09 |
| Total acid number,mg·KOH/g | 0.01 | 0.05 |
| Volume resistivity, Ω·cm, 80℃ | $1.1 \times 10^{14}$ | $2.1 \times 10^{12}$ |

### *11.1.3.3. Decomposition of PCBs*

To determine the proper irradiation intensity according to the concentrations of PCBs, additional experiments for 16 different kinds of samples were performed, and their residue PCBs concentration we measured are as shown in Table 11.2.

Fig. 11.2. represents the FT-NMR results after irradiation. The results indicate that aliphatic chloride compounds are produced with an increasing dose of irradiation. The NMR data show that the newly produced materials are mono chloro-alkane from the peak between 3-4 ppm, and di-chloro-alkane from the peak between 5-6 ppm. Therefore, aliphatic chloride compounds are produced at higher doses of irradiation.

### *11.1.3.4. By-Products*

Table 11.3 shows the concentrations of the residual PCBs isomers in ppb after irradiation at 0 kGy, 180 kGy, 240 kGy, and 300 kGy for a 37 ppm sample. The higher dose in the sample, the more the low chlorinated isomers increased. This means that the hepta-chlorinated biphenyl decomposed into hexa-chlorinated biphenyl, and then into penta-, tetra-, tri-, di-, and mono-, and finally into bi-phenyl, which is no longer a toxic compound. Compared to the concentrations of PCBs between GC/ECD and HRGC/MS, the concentrations from the HRGC were always higher than the results with GC/ECD. Therefore, the analysis from HRGC to confirm the residual PCBs is very important

TABLE 11.2. RESIDUAL CONCENTRATION OF PCBS ACCORDING TO IRRADIATION DOSE IN A BATCH SYSTEM.

| **Sample ID** | **Dose, kGy** | **Residual Concentration, ppm** | **Sample ID** | **Dose, kGy** | **Residual Concentration, ppm** |
|---|---|---|---|---|---|
| 0601 | 0 | 111.5 | 0708-2 | 0 | 27 |
| 〃 | 250 | ND | | 600 | ND |
| 〃 | 300 | ND | 0708-3 | 0 | 49 |
| 〃 | 350 | ND | | 600 | ND |
| 0602 | 0 | 13.39 | 0708-4 | 0 | 98 |
| 〃 | 50 | 4.78 | | 600 | ND |
| 〃 | 100 | 1.90 | 0708-5 | 0 | 498 |
| 〃 | 150 | ND | | 600 | ND |
| 〃 | 200 | ND | 0709 | 0 | 73.58 |
| 0606-1 | 0 | 1.83 | | 20 | 36.32 |
| 〃 | 50 | ND | | 50 | 23.87 |
| 0606-2 | 0 | 10.85 | | 100 | 8.84 |
| 〃 | 150 | ND | | 200 | 0.19 |
| 0606-3 | 0 | 27.3 | 0806 | 0 | 81.571 |
| 〃 | 150 | ND | 〃 | 200 | ND |
| 0606-4 | 0 | 98.91 | 0809-1 | 0 | 19.8 |
| 〃 | 300 | ND | 〃 | 200 | ND |
| 0606-5 | 0 | 853 | 〃 | 200 | ND |
| 〃 | 600 | 1.10 | 〃 | 200 | ND |
| 〃 | 650 | ND | 〃 | 200 | ND |
| 〃 | 700 | ND | 0809-2 | 0 | 47 |
| 〃 | 750 | ND | 〃 | 150 | ND |
| 0708-1 | 0 | 10 | 〃 | 150 | ND |
| 〃 | 600 | ND | | | |

*ND: no PCBs detected, i.e. <0.05 ppm

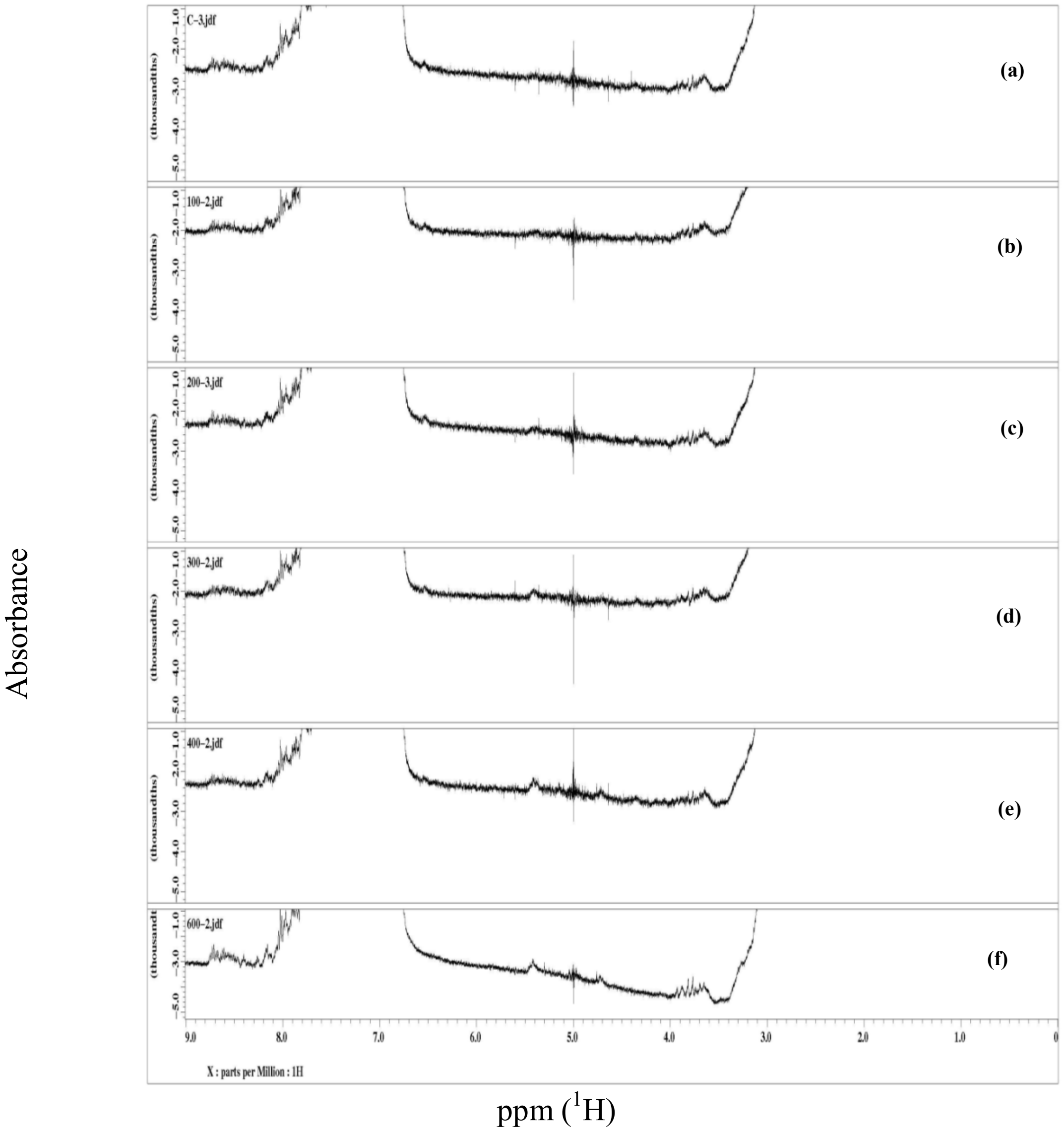


*FIG. 11.2. FT-NMR results after irradiation according to the dose of the electron*

### 11.1.4. Conclusion

From an investigation of molecular weight changes post-irradiation, electron beam irradiation seemed to transform a large molecular weight compound into a lower one; however, the impact was considered too small on the physical properties of the oil. Comparison results of the physical and electrical properties between pre- and post-irradiation revealed that the properties were almost maintained after irradiation. The residual concentrations of the PCBs after irradiation depended on the absorption dose of the electron beam energy, but aliphatic chloride compounds were produced at higher doses of irradiation. The difference between GC/ECD and HRGC/MS for the residual concentration of PCBs indicated that the analysis by HRGC to confirm the residual PCBs is very important.

Recently, the electron beam accelerator has come into the spotlight in the field of environmental conservation. Its advantages compared to other methods such as chemical destruction, biodegradation, IR, UV, and so on for the decomposition of PCBs in transformer oil are its economic benefits, massive, and lack of needed additives. It is also a simple process due to its normal temperature and ambient pressure operation.

TABLE 11.3. CONCENTRATION OF PCBS AND PCBS ISOMERS AFTER IRRADIATION WITH AN ELECTRON BEAM ACCELERATOR.

| Sample ID | 090306-0-7-0-V01 | 090306-0-7-0-V14 | 090306-0-7-0-V14 | 090306-0-7-0-V14 |
|---|---|---|---|---|
| Dose, kGy | 0 | 180 | 240 | 300 |
| PCBs by GC/ECD | 37ppm | <0.5ppm | <0.5ppm | <0.5ppm |
| PCBs isomers | | | | (unit: ng/g) |
| MoCBs | 91 | 4000 | 3100 | 2000 |
| DiCBs | 3900 | 7400 | 4000 | 2700 |
| TrCBs | 13000 | 690 | 240 | 160 |
| TeCBs | 9700 | 170 | 40 | 40 |
| PeCBs | 11000 | 16 | 0 | 7 |
| HxCBs | 13000 | 0 | 0 | 0 |
| HpCBs | 8400 | 0 | 0 | 0 |
| OcCBs | 2300 | 0 | 0 | 0 |
| NoCBs | 210 | 0 | 0 | 0 |
| DeCB | 4 | 0 | 0 | 0 |
| Total PCBs | 62000 | 12000 | 7400 | 4900 |

## 11.2. PART 2. TREATMENT OF SEWAGE SLUDGE

### 11.2.1. Introduction

Sewage sludge after dehydration is consisted of 80% water and 20% organics, and small amount of nitrogen and phosphate which are basic components for fertilizer were enriched. Most of sewage treatment plants have treated night soil together, resulted in highly presence of a coli form and a bacillus in the sewage sludge cake. Recently trace amount of harmful organic chemicals affecting to the ecological system have been detected in the sewage sludge cake. On the other hand, the amounts of a starfish caught from sea side have increased continuously. These result in desolation of fishery resources. A starfish has been known as a fish enriched with organics and a calcium carbonate. A calcium carbonate has been used to fertilizer in agricultural area. The purpose of this study is to produce a fertilizer from an electron beam treated sewage sludge and a starfish, and to evaluate their quality by comparison of the plant growth rate.

### 11.2.2. Experimental

Dehydrated Sewage sludge was obtained from sewage treatment plant. A starfish was dried and crashed before mix with sludge cake. Thin film type of sludge cake with 5 mm thickness was placed on the bottom of stainless still plate which was located under window of an electron beam. Irradiation time was determined by total dose to be absorbed. Irradiated sludge cake was mixed with powder type of a starfish. In order to evaluate the quality as a fertilizer, relative growth rate on the grass, rose tree and shrub was compared with and without irradiated sludge mixed with starfish.

### 11.2.3. Results and Discussion

Several kinds of harmful poly aromatic hydrocarbon (PAHs) were detected in the sewage sludge although their concentrations are very low. Most of PAHs were decomposed easily by irradiation dose within 10 kGy (Fig. 11.3).

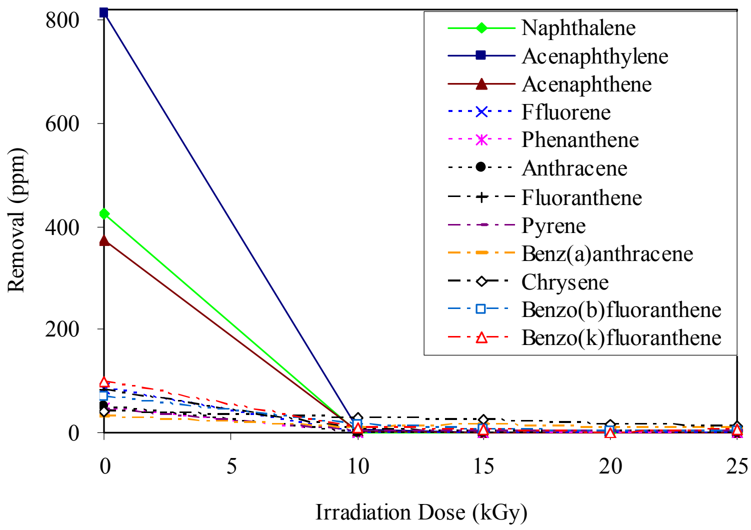


*FIG. 11.3. Decomposition of PAHs according to the applied doses.*

The Coli form and bacillus contained in sludge were irradiated and resulted in totally destruction of them by 3 kGy irradiation dose. After irradiation, most of the cell structures were completely destroyed as shown in figure 11.4.

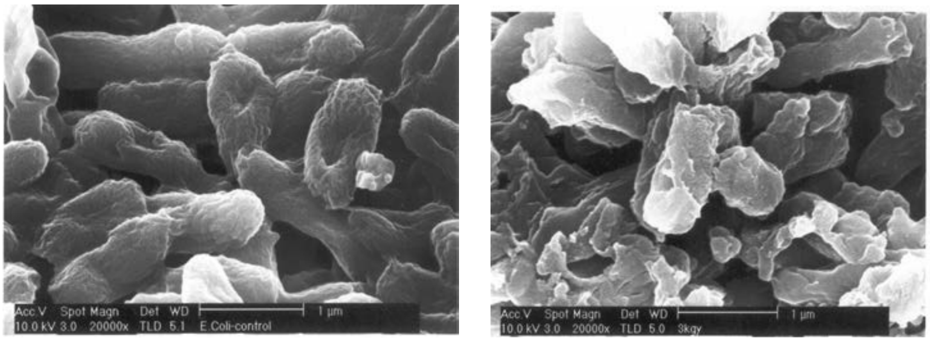
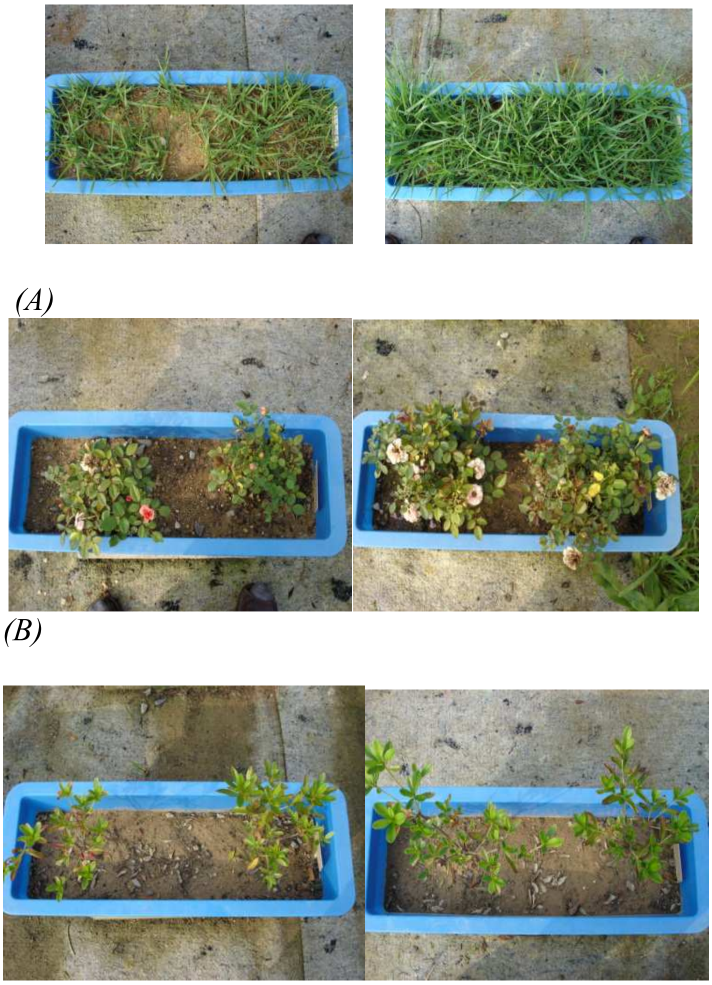


*FIG. 11.4. Destruction of microorganisms by irradiation (left: control, right: 3 kGy radiation dose).*

Figure 11.5. and 11.6. show the results of comparison on the relative growth rate for grass, rose tree and shrub with and without fertilizer mixed with irradiated sludge and a starfish. It showed that irradiated sludge mixed with a starfish acts as a good fertilizer for plant growth.



(A)

(B)

(C)

FIG. 11. 5. Comparison on the relative growth rate for grass, rose tree and shrub (left: without sludge, right: with sludge, A: grass, B: rose tree, C: shrub)

FIG. 11.6. Over view of greenhouse.

### 11.2.4. Conclusion

Most of harmful organic chemicals, PAHs, contained in the sewage sludge could be destructed by an electron beam irradiation. Microorganisms such as coli form and bacillus could be also completely disinfected by an electron beam irradiation. A significant relative growth rate for plants was observed in the irradiated sludge mixed with a starfish. A starfish seems to be a good additive when it is mixed with sewage sludge for fertilizer.

## 11.3. PART 3. RADIATION TREATMENT OF GROUNDWATER POLLUTED BY TCE AND PCE

### 11.3.1. Introduction

The pollution of groundwater with chlorinated ethylene is becoming a serious problem in industrialized areas of Korea. As a result, the government limited TCE (trichloroethylene) and PCE (perchloroethylene) concentrations in groundwater to less than 0.03 and 0.01 mg/L, respectively, since 1993. However, the contamination of groundwater with these pollutants was not decreased due to increasing industrialization and poor groundwater conservation. Thus, many techniques have been proposed for the reclamation of groundwater. Among these, adsorption onto activated carbon and air-stripping have been found to be efficient and economic, however, they remove the contaminants but do not destroy them. As noted by former researcher, this results in a mere displacement of the problem from groundwater to the carbon and atmosphere.

An attractive solution to TCE and PCE pollution is radiation-induced decomposition. The radiation treatment of the pollutants has been thoroughly studied by former researchers. They showed that the organic pollutants were completely decomposed by gamma-rays or electron-beams, and the decomposition was more efficient in the presence of ozone ($O_3$). However, there are few reports that investigate the effect of catalysts such as titanium oxide ($TiO_2$) and the effect of dissolved metal ions on the decomposition of TCE and PCE. Moreover, their catalytic or inhibitory activities in radiation treatment have not yet been characterized.

Electron paramagnetic resonance (EPR) spectroscopy and the spin-trapping method were used to characterize the gamma-irradiated $TiO_2$ and to determine the efficiency of hydroxyl radical production in this work. EPR spectroscopy is a powerful tool to characterize paramagnetic metal ions and defects in oxide catalysts, and the combination of EPR and the spin-trapping method is a sensitive and selective technique for detecting unstable radicals such as hydroxyl radicals.

### 11.3.2. Experimental

Irradiation was performed at room temperature in a $^{60}Co$. Irradiation samples were prepared in glass bottles with TCE and PCE stock solutions in distilled and deionized water ($\gamma$-rays alone) or in ozone-saturated water ($\gamma$-rays/$O_3$). For irradiation combined with $O_3$ and $TiO_2$ ($\gamma$-rays/$O_3$/$TiO_2$), four $TiO_2$-coated glass tubes were immersed into the $\gamma$-rays/$O_3$ samples. The effect of metal ions was investigated by adding metal nitrate solutions into $\gamma$-rays alone samples. TCE and PCE contents after gamma-irradiation were measured by an HPLC.

The change of titanium oxide by gamma-rays was determined using EPR spectroscopy in the X-band on a Bruker EMX spectrometer at 77 K. For the measurement of hydroxyl radicals, a nitron spin-trapping reagent, DMPO (5,5-dimethyl-pyrroline-N-oxide, Aldrich) was used. $TiO_2$ and $Cu^{2+}$ solutions were mixed with DMPO in phosphate buffer (0.1 M, pH 7.4) just before gamma-irradiation.

### 11.3.3. Results and Discussion

#### *11.3.3.1. Radiation treatment*

The removals of TCE and PCE as a function of irradiation dose are given in Figure 11.7. At a dose of 300 Gy, more than 99 % of TCE was removed. There was no significant difference between γ-rays alone, γ-rays/$O_3$ and γ-rays/$O_3$/$TiO_2$, but the combined γ-rays/$O_3$/$TiO_2$ process increased the decomposition of TCE. The effect of $O_3$ and $TiO_2$ on decomposition was more evident at low irradiation doses. Similar to TCE decomposition, more than 99 % of PCE was removed at a dose of 300 Gy. However, contrary to TCE decomposition, there is a significant difference among γ-rays alone, γ-rays/$O_3$ and γ-rays/$O_3$/$TiO_2$. The combined process of γ-rays/$O_3$/$TiO_2$ showed the most efficient PCE decomposition where $TiO_2$ explicitly enhanced decomposition.

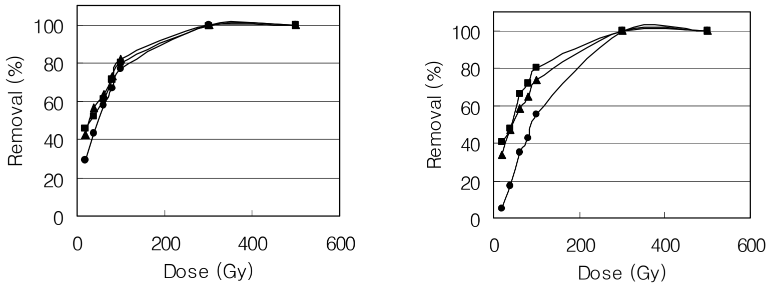


*FIG. 11.7. TCE and PCE decomposition as a function of irradiation dose. The concentration of TCE and PCE was about 10 mg/L. Legend: ● γ-rays alone; ▲ γ-rays/$O_3$; ■ γ-rays/$O_3$/$TiO_2$.*

#### *11.3.3.2. EPR Study*

The enhancement of TCE and PCE decomposition in the presence of $TiO_2$ may be caused by the formation of electron/hole pairs and defects (activated centres) in $TiO_2$ by gamma-rays. EPR spectroscopy was used to characterize the change of $TiO_2$ by gamma-rays. Figure 11.8 shows the EPR spectra of $TiO_2$ powder recorded at 77 K. Four peaks in the spectra increased by up to 15 % after irradiation. According to Lu *et al.* (1994), the peaks with $g_{\parallel} = 1.951$ and $g_{\perp} = 1.972$ can be assigned as the axial defect ($Ti^{3+}$), $g = 2.005$ as an electron trapped at an oxygen vacancy (F-centre) and $g = 1.991$ as $Ti^{3+}$ in $TiO_2$ formed after degassing at 200 $^{O}$C or reduction with 50 Torr of $H_2$ at the same temperature. These four peaks may be deeply related to the enhancement of pollutant decomposition.

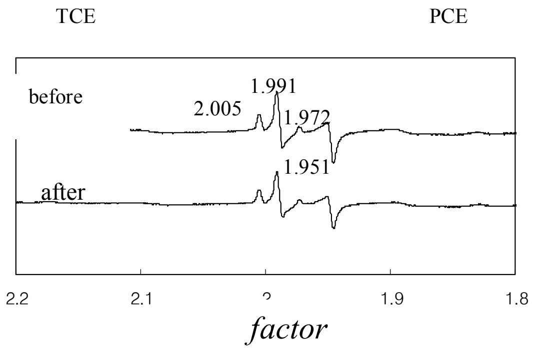


*FIG. 11.8. The EPR spectra of $TiO_2$ powder at 77 K before and after gamma-irradiation. (Irradiation dose applied was 70 kGy.)*

Hydroxyl radicals were measured by EPR/spin-trapping method since the radicals have a dominant role in the decomposition of TCE and PCE. Figure 11.9 shows the typical EPR spectra of DMPO-OH adduct that was composed of quartet lines having a peak height ratio of 1:2:2:1 (Utumi et al., 1998). Gamma-rays increased the DMPO-OH signal by around 5 %. This directly indicates that $TiO_2$ enhanced the production of hydroxyl radicals in water radiolysis, and thus increased the decomposition of TCE and PCE. In the presence of $Cu^{2+}$ ions, the DMPO-OH signal was reduced by 90 %. This strongly confirms the action of $Cu^{2+}$ ions as hydroxyl radical scavengers.

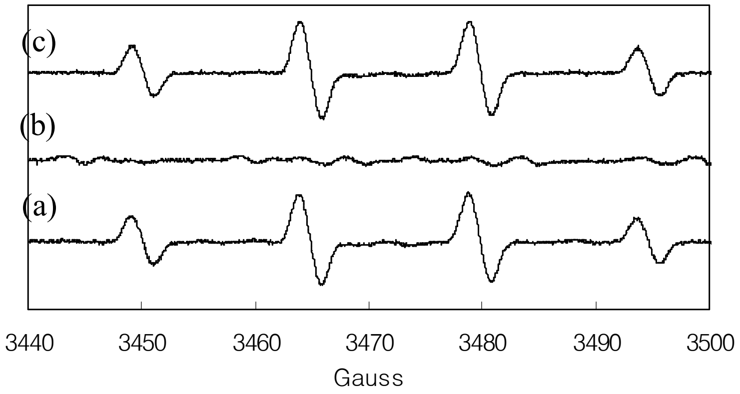


*FIG. 11.9. EPR spectra of DMPO-OH adduct at room temperature. The conditions are (a) gamma-irradiation alone, (b) $Cu^{2+}$ ions added and (c) $TiO_2$ powder added. The concentrations of DMPO, $Cu^{2+}$ and $TiO_2$ were 0.1 M, 10 mg/L and 4 g/L, respectively. Irradiation dose applied was 100 Gy.*

### 11.3.4. Conclusion

Radiation treatment of TCE and PCE in the presence of $O_3$ and $TiO_2$ removed the pollutants by almost 100 %, where the $TiO_2$ catalyst showed explicit enhancement of decomposition. The catalytic activity of $TiO_2$ was characterized by EPR spectroscopy. The four peaks of the EPR spectra that were increased by gamma-rays may be assigned as activated centres. The increase of these centres enhanced the production of hydroxyl radicals and thus increased the decomposition of TCE and PCE.

## 11.4. PART 4. FIELD DEMONSTRATION FOR THE TREATMENT OF SEWAGE EFFLUENT USING MOBILE ELLECRTON BEAM

### 11.4.1. Introduction

Most of biological environmental issues in the eco-system result from the discharge of toxic chemicals which are hardly decomposed with conventional biological treatment processes. Above all, the chemicals such as antibiotics and endocrine disrupters are regarded as new environmental contaminants when those are discharged to water streams from sewage treatment plants. The problems on sudden death of large amount of fishes and sexual disturbance of the fishes are raised from release of toxic and non-biodegrable chemicals into water streams. Therefore, it is very important to control the toxic and non-biodegrable chemicals before those are discharged to water stream. Recently, a mobile electron beam accelerator (MEB) was constructed in Korea and a demonstration study on the sterilization and decomposition of toxic chemicals contained in the effluents of sewage treatment plant was conducted. The field demonstration study was carried out in the sewage treatment plant with basic information obtained from laboratory test. The field demonstration research is surely more helpful for the commercial approach in a view of completion of its technological development.

### 11.4.2. Experimental

#### *11.4.2.1. Installation of MEB*

MEB was installed at a discharge point of a sewage treatment plant. Sewage treatment plant had treatment capacity of 43,000 $m^3$/d. The plant treated wastewater consisting of municipal sewage and livestock wastewater. The amount of livestock wastewater was less than 1% of total volume of the sewage. About 250 $m^3$/d of sewage to be treated with MEB was obtained by pumping from the effluent of the sewage treatment plant. Wastewater to be irradiated was stored in a storage tank before flowing into the irradiation reactor. Energy and beam current of MEB were set by 0.6 MeV and 20 mA, respectively. Figure 11.10 shows the view of MEB installed in sewage treatment plant

*FIG. 11.10. View of MEB installed in sewage treatment plant*

In order to study the decomposition of antibiotics and endocrine disruptors, synthetic chemicals were used because the sewage effluent contained too low concentrations of those chemicals. Lincomycin, tetracycline and bisphenol-A were prepared and mixed with the wastewater to be irradiated, and the concentration after mixing was adjusted to 0.5 mg/l, respectively.

Irradiation by MEB was conducted with a unique type of reactor. It provides a thin film flow of wastewater during irradiation. Thickness of wastewater was about 1 mm. it was set with radiation dose of 1.5 kGy at a single-time passing under a window part of MEB. Samples were obtained before and after irradiation

Analysis of irradiated wastewater was focused on toxicity reduction and decomposition of antibiotics and endocrine disruptors, and sterilization of microorganisms. Toxicity test was conducted with algae. Growth of algae was observed according to radiation dose. Measurement of chemical concentrations was conducted with HPLC.

### 11.4.3. Results and Discussion

#### *11.4.3.1. Removal of organic matters, suspended solids and nutrients by MEB*

Table 11.4 shows the characteristics on removal of organic matters, suspended solids and nutrients by the irradiation of MEB. As a result, there was negligible removal efficiency on organic matters, suspended solid and nutrients. This means that a low irradiation dose of MEB does not affect removal on organic matters, suspended solid and nutrients

TABLE 11.4. CHARACTERISTICS ON REMOVAL OF ORGANIC MATTERS, SUSPENDED SOLID AND NUTRIENTS BY MEB

| Item | Concentration of influent(mg/L) | | Concentration of Irradiated WW(mg/L) | | Removal efficient (%) | |
|---|---|---|---|---|---|---|
| | range | average | range | average | range | average |
| $BOD_5$ | 1.5~10.5 | 4.2 | 0.9~6.1 | 2.9 | 0.0~60.9 | 26.4 |
| $COD_{Mn}$ | 7.5~26.1 | 11.6 | 6.9~13.2 | 9.8 | 0.0~56.7 | 12.0 |
| $COD_{Cr}$ | 13.0~26.5 | 18.9 | 10.0~23.5 | 16.1 | 0.0~46.8 | 14.3 |
| SS | 0.9~5.0 | 2.5 | 0.1~4.9 | 2.1 | 0.0~90.9 | 20.4 |
| T-N | 9.0~13.5 | 11.5 | 8.6~13.4 | 11.3 | 0.7~9.3 | 2.5 |
| T-P | 0.2~1.4 | 0.8 | 0.2~1.3 | 0.7 | 0.0~29.1 | 3.9 |
| TOC | 6.8~13.7 | 10.0 | 6.1~13.4 | 9.0 | 0.8~26.3 | 10.1 |

#### *11.4.3.2. Removal of antibiotics and endocrine disruptors*

Table 11.5 shows removal of lincomysin, tetracycline and bisphenol-A before and after irradiation by MEB. Initial concentration of these chemicals with average of 0.468-0.437 was reduced to 0.001, 0.005 and 0.004 at the irradiation dose of 1.5 kGy, respectively. Its removal efficiency was 99.8 %. It means that these chemicals can be decomposed at a low irradiation dose.

TABLE 11.5. REMOVAL OF LINCOMYSIN BY MEB [MAX~MIN (AVERAGE)]

| Chemical(mg/L) | Before irradiation | After irradiation | Removal efficiency (%) |
|---|---|---|---|
| lincomycin | 0.468(0.329～0.586) | 0.001(0.0~0.005) | 99.8(99.0~100.0) |
| Tetracycline | 0.464(0.332~0.665) | 0.005(0.000~0.008) | 98.8(97.9~100.0) |
| Bisphenol-A | 0.437(0.410~0.454) | 0.004(0.000~0.007) | 99.1(98.3~100.0) |

### *11.4.3.3. Sterilization of coliform and microorganisms*

Table 11.6 shows sterilization of coli form before and after irradiation by MEB. Maximum concentration of coli form was 3.4x$10^5$CFU/ml while minimum was 13 CFU/ml. These results come from mixing with sewage and livestock wastewater together in the sewage treatment plant. No coli form was detected after 1.5 kGy of dose. This means coli form contained in effluent can be sterilized with less than 1.5 kGy of irradiation dose.

TABLE 11.6. REMOVAL OF COLI FORM BY MEB [MAX~MIN (AVERAGE)]

| Item | Coli form(CFU/ml) | | Removal efficient (%) |
|---|---|---|---|
| | Before irradiation | After | |
| Concentration | $2.2 \times 10^4(13\sim3.4 \times 10^5)$ | ND | 100 |

Table 11.7 shows sterilization of microorganisms before and after irradiation by MEB. Average value of microorganisms was 7.8x$10^4$ CFU/ml. These microorganisms reduced to 1.1x$10^2$ CFU/ml. This means that sterilization of microorganisms is also well conducted with less than 1.5 kGy of irradiation dose.

TABLE 11.7. REMOVAL OF MICROORGANISMS BY MEB [MAX~MIN (AVERAGE)]

| Item | Microorganism(CFU/ml) | | Removal efficient (%) |
|---|---|---|---|
| | Before irradiation | After irradiation | |
| Concentration | $7.8 \times 10^4(8.0 \times 10^2\sim5.7 \times 10^5)$ | $1.1 \times 10^2(20\sim6.5\times10^2)$ | 98.3(78.3~100) |

### *11.4.3.4. Reduction of toxicity*

Table 11.8 shows the reduction of toxicity by MEB irradiation of effluent. Of course, this effluent contains the synthetic antibiotics and endocrine disruptor. Toxicity test was conducted with algae. Initial toxicity unit with 15.0 was decreased to 1.8 by irradiation of 1.5 kGy. Figure 11.11 shows the growth of algae after irradiation. While the color of algae was originally light green before irradiation, it became denser green after irradiation. This means that toxicity of effluent can be reduced owing to removal of mother toxicity chemical such as lincomysin, Tetracycline and bisphenol-A.

TABLE 11.8. REDUCTION OF TOXICITY

| | Before irradiation | After irradiation |
|---|---|---|
| Toxicity (TU) | 15.0 | 1.8 |

*FIG. 11.11. Algae growth with and without irradiation (left: with irradiation, right: without irradiation)*

## 11.5. CONCLUSION

Field demonstration with MEB was conducted in order to remove the antibiotics and endocrine disruptors contained in effluent of the sewage treatment plant. The influence of MEB on toxicity and sterilization of coli form were also observed. By the irradiation dose of 1.5 kGy, antibiotics and endocrine disruptors could be decomposed easily, and coli form and microorganisms were also removed. Reduction of toxicity was observed using the algae test. Other kind of organic pollutants contained in effluent of sewage plant were not removed. Therefore, it was thought that additional treating methods for removal of organic pollutants should be recommended for re-using sewage effluent.

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# 12. STATUS AND PROSPECTS OF APPLICATIONS OF RADIATION TECHNOLOGY FOR ENVIRONMENTAL REMEDIATION IN THE PHILIPPINES

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**Abstract**

The Philippines' different water resources have been threatened by pollution caused by industrial, domestic, and agricultural waste water. Efforts have been made by the government to mitigate waste water pollution through implementation of appropriate policies and technologies. This paper presents opportunities for the use of radiation technology within the framework of the Philippines' waste water treatment project entitled "Metro Manila Wastewater Management Project". R & D efforts in the development of radiation grafted fibres e.g. water hyacinth, abaca and pineapple for metal adsorbent for industrial waste water treatment is also discussed. Works have also been made to address the adoption of sustainable agriculture by developing radiation modified carrageenans as plant growth promoter and elicitor, whereby decreasing draw-off pesticide / fertilizer as agricultural source of pollution

## 12.1. INTRODUCTION

The Philippines is an archipelago with around 7,100 islands. It has an area of 300,000 sq. km wherein 65% of its towns are coastal. The Philippines is endowed with water resources such as rivers, lakes, groundwater, and coastal and marine waters. The country has 18 major river and 421 principal rivers as defined by the National Water Resources Board (NWRB). Coastal and marine waters cover an area of about 266,000 sq. km, including bays and gulfs. The Bureau of Fisheries and Aquatic Resources (BFAR) reports that there are 79 lakes in the country, mostly utilized for fish production. In terms of groundwater, the country has extensive reservoir with an aggregate area of about 50,000 sq. km [12.1–12.2].

Being rich in water resources, the economic development of the country points to water as one critical resource which has to be managed effectively and efficiently. This is seen in the nation's water resources which have been utilized mainly in the agricultural industry in livestock and poultry production, crops' irrigation and aquaculture.

The population in the Philippines in 2013 was approximately 99 million with a growth rate of 1.89% [3]. The number of Filipinos is still expected to rise over the years. With this exponential increase in population, it is inevitable that this growth would have a direct repercussion on the declining quality of water resources. In fact it is quite alarming to note that as many as 50 of the 421 rivers in the Philippines are already considered "biologically dead" [12.1]. The major source of water pollution can be categorized as follows:

a) Industrial wastewater: The kind of pollutants found in industrial wastewater varies according to the types of industries involved, but some common pollutants are chromium, cadmium, lead, mercury, and cyanide.

b) Agricultural wastewater: This can include organic wastes such as decayed plants, livestock manure, and dead animals, soil runoff due to erosion, and pesticides and fertilizer residues.

c) Domestic wastewater/sewage: Domestic effluents are generated from activities such as bathing, laundry, cleaning, cooking, washing, and other kitchen activities. This contains a large amount of organic waste with suspended solids and coliforms.

d) Other sources of water pollution include oil and/or chemical spills, mine tailings or spills, and the illegal dumping of wastes in or near bodies of water.

Pollution sources revealed that domestic wastes are the major source of pollution (33%), followed by livestock (29%) and industrial sources (27%) [12.1–12.2].

The Environmental Management Bureau reports that domestic wastewater discharges contribute highest to the BOD load as the lack of sewage treatment system allows more than 90 percent of inadequately treated domestic sewage to be discharged into surface waters, which contain bacteria and viruses that threaten human life[1].

Agricultural wastewater is considered as the major source of pollution in rural areas as a number of these farms, including backyard animal farms, have no appropriate wastewater treatment facilities. An impact of using agrochemical inputs on groundwater resources, especially during the wet season is also a source of pollution.

Effluents from industrial waste water show that the volume and characteristics of industrial effluents vary by type of industry and are influenced by different factors such as production processes and the scale of production used. Industries that are found to be water-intensive are food and dairy manufacturing, pulp, paper and paperboard products, and textile products.

Even as early as 1999, United Nations Industrial Development Organization (UNIDO) already reports that the situation is critical with regard to hazardous wastes. Approximately 2,000 cubic meters of solvent wastes, 22,000 tons of heavy metals, infectious wastes, biological sludge, lubricants, and intractable wastes, as well as 25 million cubic meters of acid/alkaline liquid wastes are improperly disposed of annually in the Metro Manila area alone [1]. The numbers could have increased tremendously by now with the absence of an integrated treatment facility for hazardous wastes in the country.

Various efforts have been undertaken to address the problems on water pollution, especially chemical pollution. These include the formulation of various policies, monitoring and analysis, and researches among the key stakeholders as implemented by concerned agencies. Technical capabilities for waste water treatment have been reinforced limiting their options only to the conventional procedures with the use of various engineering processes for activated sludge systems, membrane filtration, settling tanks, anaerobic filtration and aerobic filters and lagoons, natural treatment systems for settled wastewater among other methods.

Radiation technology has emerged as an environment-friendly, commercially viable technology with broad applications that can essentially contribute to achieve the goal of sustainable development. Radiation technology has been successfully used for wastewater treatment in the decontamination of sewage. It has also been demonstrated that degradation of organic pollutants such as PCBs, PAHs, halogenated compounds, dyes, and so many other organic compounds is achieved effectively with E-beam irradiation and sometimes in tandem with other processes e.g. ozone treatment. While this option for waste water treatment is already available, little is known about this technology. In the Philippines, the conventional processes of waste water treatment still remain to be the exclusive choice of stake holders. Thus, efforts should be made to promote this technology in order that radiation technology for wastewater treatment could be known and would then be part of their alternatives. In the meantime, the Philippine Nuclear Research Institute (PNRI) for the past years has taken much effort in pursuing studies on the radiation grafting of synthetic and natural polymers for use as adsorbent for metals in waste water. Likewise, it has contributed to the adoption of sustainable agriculture by developing radiation modified carrageenans as plant growth promoter and elicitor, whereby decreasing draw-off pesticide / fertilizer as agricultural source of pollution.

## 12.2. OPPORTUNITIES FOR WASTEWTER TREATMENT BY RADIATION TECHNOLOGY

Metro Manila, the national capital region has a population of about 12 million people. It consists of 16 cities and one municipality. Metro Manila is located in the hydraulic zone of Laguna lake-Pasig River-Manila Bay corridor, which is interconnected by more than 30 tributaries in the urban area. Pasig River connects the Manila Bay and Laguna Lake. The pollution level in the Pasig River and its tributaries is very high. Domestic wastewater in Manila Bay watershed contributes approximately 70% of the Biological Oxygen Demand. Metro Manila has an extremely inadequate sewerage system. About 11% of the population of Metro Manila are served by piped sewerage. The majority of sewage is conveyed through open ditches and canals untreated into Manila Bay [12.4].

Concerns over the alarming continuous decline of water quality in the Philippines led the Government to enact the “Clean Water Act” in 2004. This policy presents an integrated, decentralized and participatory approach to abating, preventing and controlling water pollution. A continuing mandamus was also issued by the Supreme Court last December 2008 on the clean-up of Manila Bay. With this background, The Philippines borrowed a loan from the World Bank for a Project entitled “Metro Manila Wastewater Management Project” amounting to US$ 371.70 million from 2012–2017 [12.5]. This will be implemented by the two concessionaires that provide water and wastewater services to the Metro Manila region - Manila Water Company, Incorporated (MWCI) and Maynilad. The objective is to improve wastewater services in selected sub-catchments of Metro Manila. The elements of the project consist of construction of a sewage treatment plant and associated sewage lines, wastewater collection and treatment, septage management and consultancy services.

Looking at the large investment by the government on this project and the technical aspect of their plan of action, one may wonder why radiation technology cannot be part of this Master Plan. Radiation technology may very well fit into the picture. Perhaps it is just a matter of approaching the right people and selling to them what this technology can offer above all the advantages of the conventional processes of wastewater treatment. The PNRI for her part had been joining and promoting this technology to some focus group discussions. However, it can be so limited without the actual demonstration and the economics of wastewater treatment by e-beam technology. Something more tangible to the stake holder has to be done. A more daring stance in promoting this technology may have to be taken. The challenge is how will the partnership of IAEA with its Member States take this opportunity and similar opportunities in the future?

## 12.3. RESEARCH AND DEVELOPMENT EFFORTS ON WASTE WATER MITIGATION

The Philippines in its effort to mitigate waste water pollution from industry has done R&D works on the development of natural fibres and non-woven matrices as metal adsorbents for industrial waste water.

The whole process of waste water treatment involves several mechanical and chemical steps. The initial procedure is focused on separating the large debris present in the waters using filters while the advanced treatment steps include decreasing of nitrogen, phosphorus and heavy metal concentrations to limits determined by national law. In this advanced part of waste water treatment, ion exchange resins and activated carbons are commonly utilized by treatment facilities. However, most resins and activated carbons are operated at low flow rates because the process is diffusion controlled. Moreover, the high price of these materials limits their use mostly to large industries. Our research group attempted to modify several materials from cheap and abundant natural sources through radiation-induced grafting. The grafted materials were further functionalized to introduce functional groups that can remove certain metals from waste water through chelation of ion exchange. Previous studies confirmed that grafted fibrous polymers can be operated at high flow rates compared to resins in removal of heavy metals [12.6, 12.7].

### 12.3.1. Water Hyacinth Fibers

Water hyacinth fibres (*Eichhornia crassipes*) were functionalized using radiation-induced graft polymerization of glycidyl methacrylate by γ-rays from $^{60}$Co source. The simultaneous grafting technique was employed wherein the water hyacinth fibres were irradiated in nitrogen atmosphere in the presence of glycidyl methacrylate dissolved in water/methanol solvent. The effects of different grafting parameters to the grafting yield were evaluated. Fig. 12.1. shows the variation of degree of grafting with absorbed dose at different monomer concentrations. The optimal values of solvent, radiation absorbed dose, dose rate, concentration of monomer were found to be 1:3 (volume/volume) water-methanol solvent, 10 kGy, 8 kGy hour$^{-1}$ dose rate and 5% (volume/volume) glycidyl methacrylate, respectively. Using the optimum conditions, degree of grafting of approximately 58% was achieved [12.8].

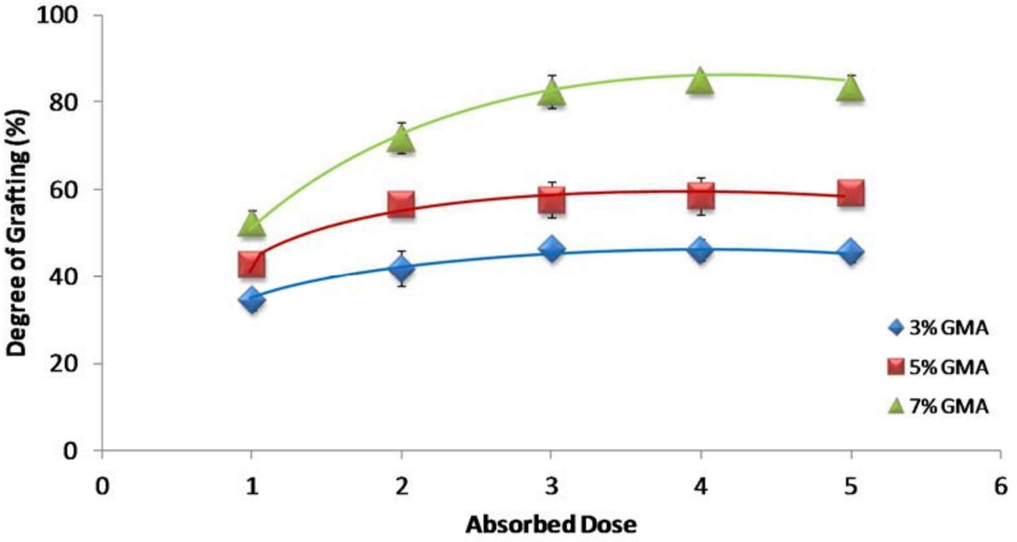

*FIG. 12.1. Effect of absorbed dose on degree of grafting (%) for radiation induced grafting of GMA onto water hyacinth fibres. Grafting conditions: 8 kGy hour$^{-1}$, 1:3 water/methanol.*

An amine group containing fibrous adsorbent was prepared by reaction of grafted water hyacinth fibres with ethylenediamine. The conversion of the epoxy group from GMA into amine group was investigated. The concentration of ethylenediamine solution that gave the highest amine functional group density was 50% by volume in 2-propanol. The grafted and amine functionalized water hyacinth fibres were characterized using Attenuated Total Reflectance-Fourier Transformed Infrared Spectroscopy (ATR-FTIR), Thermogravimetric Analysis (TGA), and Energy Dispersive X-ray Spectroscopy (EDX). Information derived from these analyses confirms the successful grafting and conversion of the epoxy group. The amine-type adsorbent was evaluated for its uptake of $Pb^{2+}$, $Cu^{2+}$ and $Cr^{3+}$ from aqueous solutions. Figure 12.2. shows the amount of metal uptake per unit mass of the amine type adsorbent from 150 ppm solutions of each metal.

From the obtained data, it can be observed that generally, the adsorption of metals onto amine functionalized fibres reach equilibrium faster than the adsorption of metals onto unmodified water hyacinth fibers. At the same time, the amount of $Pb^{2+}$, $Cu^{2+}$ and $Cr^{3+}$ adsorbed by unmodified water hyacinth fibres is less than the amount adsorbed by the amine functionalized water hyacinth fibres at equilibrium. This indicates that gamma radiation-induced grafting of GMA and subsequent functionalization enhanced the overall adsorption ability of water hyacinth fibres. The initial concentration of the metal ions and pH of the solutions were found to influence the amount of metal ions adsorbed by the amine-type adsorbent. The kinetics of adsorption was observed to follow Lagergren's first order equation. Results of ion sorption studies indicate that gamma radiation-induced grafting and subsequent chemical modification improved the ion sorption behavior of water hyacinth fibres [12.9].

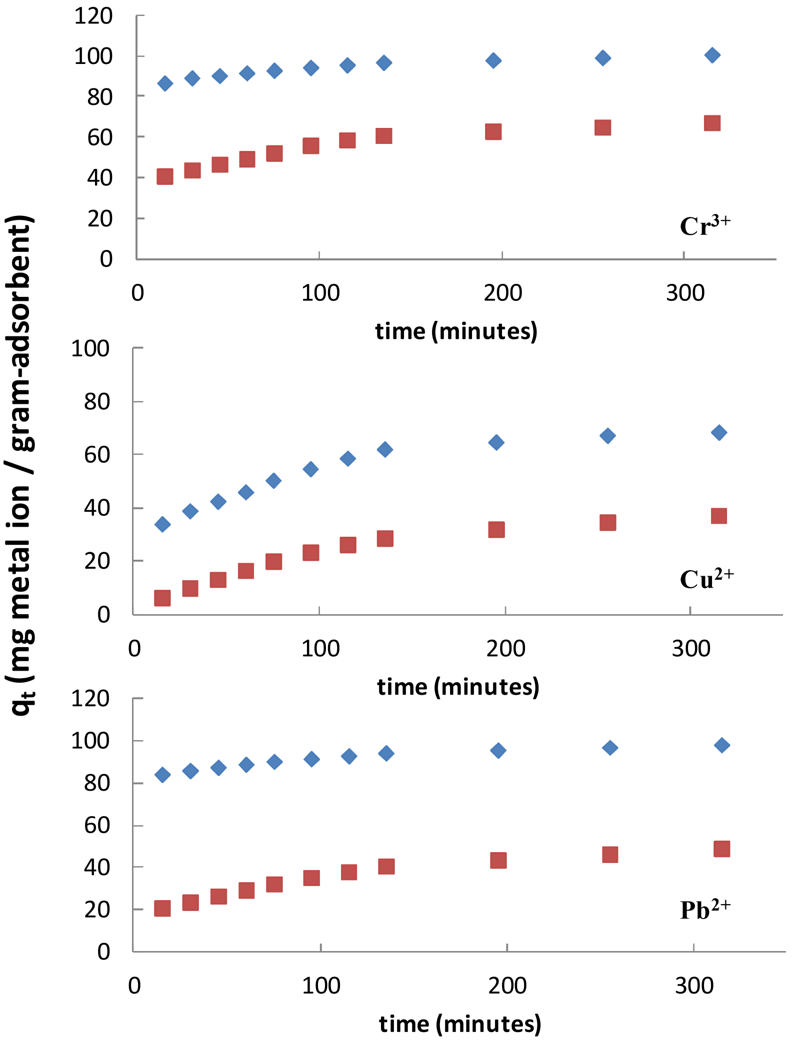

*FIG. 12.2. Time profiles for the adsorption of $Cr^{3+}$, $Cu^{2+}$, and $Pb^{2+}$ from 150 ppm solutions onto amine functionalized water hyacinth fibres (◆) and unmodified water hyacinth fibres (■).*

### 12.3.2. Abaca/Polyester Nonwoven Fabric

A metal ion adsorbent was developed from a nonwoven fabric trunk material composed of both natural and synthetic polymers. Pre-irradiation technique was used for emulsion grafting of glycidyl methacrylate (GMA) onto an electron beam irradiated abaca/polyester nonwoven fabric (APNWF). The dependence of degree of grafting (Dg), calculated from the weight of APNWF before and after grafting, on irradiation dose, reaction time and monomer concentration were evaluated. Fig. 12.3. shows the relationship between Dg and grafting time at different irradiation doses [12.10].

After 50 kGy irradiation with 2 MeV electron beam and subsequent 3-hour reaction with an emulsion consisting of 5% GMA and 0.5% polyoxyethylene sorbitan monolaurate (Tween 20) surfactant in deionized water at 40°C, a grafted APNWF with a Dg greater than 150% was obtained. The GMA-grafted APNWF was further modified by reaction with ethylenediamine (EDA) in isopropyl alcohol at 60°C to introduce amine functional groups. After a 3-hour reaction with 50% EDA, an amine group density of 2.7 mmole/gram adsorbent was achieved based from elemental analysis. Batch adsorption experiments were performed using $Cu^{2+}$ and $Ni^{2+}$ ions in aqueous solutions with initial pH of 5 at 30°C. The effect of contact time on the adsorption of $Cu^{2+}$ and $Ni^{2+}$ ions by aminated APNWF and DIAION WA20, a commercial ion exchange resin, were investigated and the results are shown in Fig. 12.4.

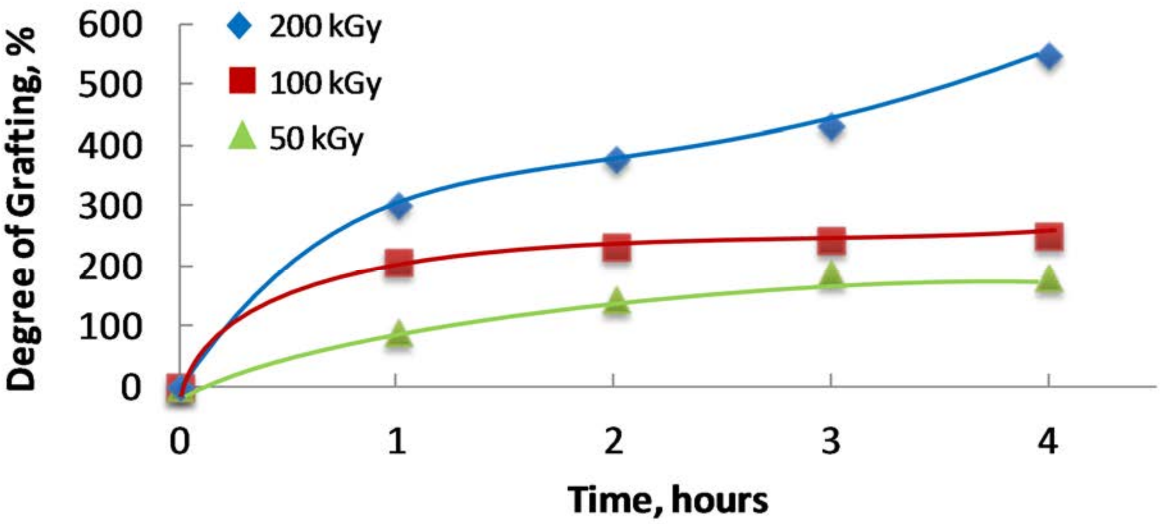

*FIG. 12.3. Effect of dose on Dg after grafting in aqueous emulsion of 5% GMA and 0.5% Tween 20 at different reaction time*

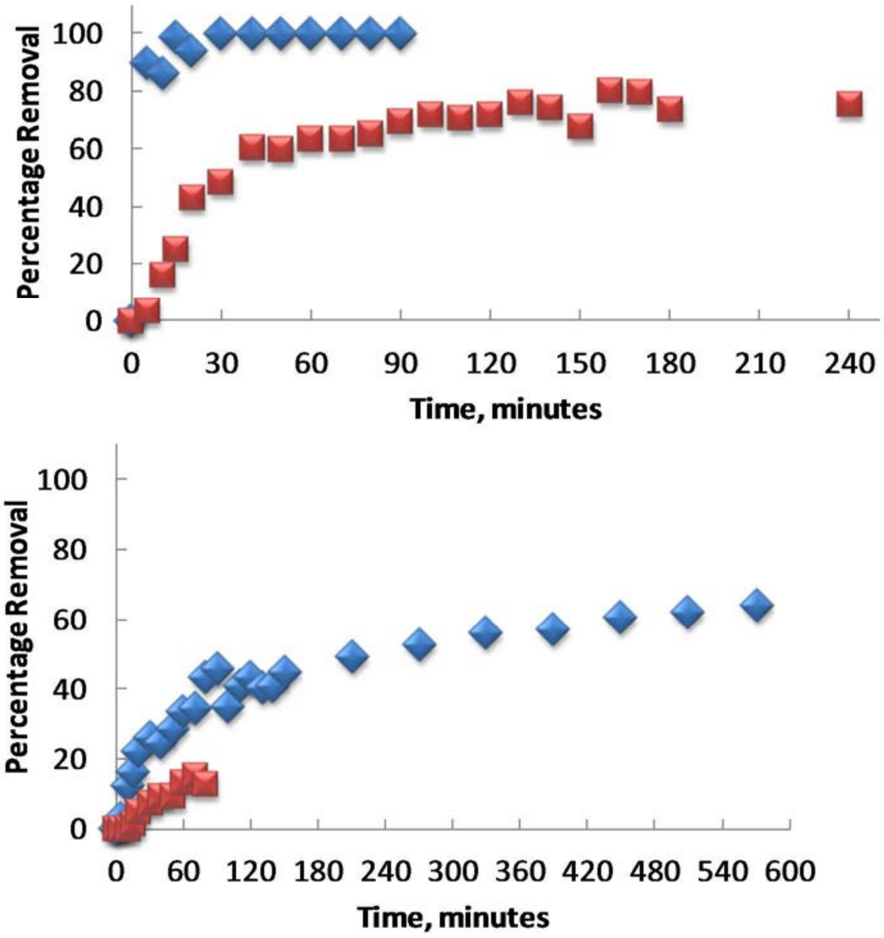

*FIG. 12.4. The relative amount of (a) Cu$^{2+}$ and (b) Ni$^{2+}$ ions removed from 10 ppm solution as a function of time by aminated GMA-grafted APNWF (◆) and DIAION WA20 ( ■) at pH 5 and 30°C.*

Fig. 12.4a shows that the aminated APNWF removed almost 90% of the Cu$^{2+}$ ions after 5 minutes of contact with the solution. This is significantly higher compared to 3.3% removed by the commercial resin DIAION WA20 at the same period of time. Complete uptake of Cu$^{2+}$ ions in the solution by the aminated APNWF was achieved after stirring for 30 minutes. The amount of Cu$^{2+}$ removed from the solution by DIAION WA20 increased fast, reaching 60.2% after 40 minutes, followed by a slow steady increase until it reached an almost constant value of 77.2% after 130 minutes of stirring.

A trend similar to that of Cu$^{2+}$ adsorption was observed for Ni$^{2+}$ ion removal by both the synthesized adsorbent and the commercial resin. It can be seen from Fig. 12.4b that the amount of Ni$^{2+}$ ions removed by aminated APNWF increased up to 33.4% after 60 minutes of stirring. Afterwards, gradual increments in Ni$^{2+}$ removal were observed until the percentage removal leveled at approximately 62.1% after 450 minutes. DIAION WA20 showed even lower adsorption of Ni$^{2+}$ ions. It adsorbed negligible amounts of Ni$^{2+}$ for the first 20 minutes and reached only 13.8% removal after 60 minutes of adsorption.

### 12.3.3. Pineapple Fibers

Fibers from pineapple leaves were modified using radiation-induced graft polymerization of glycidyl methacrylate in methanol solvent. The simultaneous grafting technique was used wherein the monomer and the pineapple fibers were irradiated simultaneously under nitrogen atmosphere. The degree of grafting at different absorbed radiation dose was evaluated at 3%, 5%, 7%, & 10% (wt./wt.) glycidyl methacrylate concentration. Fig. 12.5 shows the variation of degree of grafting with absorbed dose at different monomer concentration.

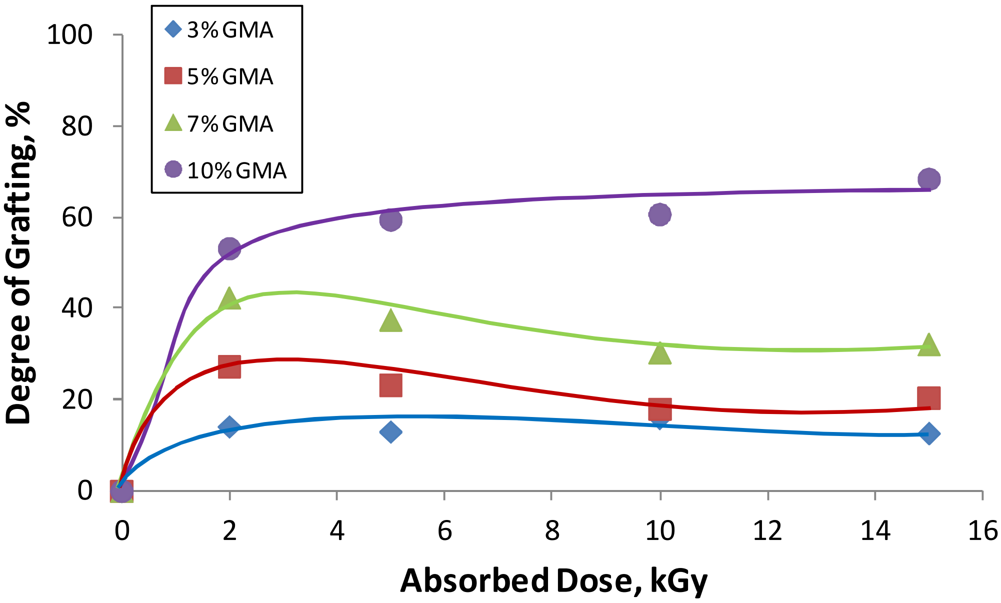

*FIG. 12.5. Effect of absorbed dose on Dg after grafting of pineapple fibres in3%, 5%, 7% and 10% glycidyl methacrylate in water/methanol solvent.*

A 65% degree of grafting was achieved after using the following grafting conditions: 2 kGy absorbed dose, 10% (wt./wt.) glycidyl methacrylate concentration, 6 kGy/hour dose rate and 1:1 water/methanol solvent. The epoxy groups on the grafted pineapple fibres were converted to amine functional groups through ring opening reaction with ethylenediamine in isopropanol. The grafting of poly (glycidyl methacrylate) on pineapple fibres and its conversion to the amine functional group was confirmed with Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance (FTIR-ATR). Results from Scanning Electron Microscopy (SEM) shows that the after grafting and functionalization, the fibres remain intact and has almost similar morphology as the unmodified fibres.

The amine functionalized pineapple fibres were tested for their copper and lead ion uptake. Fig. 12.6 shows the comparison in the Cu (II) and Pb (II) uptake ability between the grafted and ungrafted pineapple fibres. The percentage of copper removal from synthetic solutions increased 10 times after grafting while the percentage of lead removed by the grafted and functionalized pineapple fibres is only about 10% higher than the unmodified pineapple fibres.

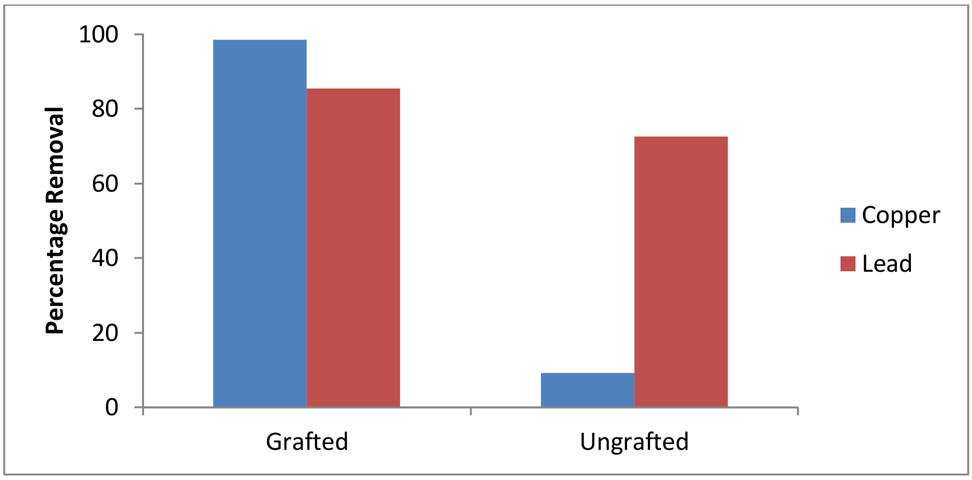

*FIG. 12.6. Copper and lead ion uptake of the grafted and ungrafted pineapple fibres.*

### 12.3.4. Future researches and partnership with end-users

The results for ion sorption tests were all obtained using batch adsorption. Future works involve doing laboratory and bench scale column tests for ion sorption and competitive adsorption of metal ions. While the isotherm testing provides an indication of how well an impurity may be removed, it cannot give definitive scale-up data due to two factors: (1) in column mode, dynamic adsorption occurs because the impurity concentration changes as the mass transfer zone moves through the bed and (2) regeneration effects on multiple cycles cannot be studied since the isotherm test procedure uses the adsorbent only in a once-through adsorption process. Because of these factors, bench scale column tests will be performed. The bench-scale column test system will be composed of four columns operating in series in order to determine important column parameters. Fig. 12.7. shows the experimental set-up for the bench scale column test of the grafted nonwoven fabric.

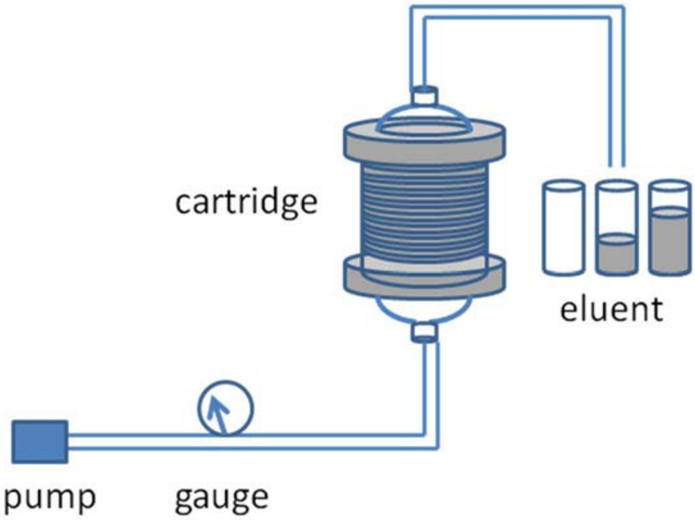

*FIG. 12.7. Bench scale column test set up for the grafted nonwoven fabric.*

Discussion about the testing of the grafted materials with possible end-user from the leather tanning industry was initiated. Currently they are using nanofiltration to lower the concentration of the heavy metals to meet the regulatory limits. They agreed to provide waste water samples that can be used for testing the efficiency of the grafted material in laboratory and bench scale tests.

## 12.4. RESEARCH AND DEVELOPMENT EFFORTS ON SUSTAINABLE GREEN AGRICULTURE

Under the auspices of International Atomic Energy Agency (IAEA) and the Forum for Nuclear Cooperation in Asia (FNCA), a regional cooperative project on "Radiation Processing of Natural Polymers" have demonstrated the usefulness of radiation modified polymers (chitosan, alginates and carrageenan) as growth promoter and protector of crops. Numerous studies have been carried out in Member States, including the Philippines, to investigate the plant growth promotion and plant protection effect of radiation processed polysaccharides in a variety of crops under different environmental conditions.

Radiation degraded polysaccharides can induce various kinds of bioactivities such as growth promotion of plants, suppression of heavy metal stress on plants, anti-microbiological and anti-viral activities (Kume, 2000). Upon irradiation, polysaccharides can be depolymerized to form shorter fragments. As compared to the conventional techniques, like acid or base hydrolysis or enzymatic methods, radiation processing offers a clean one step method for the formation of low molecular weight polysaccharides and oligomers in aqueous solutions even at high concentrations.

For the past years, the Philippines has been doing R & D works on the use of irradiated carrageenan as plant growth promoter and elicitor. It has been demonstrated to increase yields in plants, i.e., bokchoi, rice, mungbean, peanuts and corn. In addition, preliminary results in rice indicated that rice fields which were treated with radiation modified carrageenan and chitosan were not infested with the Tungro disease as shown in Figure 12.8, whereas neighboring rice paddies were affected and infested with the disease. Oligocarrageenan and oligochitosan treated paddies stood out to be green and unaffected by Tungro disease.

The biodegradable properties of natural polymers have been an additional advantage to be used as plant growth promoters and elicitors. The replacement of hazardous organic chemicals with biodegradable natural polymers from radiation processed materials will not only enhance agricultural production but will also decrease the overall utilization and dependence of chemical fertilizer hence will help mitigate environmental pollution by reducing runoff of toxic chemicals into aquatic environments thereby promoting a cleaner ecosystem and sustainable green agriculture.

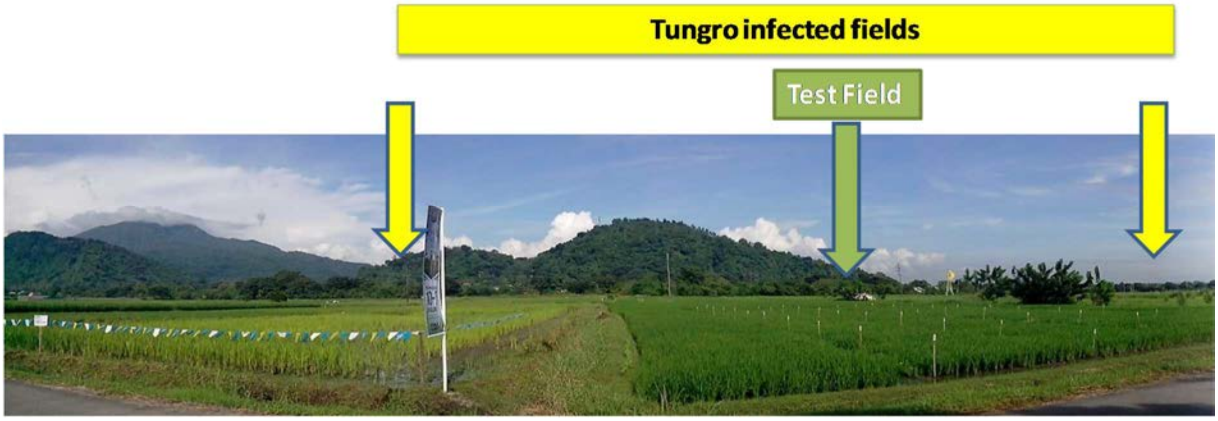

*FIG. 12.8. Field trials on the application of radiation modified carrageenans on rice.*

## 12.5. CONCLUSION

Radiation technology offers many possibilities for developing countries like the Philippines in providing a cleaner and greener environment. It can be utilized to mitigate the escalating problem of waste water pollution through the following fields of application: a) e-beam or gamma radiation treatment of sewage and industrial waste; b) development of radiation grafted materials to adsorb metals and organic pollutants from industrial waste water; and c) development of biodegradable radiation modified polysaccharides to decrease runoff of toxic chemicals from chemical pesticides and inorganic fertilizers. While appropriate radiation technologies are already available in developed countries, efforts have to be done to partner with these countries for a more realistic and effective dissemination of information. Promotion of the technology can best be achieved using first-hand information and actual demonstration of the capability of the technology. Given the proper back-up support, radiation technology may become part of the options of the institutes within the government mandated to clean-up the aquatic environment or private companies wishing to invest on waste water treatment.

## ACKNOWLEDGEMENT

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# 13. EVALUATION OF EB TECHNOLOGY FOR GAS POLLUTANTS EMISSION CONTROL FOR DIFFERENT EMISSION SOURCES

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**Abstract**

This article reviews the current status of electron beam (EB) technology application for gas pollutants control for different emission sources. $SO_2$ and NOx removals from flue gases emitted from coal and oil fired boiler, diesel engine under EB irradiation are discussed. Moreover, other type gas pollutants, such as volatile organic compounds (VOCs), polycyclic aromatic organic compounds (PAHs), dioxins, mercury, and their removal from air or waste off-gases under EB irradiation were presented too. It shows that EB is one of the promising technologies to be applied in industrial scale to remove multiple gas pollutants from different emission sources.

## 13.1. INTRODUCTION

Electron beam (EB) flue gas treatment technology for purification of gaseous effluents from coal fired boilers after testing in Japan, the US, Germany, Poland, China and Bulgaria has been implemented in industrial scale in Pomorzany Power Plant, Szczecin, Poland [13.1]. The power of accelerators used is bigger than 1 MW (700 keV). It was only full scale application; however most of the big scale boilers using coal as a fuel have been equipped by $deSO_x$ and $deNO_x$ conventional type installation. Some of these boilers are used for biomass/coal co-firing what leads to volatile organic compounds (VOCs) emission. The electron beam flue gas treatment (EBFGT) is potential process to control these emissions as well. The removal efficiency is high; however the toxicity equivalent units have to be used as a performance factor, since the new organic byproducts can be formed in irradiated gas. Another problem concerning Europe is emission of pollutants from big cargo ships which by the year 2020 will be bigger than those from stationary on-shore sources. The main problem regarding EB process applications is high $NO_x$ emissions which require high dose treatment, some hybrid processes may be a solution. Finally oil fired boilers are becoming a problem, especially when high sulfur oil is used as fuel. Main components of the technology are available on the market, some of them like ESP, have to meet process requirements. However the success of the technology depends on the development reliable high power accelerators (ca.500 kW, up to 1 MeV) which may be operated continuously at least 7500 hours per year. The harsh industrial conditions require special primary and secondary window construction, the maritime applications require single window construction what is challenge for accelerator manufactures (300 keV systems). The results of the tests for the above listed emitters and feasibility studies for discussed solutions are presented in this paper.

## 13.2. EB PROCESS DESCRIPTION

When fast electrons from electron beams are absorbed in the off-gases, they cause ionization and excitation process of the nitrogen, oxygen and water molecules. Primary species, secondary electrons and radicals are formed. These primary species, secondary electrons and radicals cause pollutants removal from off-gases with or without scrubber. Schema of EB process for $SO_2$, NOx pollutants removal is presented in Fig.13.1. as an example.

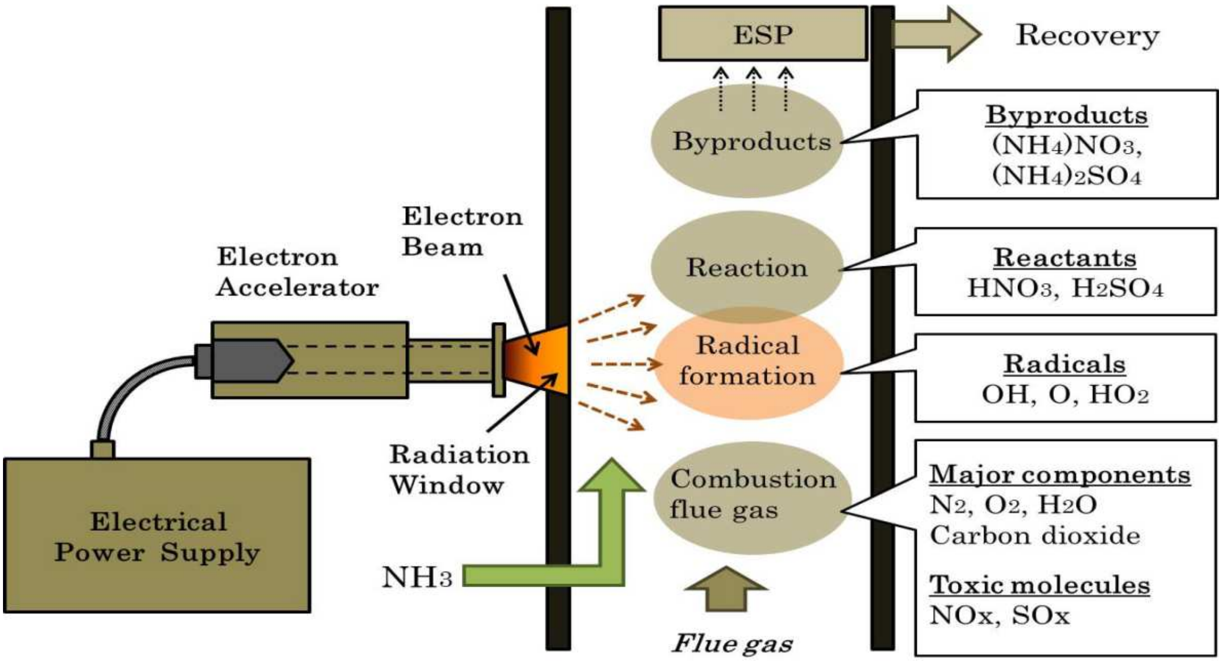

*FIG. 13.1. Scheme of EB process for $SO_2$, NOx pollutants removal*

## 13.3. EB TECHNOLOGY FOR GAS POLLUTANTS EMISSION CONTROL FOR DIFFERENT EMISSION SOURCES

During the fuel (coal, oil, diesel) combustion process, different types of pollutants are formed in the off-gases. These pollutants include $SO_2$, NOx, VOCs, PAHs, Hg and dioxins.

### 13.3.1. EB technology for gas pollutants control for flue gas emitted from coal-fired boiler

#### *13.3.1.1. EB technology for $SO_2$ and NOx removal from flue gas emitted from coal-fired boiler*

EBFGD is a well-developed technology for simultaneous SOx and NOx removal from coal-fired boiler. The biggest industrial plant has been built in EPS Pomorzany, Szczecin where it treats 270, 000 Nm³/h. Removal efficiencies of $SO_2$ and NOx at 8.0 kGy are about 90% and 60%, respectively (Fig. 13.2)[1]. With the addition of ammonia, usable product – fertilizer was generated (Table 13.1 & Fig. 13.3) [13.2]

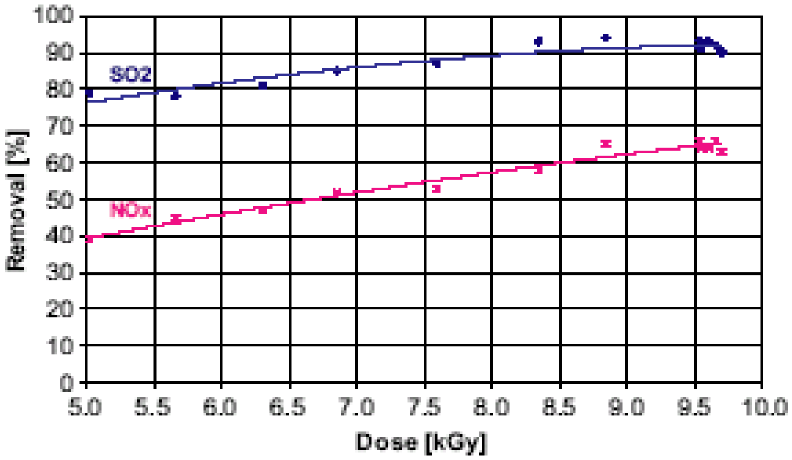

*FIG. 13.2. Removal efficiency of $SO_2$ and NOx versus dose*

TABLE 13.1 CONTENTS OF HEAVY METALS (MG/KG) IN THE BYPRODUCT AND LIMITS FOR HEAVY METALS CONTENT IN THE NPK FERTILIZER ESTABLISHED IN SOME COUNTRIES

| As | Cd | Cr | Co | Pb | Hg | Ni | Zn | Remarks |
|---|---|---|---|---|---|---|---|---|
| <0.02 | <0.01 | 0.43 | 0.03 | 1.01 | <0.03 | 63.5 | 18.3 | averaged values for byproducts collected by cartridge bag filter |
| 0.24 | 0.09 | 1.61 | 0.03 | 0.54 | 1.41 | 22.80 | 1476 | byproducts collected by ESP |
| Limits for heavy metals content in NPK fertilizer | | | | | | | | |
| 41 | 39 | | | 300 | 17 | 420 | 2800 | US EPA CFR40 Part. 503 |
| 75 | 20 | | 150 | 500 | 5 | 180 | 1350 | Canadian Fertilizer Act (1996) |
| 50 | 50 | | | 140 | 2 | | | Polish standard |
| | 32.2 | 276.8 | 12.9 | 17.8 | | 72.3 | | mean values of heavy metals concentrations in fertilizers marketed |

*FIG. 13.3. NPK fertilizer*

### *13.3.1.2. EB technology for VOCs removal from air*

Electron beam irradiation technology is one of the most promising technologies for purification of dilute pollutants, mostly VOCs, with high flow-rate gas stream released from industrial off-gases. VOCs removal under EB irradiation was intensively studied, most of them were studied in bench scale[3]. Under EB irradiation, VOCs are oxidized into irradiation by-products as well as $CO_2$ and CO. However, some of these irradiation by-products have adverse effect on environment and human beings.

A new technology which combines EB and catalyst together to treat aromatic VOCs, e.g., toluene [13.4–13.6], styrene[13.5], o-xylene [13.7–13.8] and ethylbenzene [13.9] was developed in the aim of enhancing higher oxidation efficiencies of VOCs into $CO_2$. Removal efficiency of toluene, styrene and ethylbenzene increased by 10%, 20%, and 20% in an EB-catalyst hybrid system in comparison with that achieved in catalyst-only method at approximately 10 kGy absorbed dose[5]. Removal efficiency of ethylbenzene in the EB-catalyst hybrid was 30% higher than that of EB-only treatment. Ethylbenzene was decomposed more easily than toluene by EB irradiation. The G-values for ethylbenzene increased with initial concentration and reactor type: the G-values vary in the range of 7.5–10.9 (EB-only) and 12.9–25.7 (EB-catalyst hybrid) by reactor type at the initial concentration of ethylbenzene being 2800 ppm. Son et al.[9] and Jeon et al. [13.6] also studied different catalysts (Pt, Pd, Cu and Mn) and humidity influence on removal efficiency of toluene using EB-catalyst hybrid system. It was found that removal efficiency of toluene was increased by 36.9%, 35.3% and 22% in the presence of Pt, Pd , Mn and Cu catalysts comparing with EB only for initial concentration of toluene being 1500 ppm, the selectivity to $CO_2$ with Pt and Pd coupling were relatively higher than those of Cu and Mn. Especially the $CO_2$ selectivity of EB–Pt coupling was significantly high at a relatively low absorbed dose. The catalytic activity for EB–catalyst coupling system was in the order of Pt, Pd, Mn and Cu. There was no significant difference of removal efficiency of toluene among 0.1, 0.5 and 1.0 wt% loading of catalyst. No significant water effect was observed in EB-catalyst hybrid system [13.9].

Other type of catalysts such as $TiO_2$ was used to study xylene decomposition under EB irradiation in lab scale experimental work [13.7]. It was found that removal efficiency of xylene and $CO_2$ formation were increased with the presence of $TiO_2$ catalyst, the similar phenomenon was observed when Kim study toluene decomposition using Pt as catalyst [13.5].

Hakoda, et al. [13.8] also studied xylene decomposition using $MnO_2$ (an $O_3$ decomposition catalyst), $\gamma$-$Al_2O_3$ was selected as a base material of the catalyst. The combination process at temperatures of about 100ºC using $MnO_2$ placed downstream enhanced the oxidation of the by-products of xylene into $CO_2$ by active oxygen produced from the $O_3$ decomposition when the $MnO_2$ bed was placed downstream of an irradiation space. Furthermore, EB-irradiated $\gamma$-$Al_2O_3$ surface was found to be active, and the oxidation of organics was enhanced by primary electrons. The combination process using $\gamma$-$Al_2O_3$ reduced dose to 33% of a single EB process to obtain the same conversion of xylene to $CO_2$.

Ighigeanu et al. [13.10] studied VOCs (Toluene, hexane+toluene mixture diluted in air) decomposition by using combination of three different technologies (EB, microwave (MW) and catalysts): (EB+MW+catalyst); (MW+catalyst) and (EB+catalyst). They found that decomposition efficiency (De) and oxidation efficiency (Eo) of toluene increase significantly for the (EB+MW+catalyst) treatment as compared with (MW+catalyst) and (EB+catalyst) treatments, at initial concentration of toluene being in the range of 180 ppm – 523 ppm; and CO2 and CO concentrations after treatment were higher for the (EB+MW+catalyst) treatment than for (MW+catalyst) and (EB+catalyst) treatments. De and Eo of toluene were, respectively, as follows: 59.5% and 82.2% for the (MW+catalysis), 77.2% and 87.1% for the (EB+catalyst) and 92.8% and 90.5% for the( EB+MW+catalyst). For air mixture contained toluene and hexane, removal efficiency of toluene and hexane in (EB+MW+catalyst) system was higher than that in (MW+catalyst) system or in (EB+catalyst) system, about 88.5% toluene and 87.8% hexane was decomposed for initial toluene and hexane concentration being 250 ppm respectively.

Kim et al. [13.11] also studied the decomposition of VOCs using an electron beam (EB)–catalyst coupling system in pilot scale (gas flow was 1000 $m^3$/h). They found that the removal efficiencies for toluene and o-xylene at 10 kGy dose were 92.4% and 94.5% in EB-catalyst system, which were higher than the results of 45.7% and 52.3% when EB-only was used, respectively, for the inlet concentration of toluene and o-xylene being 1800ppmC and 1500 ppmC, respectively. The Main by-products were $CO_2$.

#### *13.3.1.3. EB technology for PAHs removal from flue gas emitted from coal-fired boiler*

16 kinds of toxic PAHs were investigated under electron beam irradiation in the pilot plant in Electric Power Station Kawęczyn, Poland[12]. The investigation was carried out under the following experimental conditions: flue gas flow rate 5000 $Nm^3$/h; humidity 4.5%; inlet concentrations of $SO_2$ and NOx that were emitted from the power station were 192 and 106 ppm, respectively; ammonia addition was 2.75 $Nm^3$/h; alcohol addition was 600 l/h, the absorbed dose was 8 kGy. The results was presented in Fig. 13.4. It was found that under these experimental conditions the concentrations of naphthalene (NL, $C_{10}H_8$), acenaphthene (AC, $C_{12}H_{10}$), fluorene ($C_{13}H_{10}$), phenanthrene ($C_{14}H_{10}$), anthracene ($C_{14}H_{10}$) were decreased, while the concentrations of acenaphthylene ($C_{12}H_8$), fluoranthene ($C_{16}H_{10}$), pyrene ($C_{16}H_{10}$),

benzo(a)anthracene ($C_{18}H_{12}$), chrysene ($C_{18}H_{12}$), benzo(b þ k)fluoranthene ($C_{20}H_{12}$), benzo(e)pyrene ($C_{20}H_{12}$), benzo(a)pyrene ($C_{20}H_{12}$), perylene ($C_{20}H_{12}$), dibenzo(a; h)anthracene+indeno(1,2,3-cd) pyrene ($C_{22}H_{14}$), benzo(g; h; l)perylene ($C_{22}H_{12}$) were increased. Removal efficiencies of $SO_2$ and NOx were 61.6% and 70.9%, respectively. The concentration of hydrocarbons of small aromatic ring (PAHs, like naphthalene ($C_{10}H_8$), acenaphthene ($C_{12}H_{10}$), fluorene ($C_{13}H_{10}$), anthracene ($C_{14}H_{10}$)) was reduced, while the concentration of fluoranthene was increased remarkably after irradiation.

Similar experiments were carried out in EPS Kawęczyn with ammonia presence but without alcohol addition [13.13,13.14]. It was found that removal efficiency of PAHs ranges from 40% up to 98%.

Callén et al. [13.15] studied PAH removal from lignite-combustion flue gas from Bulgarian Maritza-East thermal power plant (TPP) and obtained that PAHs concentration after EB irradiation resulted in ~ 10 fold decrease in studied PAHs emissions. The removal efficiency of PAH removal at the dose of 4 kGy was 85% (weight/weight). High PAH removal efficiency was obtained especially for 2 and 3 rings PAH, this result was similar to that obtained in our previous work [13.12].

The concentration of PAHs in by-product was also examined. It was relatively low, varied from few up to 12 µg per kg of fertilizer for the experimental work carried out in EPS Kawęczyn, Poland. Less than 3% of PAH were removed in adsorption on the by-product surface[14]. The study in Maritza-East TPP allowed PAH assessment in solid by-products obtained from EB lignite-combustion flue gas. The determined PAH content was reasonable, ~ 60 microg/kg and was lower than PAHs background in Bulgarian soils. These results demonstrated the insignificant role of adsorption for PAHs removal [13.15].

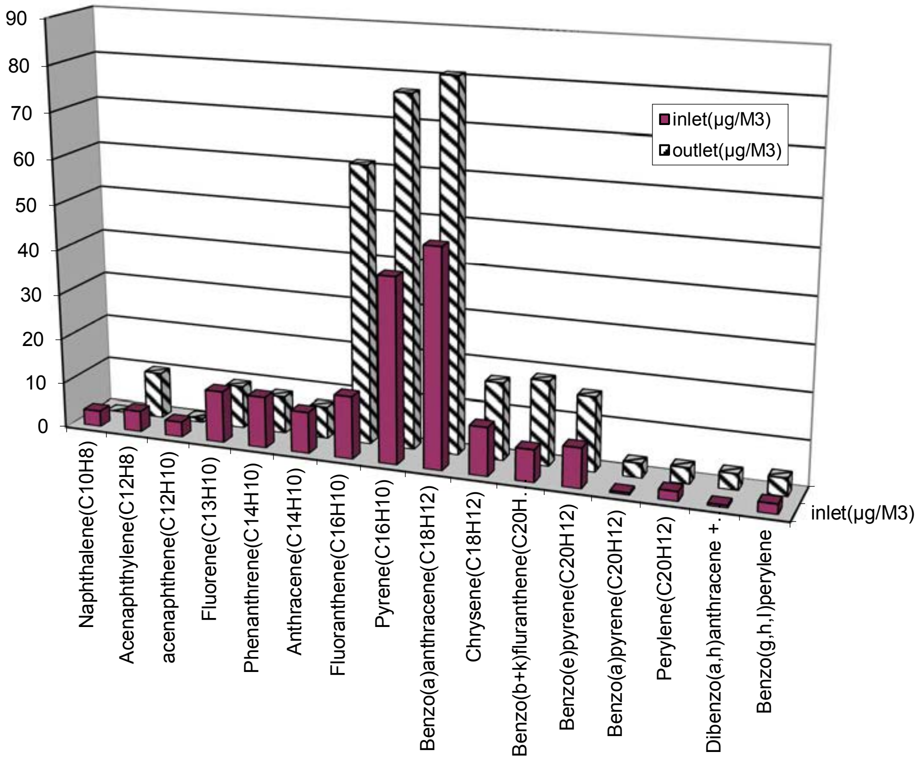

*FIG. 13.4 EB irradiation influence on PAHs removal*

#### *13.3.1.4. EB technology for Dioxins removal from flue gas emitted from waste incinerator*

Dioxins were formed in waste incinerator due to materials containing chlorinated compound, such as plastic wastes. Dioxins reduction from waste incinerator was studied using EB technology in Japan [13.16] and in Germany [13.17]. Hirota et al. [13.16] studied reduction the emission of polychlorinated dibenzo- p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in a flue gas of 1000 $m^3N/h$ from the municipal solid waste incinerator (MSWI), located at Takohama Clean Center which treats 450 t ( 150 t * 3 furnaces) of solid waste in 1 day, at a temperature of 200 °C. they found that more than 90% PCDD/Fs w

as removed at 14 kGy when initial concentration of PCDD was in the range of 0.22-0.88 ng-TEQ/$m^3N$ and PCDF in the range of 0.35–12.4 ng-TEQ/$m^3N$. Paul et al. (1998) also reported that over 90% PCDD was removed at 12 kGy dose for inital concentration of PCDD being 21-110 ng/$m^3N$ (AGATE-M plant, Germany).

#### *13.3.1.5. EB technology for Hg removal from air*

Mercury (Hg) as a highly toxic pollutants tends to bioaccumulation and has adverse effects on human health. Coal-fired boilers are reported as the largest single-known source of anthropogenic Hg emission in the USA. In the flue gas, elementary mercury ($Hg^0$) is dominant. However Hg(II) is preferable due to its water solubility. Hg oxidation in air by using electron beam irradiation was studied in bench scale by Kim et al. [13.18]. It was found that approximately 98% of gaseous mercury vapor was readily oxidized for the initial $Hg^0$ concentrations about 16 μg/$m^3$ at 5 kGy dose. Electron beam irradiation demonstrated high levels of mercury oxidation at the bench scale, and this technology might help improve mercury removal in wet scrubbers or wet ESPs when employed as a primary or secondary mercury oxidation technique[18].

### 13.3.2. EB technology for $SO_2$ and NOx removal from flue gas emitted from oil-fired boiler

Another promising market for EBFGT application is for $SO_2$ and NOx removal from high sulfur oil fired boilers. Pilot test in a refinery plant in Saudi Arabia was given as an example[2] (Fig. 13.5 & 13.6).

### 13.3.3. EB technology for gas pollutants control for flue gas emitted from diesel engine

In the year 2020 $SO_2$ and NOx emission from international cargo ship will be expected to exceed their emission from land-based emission sources. It is urgent to develop new technology for $SO_2$ and NOx removal from emission of cargo diesel engine. Laboratory test for high concentration of NOx removal without $NH_3$ addition was carried out in INCT. It shows that removal efficiency of NOx is influenced by inlet gas temperature and $SO_2$ concentration (Figs. 13.7–13.8). When the sea water was used as scrubber, more than 80% $SO_2$ and 55% NOx was removed from gas phase[2].

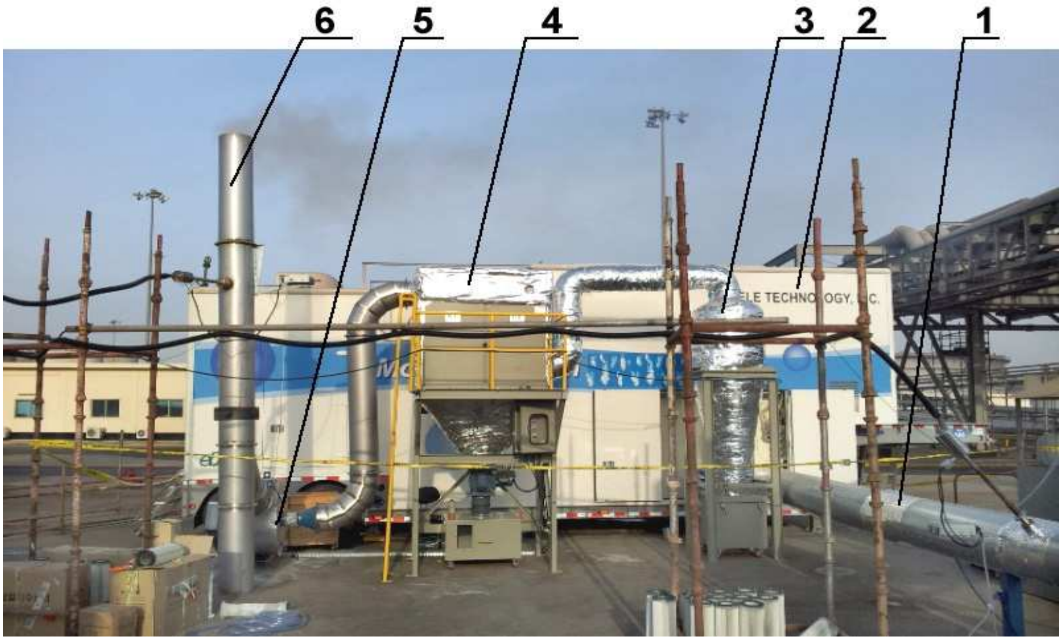

*FIG.13.5. Saudi Arabia pilot plant process units, 1. Ammonia addition, 2. EB-TECH mobile unit, 3. cyclone, 4. cartridge filter 5. ID fan 6. Stack*

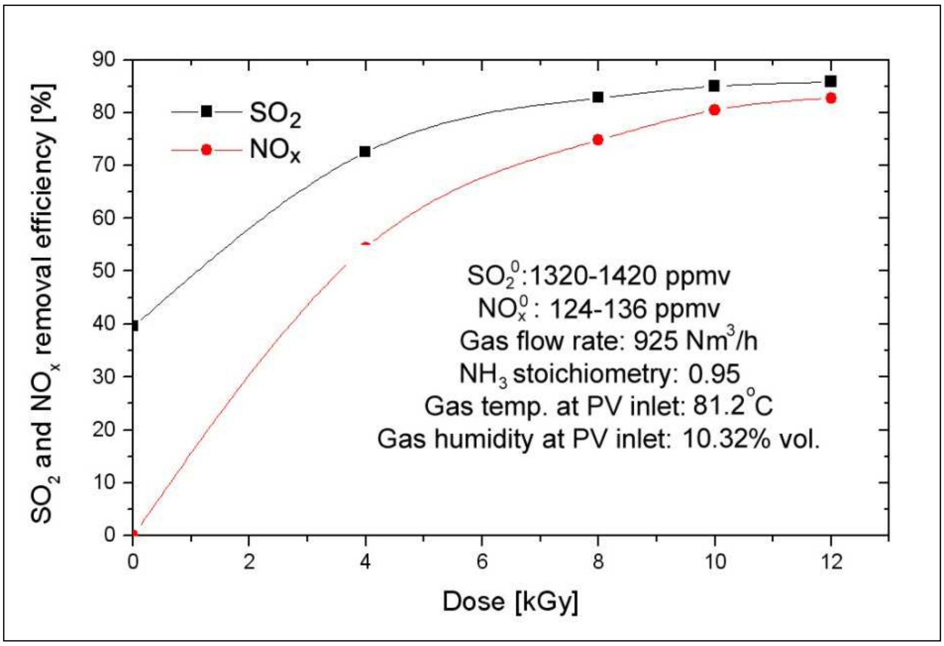

*FIG.13. 6. Removal efficiency of $SO_2$ and NOx vs. dose from flue gas emitted from oil fired burner (pilot plant test result in a refinery in Saudi Arabia*

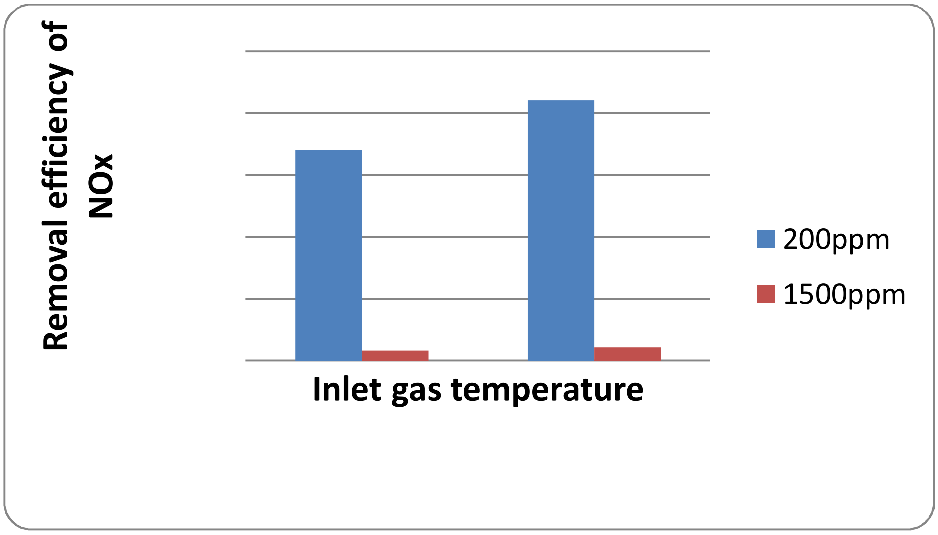

*FIG.13.7. Inlet gas temperature influence on NOx removal efficiency at 8.8 kGy dose without $NH_3$ addition ($SO_2$ = 700 ppm)*

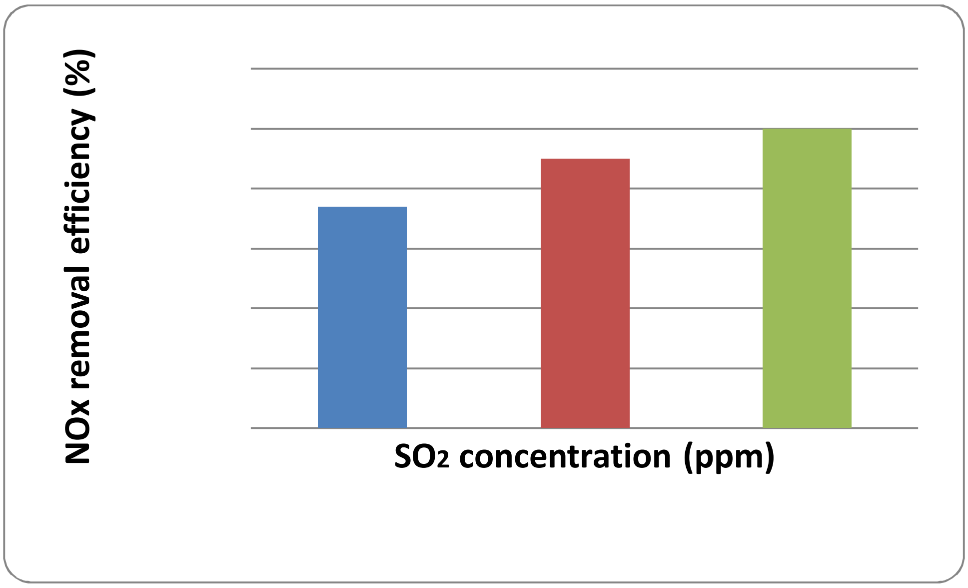

*FIG 13.8. Inlet concentration of $SO_2$ influence on NOx removal efficiency (NOx =1000ppm, dose=8.8 kGy)*

## 13.4. CONCLUSIONS

Tests in industrial plant EPS Pomorzany, Poland proved that EBFGT is a very competitive technology to remove $SO_2$ and NOx from flue gas generated from fossil fuel. Pilot test in a refinery plant in Saudi Arabia shows that it is a promising technology to remove $SO_2$ and NOx from flue gas emitted from oil burners. In the future, it can be used to remove $SO_2$ and NOx with sea water as scrubber from waste gas emitted from cargo ship which is the major pollution sources for $SO_2$ and NOx emission in the near future. Based on pilot plant results of removal of VOCs, PAHs and dioxins and lab experimental results of mercury removal by using EB technology, it shows that EB is one of the promising technologies to be applied in industrial scale to remove multiple gas pollutants from different emission sources.

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# 14. APPLICATIONS OF RADIATION TECHNOLOGIES FOR DEVELOPING “GREEN” PROCESSES FOR TREATMENT OF BIOLOGICAL HAZARDS

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**Abstract**

In the framework of three CRPs - 1) The Development of Irradiated Foods for Immuno-Compromised Patients; 2) Remediation of Pollutants Using Radiation Technology and 3) Radiation treatment of wastewater for reuse – Portugal has worked on growth and inactivation patterns of microbial populations of environmental matrices for the development of treatment processes.

1) *Ionization radiation treatment of fruits and vegetables for immuno-compromised patients – feasibility study*: The research developed has focused on the evaluation of the irradiation effects on fruits microbiota and the potential extension of shelf-life. The analyzed fruits were raspberries, blackberries, sweet cherries, and cherry tomatoes. Alongside, other study has been conducted aiming at to assess the effects of gamma irradiation on the microbial burden of dried medicinal plants, namely *Melissa officinalis*. Samples of packed fruits and dried plants were irradiated at a Co-60 source at dose range of 0.5 up to 6 kGy (depending on the type of product). Inactivation studies of natural fruits microbiota and inoculated microbial potential hazards (e.g. *Salmonella enterica* serotype Typhimurium; *Escherichia coli*) were performed. Furthermore, shelf-life assessment was carried out up to 14 days of storage at 4°C for some of the analyzed products. Generally, the obtained results indicated a microbial inactivation of ≤2 log reduction for the applied gamma radiation doses, depending on the level and type of microorganisms present on food products. The results indicated a potential shelf-life extension for irradiated raspberries, blackberries and cherry tomatoes.

2) *Survival and inactivation patterns of viral threat agents in the environment: assessment of ionizing radiation as decontamination tool:* The developed work was based on the optimization and validation of the methods to assess the virucidal effect of gamma radiation. Human Norovirus (HNoV) is considered the leading cause of gastroenteritis worldwide, however this human virus cannot be replicated in cell culture, as so it was used a Murine Norovirus as surrogate model of HNoV. The prevalence of viruses on different food surfaces has been linked to their high stability in the environment, being aware of this in the validation of the methodologies it was used a surface test where the virus was in a dried surface biofilm to mimic an environmental hard condition. The virus film was exposed to several sub-lethal doses (≤10 kGy) at a Co-60 source and the infectivity of the virus was assessed by the plaque assay technique. Concerning the MNV-1 inactivation studies the attained results indicated that gamma radiation presented a virucidal activity against MNV and for the applied conditions the MNV presented exponential inactivation kinetics and a D-value of 3.7 kGy. The data obtained, showed that MNV titer could be effectively reduced by 3 log, representing a virucidal efficacy of 99.9% by a gamma radiation dose of 10 kGy.

3) *Application of ionizing radiation on the cork wastewater treatment:* The aim of this work was to find out if ionizing radiation treatment could increase the biodegradability of recalcitrant compounds using a microbial consortium from cork wastewater treatment sediment tank, and a mixed solution of four phenolic acids as a model. A preliminary HPLC and GC-MS analysis were performed to detect the major phenolic compounds in cork wastewater samples. Results indicated the presence of gallic, protocatechuic, vanillic and syringic acids in cork boiling water and gallic, protocatechuic and vanillic acids in sediment tank samples. The microbial growth was assessed in non-irradiated (0 kGy) and irradiated (100 kGy) mixed phenolic acids cultures during incubation time. The Colony Forming Units counts pointed out to a decreasing tendency along the incubation time for phenolic acids cultures (0 kGy and 100 kGy) suggesting a non-degradation trend. The selected microbial consortium was not able to metabolize the phenolic compounds solutions at the used conditions. This could be due to the detected radiolytic degradation dynamics of the phenolic acids considering the antimicrobial activity of these compounds.

## 14.1. OBJECTIVE OF THE RESEARCH

Environmental matrices have a complex dynamics among living and nonliving matter. Our objectives focus on the development and optimization of radiation technologies either as a mitigation tool for food- and water-borne microbiological hazards, or as an adjuvant process for wastewater bioremediation purposes.

## 14.2. INTRODUCTION

During the last few decades, increasing foodborne diseases and environmental generated illnesses became highly challenging issues. Especially important are enteric pathogenic microorganisms that can enter the environment through the discharge of wastes from infected individuals; contaminate food products and drinking and recreational waters; and be transmitted back to susceptible individuals to continue the cycle of infection [14.1]. Human enteric pathogens (e.g. *Escherichia coli*, *Salmonella enterica*, Noroviruses) are frequently detected in environmental systems and have been implicated in many outbreaks [14.2]. As the epidemiology of environmental diseases is changing, there is a growing global public health concern about new and re-emerging infectious diseases that are occurring through a complex interaction of social, economic, evolutionary, and ecological factors [14.2]. Therefore, controlling an outbreak depends on identifying and removing the source of contamination.

Ensuring the security of current and future food supplies is one of the main challenges facing governments around the world, driven by the need to feed an increasing world population and consumer demand for freshness and variety. But, there is also a need to address issues associated with the supply of safe and healthy food. Fresh fruit and vegetables are important components of a healthy and balanced diet; their consumption is encouraged in many countries by health agencies to protect against a range of diseases. Food products, that are consumed raw, are increasingly being recognized as important vehicles for transmission of human pathogens that were traditionally associated with foods of animal origin [14.3–14.4]. Moreover, during growth, harvest, transport and further processing and handling, these products can be contaminated with pathogens from human or animal sources [14.5]. Currently, chlorine-based sanitizers are widely used in the fresh food industry as the primary disinfection method for pathogen removal. However, it was demonstrated that these sanitizers are not effective against several human biological hazards [14.6]. Therefore, appropriate postharvest decontamination treatment is required to control the population of foodborne pathogens and reduce the burden of disease transmission from raw produces.

Contamination of water is also a serious problem caused by polluted effluents from municipalities and industry. Conventional technologies and others for wastewater purification do not solve all existing problems. The destruction of non-biodegradable organic compounds is one issue and the biological contamination of effluents is another. Particularly, wastewater from cork processing industry present high levels of organic compounds such as phenolics that must be degraded before discharge into the municipal sewer or into public water courses. In fact, these compounds present a low biodegradability and a significant toxicity due to their recalcitrant and bioaccumulation potential, rending the phenolic acids as a significant environmental concern [14.7]. New methods for their purification are required.

In general, chemical treatments are efficient but leave pollutants that are harmful to the environment and the human health. Research has demonstrated that enteric pathogens can be resistant to conventional treatments and common disinfectants [14.8]. Green Chemistry is one alternative, involving specially designed chemical processes and products that reduce or eliminate the use and generation of hazardous substances [14.9]. Similarly, radiation processing, using electron beam accelerators and gamma sources, is an additive-free process that uses the short lived reactive species (formed by radiolysis and/or other reactions) for efficient decomposition of the hazard pollutants in the product. Ionizing radiation covering a high energy range that is safely kept below the radioactivity threshold proved to be a clean and environmental friendly technology with the potential to solve the problems left by the conventional methods and an alternative for some of the chemical treatments [14.10]. Radiation processing has been widely accepted for use in many areas of the global economy. Sterilization, polymer cross-linking and tire component curing are well established technologies [14.11].

Ionizing radiation is being used more frequently as a useful and effective means of disinfection and can be an alternative technology for fresh food treatment. Food irradiation is one of the few technologies that address both food quality and safety by virtue of its ability to control spoilage and foodborne pathogenic microorganisms without significantly affecting sensory or other organoleptic attributes of the food. Irradiation has several advantages: it does not significantly raise food temperature and the food does not cook; unlike chemical treatments, irradiation does not leave potentially harmful residues; and it can be used to treat packaged food, which will remain safe and protected from microbial contamination after treatment. Beneficial effects of irradiation include reduction of storage loss, shelf-life extension, and improvement of microbiological and parasitological safety of foods, while being safe to the environment.

Biodegradation is considered as a sustainable process of wastewater treatment which, under appropriate conditions, can promote an efficient reduction of the organic matter content with minimal energy requirements and low costs [14.7]. The organic compounds naturally produced could be used as carbon and energy source by some microorganisms. The simple biological treatment and/or combined with other processes could be an option to the wastewater treatment [14.7]. In wastewater treatment, ionizing radiation could also be an alternative process for cork wastewater treatment. Advanced oxidation processes are being studied as potential technologies to reduce the COD, BOD and TOC levels, increasing the biodegradability of wastewaters [14.12–14.14]. Ionizing radiation has the same mechanism of Fenton oxidation, i.e., the generation of free radicals to promote compounds degradation but without additives. Therefore, ionizing radiation seems to be a potential technology to be applied in order to increase the biodegradability [14.15–14.17]. The use of natural bacteria from wastewater as degraders could be a promising approach to remediation of wastewaters [14.7].

The goal of our works is to develop radiation technologies applications to investigate and/or remediate issues in human health, food supply, and environment that are inaccessible or poorly addressed by more conventional techniques.

## 14.3. MATERIALS AND METHODS

### 14.3.1. Sampling

Raspberries (*Rubus idaeus* L., cv. Amira) and blackberries (*Rubus fruticosus*, cv. Primark) were grown in Fataca experimental field (Odemira, Portugal). Samples of the sweet cherries (*Prunus avium* L., cv Sweetheart) at commercial maturity were obtained from the fields of Amplos Caminhos Lda. (Fundão, Portugal). Freshly cherry tomatoes (*Solanum lycopersicus* var. *cerasiforme*) were acquired from local retail market. The analysed fruits were packed in polystyrene boxes (250 g/package) with a lid and holes for air circulation. *Melissa officinalis* dried samples were obtained from "MaisErvas - Aromáticas e Medicinais" company, and packed in sterile polyethylene plastic bags until analysis.

### 14.3.2. Bacterial strains

Three bacterial reference strains supplied by the American Type Culture Collection (ATCC) were included in the study: *Salmonella enterica* serotype Typhimurium ATCC 14028, *Escherichia coli* ATCC 8739and *Staphylococcus aureus* ATCC 6538. The reference strain cultures were routinely grown on Tryptic Soy Broth (TSB) and enumerated by plate count on Tryptic Soy Agar (TSA) at 37 °C for 18 h.

### 14.3.3. Virus and cells

RAW 264.7 cells were cultured in complete minimum essential medium (MEM) containing 10% low endotoxin fetal bovine serum (Lonza) for Murine Norovirus (MNV) assays. MNV stocks were prepared using an 80-90% confluent monolayer of RAW cells in 150 $cm^2$ tissue culture flask that were infected with MNV virus stock by using a multiplicity of infection (MOI) of 0.05. Following 1 h of adsorption, the inoculum was removed and fresh cell maintenance media was added. The flask was incubated at 37ºC in 5% $CO_2$ until >90% of the cells presented cytophatic effect (5 days). MNV was harvested after three freeze-thaw steps, followed by a centrifugation step of 30 min at 3000 rpm. All viral stocks were stored at -80ºC.

### 14.3.4. Irradiation

Irradiations were carried out at the Co-60 experimental equipment (Precisa 22, Graviner, Lda, UK) in the Ionizing Radiation Unit located in the Campus Tecnólogico e Nuclear, Bobadela, Portugal. Dosimetric studies were performed using Fricke reference dosimeter to establish the irradiation geometry and estimate the dose rate (2 kGy/h).

For each fruit type it were performed three independent irradiation batches. The packages of food product were irradiated at doses ranging from: 0.5 kGy up to 1.5 kGy for raspberries; 1 kGy up to 3 kGy for blackberries; 0.5 kGy up to 4 kGy for sweet cherries; and 0.5 up to 6 kGy for cherry tomatoes. Absorbed doses were monitored by routine dosimeters (Amber Perspex Harwell®, Batch V and X). The obtained dose uniformity was aproximatly 1.2. After irradiation, irradiated and non-irradiated samples were stored at 4ºC (regular retail and consumers home storage temperature) until analysis.

Dried *Melissa officinalis* samples were irradiated at doses ranging from 1 kGy up to 5 kGy. Samples were maintained at room temperature until analysis (in the same day of irradiation).

Regarding the challeging tests with reference bacterial strains, the artificially contaminated fruit samples (25 g of fruit) were irradiated at doses ranging from 0.5 kGy up to 1.5 kGy (in triplicate for each dose).

MNV samples (0.5ml of viral stock) were irradiated in glass petri dishes at three doses (2.0 kGy up to 10 kGy; triplicate samples per dose).

Non-irradiated samples followed all the experiments.

### 14.3.5. Microbiological inactivation studies

#### *14.3.5.1. Natural microbiota*

Fruit samples of 25 g were blended on 100 mL of physiological solution with 0.1% of Tween 80 and homogenized in a stomacher equipment (Stomacher 3500; Seaward, UK). Serial decimal dilutions were performed before plating. Aerobic mesophilic counts were carried out, in triplicate, on Tryptic Soy Agar (TSA, Merk) at 30ºC during 7 days. Microbiological counts were expressed as mean log colony forming units per gram of fresh fruit (CFU/g).

The dried plant samples (1 g) were homogenized in a stomacher equipment during 15 minutes and filtrated using nitrocellulose membranes with a pore size of 45 µm. Bacterial and fungi counts were carried out, in triplicate, on Tryptic Soy Agar (TSA, Merk) and Malt Extract Agar (MEA, Merk) at 30 ºC during 7 days. Microbiological counts were expressed as log colony forming units per gram.

All colonies were macroscopically (e.g.: pigmentation, texture, shape), microscopically and biochemically typed by gram staining, catalase activity and oxidase test. The isolates were organized into typing groups according with Bergey's Manual of Determinative Bacteriology [14.18]. Morphological identification of fungi was achieved through macro and microscopic characteristics as described elsewhere [14.19]. The frequency of each phenotype was calculated based on the number of isolates and their characterization.

#### *14.3.5.2. Challenging tests*

For the challenging tests with bacterial reference strains, 25 g of fruits and 1 g of dried plants (each in triplicate) were inoculated with a known concentration ($10^6$ CFU/ml) of bacterial suspensions in sterile saline solution. Inoculated samples were air dried in a laminar flow cabinet for 60 min. After drying the artificially contaminated samples were irradiated as described in Irradiation section. After irradiation, the samples were analyzed as described previously.

A surface test was applied using a 0.5 ml of virus stock that was spread uniformly in a 90 mm sterile glass petri dish with a cell scraper. The virus was air dried at room temperature dried in a laminar flow cabinet until visibly dry (approximately 60 min). The virus films samples were then irradiated as previously described. After irradiation, 0.5 ml of infection media (DMEM with 2% FBS) was added and the mixture was scraped from the surface of the dish. To determine the infectious titre of MNV, standard plaque assay technique was used. RAW 264.7 cells were dispensed in 60 mm diameter cell culture plates (Nunc) at a density of $1\text{x}10^5$ cells per plate and grown to 80 to 90% confluence (approximately 5 days) in 5 ml of complete cell maintenance media at 37ºC. Cell monolayers were infected with 0.1 ml (in duplicate) of 10-fold serial dilutions of the virus during 1 h at 37ºC. After removal of the inoculum, cells were overlaid with 3 ml of overlay medium (2xMEM) with 0.5% of agarose (SeaKem ME, Lonza) and incubated during 48h. Plaques were subsequently counted 8 to 24 h after a second agarose overlay (3 ml) with 0.6% of a neutral red solution (3.3 g/L, Sigma). Plates with 5 to 50 plates were used to determine the virus titre in PFU. The following controls were included: (i) Cell viability control: non infected cell culture plates. This control demonstrates that cells remain viable and non-contaminated throughout the course of the assay period; (ii) Non-irradiated virus controls: the virus was tittered at the beginning time of the assay and at the end of the assay to determine the loss of infectivity of the virus during the assay time.

### 14.3.6. Assessment of shelf-life extension

In order to evaluate shelf-life of fruit, microbiological parameters were assessed for fruits after irradiation (0 days of storage; T0) and after storage at 4ºC as described previously. For sweet cherries and blackberries it was assayed three and seven days of storage. Regarding raspberries and cherry tomatoes, microbiological analysis (total counts) were performed after 7 and 14 days of storage.

### 14.3.7. Batch biodegradation experiments

A minimal phenolic acids media [170.90 mg L-1 gallic acid, GA; 154.35 mg L-1 protocatechuic acid, PA; 168.53 mg L-1 vanillic acid, VA and 198.50 mg L-1 syringic acid, SA; plus 1% salt solution: 8.05 g L-1 CaCl2, 608.8 mg L-1 FeCl3.6H2O, 1.00 g L-1 MnSO4.H2O, 1.00 g L-1 MgSO4.7H2O, 5.01 g L-1 K2HPO4, 13.03 g L-1 KH2PO4] was used as a model. A non-irradiated minimal phenolic acid media (0 kGy) and an irradiated minimal phenolic acid media (1 Liter; irradiated in the Co-60 equipment at 100 kGy with a dose rate of 2 kGy/h) were used in the batch biodegradation experiments in order to assess the biodegradability of the phenolic acids radiolytic products.

An autochthonous mixed culture of four bacterial strains naturally present in sedimentation tank samples was selected, due to its adaptation to this environment and its potential metabolizing capacity. The morphological characterization of the four isolates was carried out by conventional bacteriological techniques (e.g. cell morphology; gram staining; biochemical tests). The biodegradation experiments were performed into 250 mL Erlenmeyer flasks containing: the minimal phenolic acids media (0 kGy and 100 kGy), TSB solution (as positive medium control) and ultra-pure water with concentrated salt solution (as negative medium control). The selected microbial consortium was inoculated in all culture media at a concentration of $10^5$ CFU/ml and incubated at 30 ºC in an orbital shaker (150 rpm). Sample aliquots for each culture assay were withdrawn at regular time intervals (time-aliquots) and analyzed for total viable biomass (Colony Forming Units – CFU/L counts), TP and HPLC analysis. CFU counts were performed by direct plating into Tryptic Soy Agar of triplicate aliquots of serial decimal dilutions of culture assays. A period until the residual concentration of phenolic compounds and the amount of biomass in flask had reached asymptotic values in time was carried out for each experiment. Results obtained from the same set of triplicate experiments were averaged and are reported.

## 14.4. RESULTS

### 14.4.1. Microbiological inactivation studies

#### *14.4.1.1. Natural microbiota*

The microbiological results indicated that raspberries and blackberries presented an initial bioburden of 4.3±0.1 log CFU/g and 3.0±0.1 log CFU/g, respectively. Regarding sweet cherries and cherry tomatoes, the estimated average bioburden value was 2.6±0.1 log CFU/g. In order to analyze the response of fresh fruits microbial population to gamma radiation survival plots were constructed based on the logarithmical values of the number of survivors in function of the absorbed dose (Figure 14.1) during storage time.

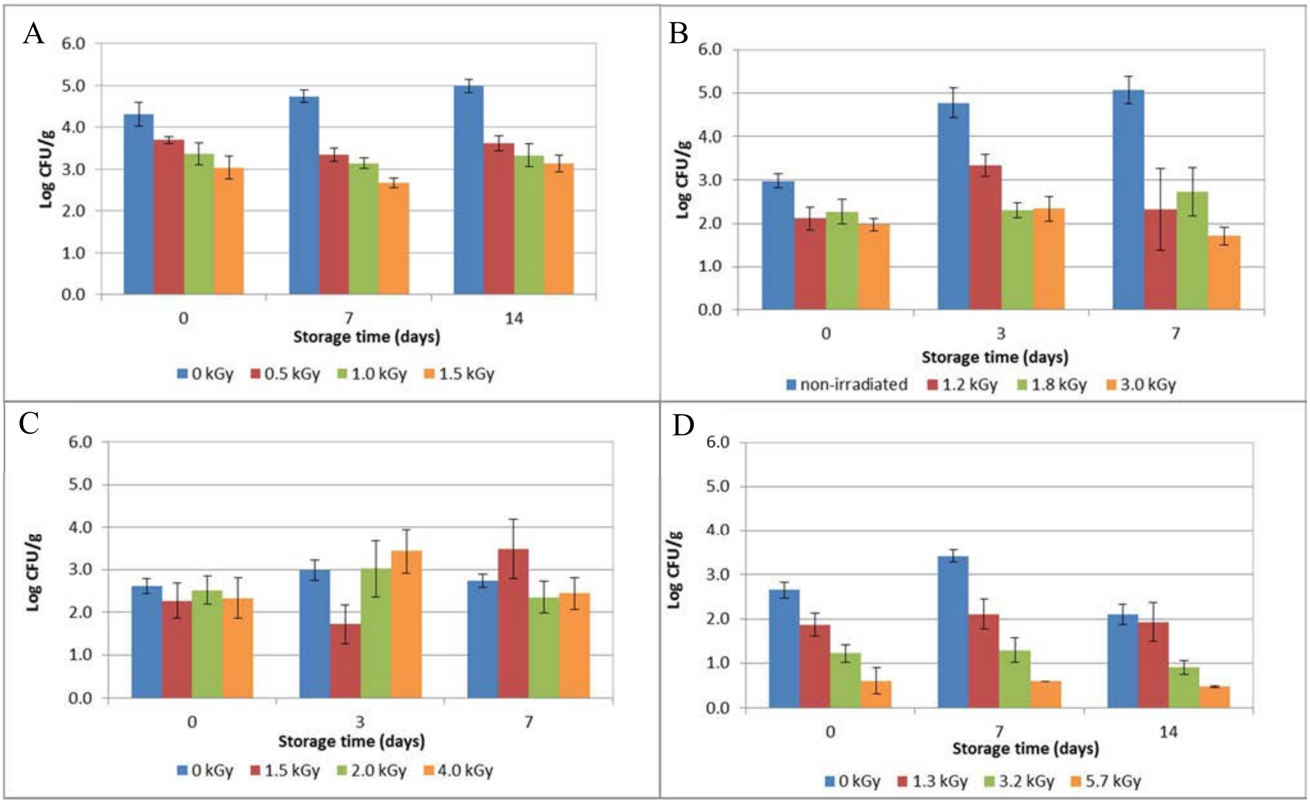

*FIG. 14.1. Total aerobic mesophilic counts for non-irradiated and irradiated fruits during storage time: A) raspberries; B) blackberries; C) sweet cherries and D) cherry tomatoes. Standard deviation bars correspond to 95% confidence intervals about mean values (n= 18; α = 0.05).*

The mesophilic microbial populations of raspberries and cherry tomatoes showed a linear inactivation kinetics, with a maximum inactivation efficiency of 95% (1.4 log decimal reduction for 1.7 kGy) and 99% (2 log decimal reduction for 5.7 kGy), respectively. For these both types of fruit the observed reduction in the microbial load remained almost constant during the 14 days of storage. Concerning blackberries and sweet cherries, the obtained results did not show an inactivation tendency for the applied gamma radiation, and a limited log reduction (≤1 log) was verified immediately after irradiation (zero days of storage). However, after seven days of refrigerated storage, it was detected a 3 log reduction (at 3 kGy) for the microbial load of irradiated blackberries comparatively to the obtained for stored non-irradiated fruits. For sweet cherries, no significant effect of microbiota reduction was observed during storage time at the applied gamma radiation doses. Previous studies of gamma radiation effects on berries pointed out to limited microbial inactivation. For blueberry it was reported that inactivation of microbial load after irradiation, at doses between 0.5 kGy up to 3 kGy was reduced by approximately 1.5 log [14.20].

The microbiota from non-irradiated and irradiated fruits was phenotypically characterized in order to evaluate the dynamics of the microbial communities and its patterns with radiation doses. In respect to raspberries, the most frequent morphological types in non-irradiated samples were filamentous fungi (41%) and the gram-negative, oxidase-negative, rods (34%). The surviving microbial population was mostly constituted by filamentous fungi (80-90%) that remained persistent during storage time. The initial microbial population of non-irradiated blackberries was mainly characterized by yeasts (76%), that persisted (70–99%) after irradiation and along storage time. The mesophilic microbial population of non-irradiated sweet cherries was predominantly defined by filamentous fungi (57%) and yeasts (28%). The surviving microbiota of irradiated sweet cherries seems to be homogenous along storage time, with the prevalence of yeast (95-100%). The cherry tomatoes presented a distinct initial microbiota of gram-negative, oxidase-negative, rods (88%), which were not detected after irradiation. During the storage time, the microbial contamination pattern of cherry tomatoes shifted to gram-negative, oxidase-positive, rods (78-100%) in the non-irradiated and irradiated samples.

The characterization of the microbiota of dried *Melissa officinalis* showed an average bioburden value of 2.50±0.02 log CFU/g and a microbial population predominantly constituted by one morphological type: gram-positive rods (74%). The inactivation studies of the dried plants mesophilic population indicated a linear inactivation kinetics (Figure 14.2), with a one log reduction of microbial burden (90% inactivation efficiency) for 4 kGy. The survivor microbiota was mainly phenotype as gram-negative rods (75%).

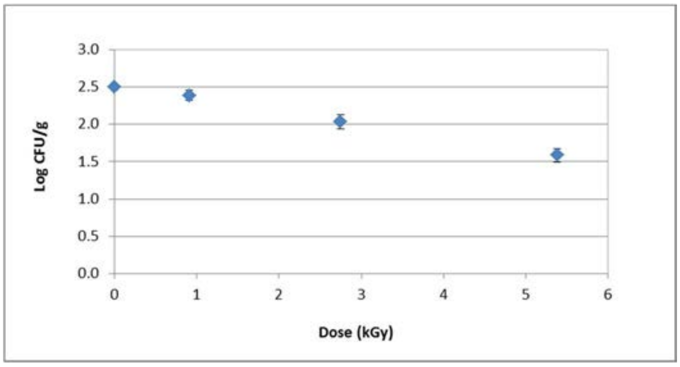

*FIG. 14.2. Total mesophilic microbial population survival curve of dried Melissa officinalis. Standard deviation bars correspond to 95% confidence intervals about mean values (n= 18; α = 0.05).*

The obtained results stress out the type of microorganisms present in the products as a key factor in the microbiocidal effect of ionizing radiation. The cumulative amount of absorbed radiation energy required to inactivate microorganisms depends on several factors. Thus, the dose required for each individual application should be established taking into consideration the contamination level, the hazard(s) involved and irradiation conditions (temperature, dose rate, oxygen presence).

### *14.4.1.2. Challenging tests*

Radiation resistances, even under comparable conditions, vary widely among different microorganisms. The resistance can differ from species to species and between strains of the same species. This radiation sensitivities differences among similar groups of microorganisms are correlated to their inherent diversity with respect to the chemical and physical structure as well their capacity to recover from radiation injuries.

Radiation survival follows in most cases the exponential kinetics. In order to characterize organisms by their radiation sensitivity, the $D_{10}$ value is used, which is defined as the dose required to inactivate 90% of a population or the dose of irradiation needed to produce a 10-fold reduction in the population.

The effects of gamma radiation treatment on microbial viability of potential pathogenic bacteria on inoculated food products were evaluated (Table 14.1). The results indicated that the same microorganism could present different $D_{10}$ values depending whether the product on/in it is present.

TABLE 14.1. $D_{10}$ VALUES FOR POTENTIAL PATOGHENIC MICROORGANISMS IN DIFFERENT SUBSTRATES.

| Microorganism | $D_{10}$ values ± Standard Error (kGy) | Substrate |
|---|---|---|
| *Salmonella* Typhimurium | 0.30 ± 0.01 kGy | Cherry tomatoes |
| | 0.2 – 0.3 k Gy | Shell eggs [21] |
| *Escherichia coli* | 0.71 ± 0.04 kGy | Cherry tomatoes |
| | 0.54 ± 0.04 kGy | Dried *Melissa officinalis* |
| *Staphylococcus aureus* | 0.45 ± 0.02 kGy | Cherry tomatoes |
| Murine Norovirus (MNV) | 3.7 ± 0.2 kGy | Surface |

Since part of the effect of ionizing radiation on a microorganism is due to indirect action mediated through radicals, the nature of the medium in which the microorganisms are suspended could play an important role in determining the dose required for a given microbiocidal effect. The more complex the medium, the greater is the competition by its components for the radicals formed by irradiation within the cell, thus “sparing” or “protecting” the microorganisms, since microorganisms and chemical species are dynamically inter-dependent.

### 14.4.2. Batch biodegradation experiments

The purpose of this study was two-fold: a) to study the biodegradation of cork wastewater, after irradiation, in order to assess its potential for biological treatment, and b) to find out if the radiolytic degradation of the phenolic acids in conjunction with microbial degradation could increase the treatment efficiency.

The assessment of microbial growth during incubation time on minimal phenolics acids media (non-irradiated and irradiated) was performed by CFU counts as presented in Figure 14.3.

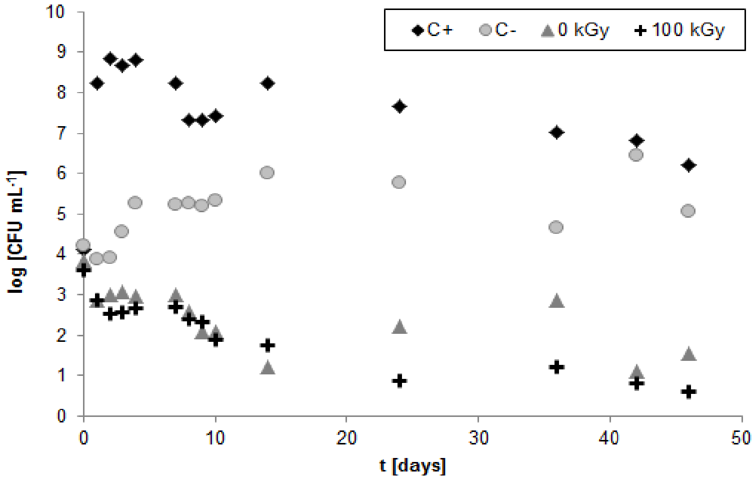

*FIG. 14.3. Log Colony Forming Units counts (CFU) for culture assays in phenolic acids medium and controls during incubation time.*

As expected, the CFU counts for the positive control (C+) increased during the initial incubation time, indicating the adequacy of methods to evaluate the growth of tested bacteria.

A rapidly bacteria growth along time is seen to C+ (in two days it reached exponential phase) so it is our comparison parameter.

As for the negative control (C-) it was not observed substantial variations in growth during incubation time. As presented in Figure 14.3, the results point out to a decrease in CFU counts in phenolic acids cultures. Therefore, the radiolytic by-products seem to have a negative effect on the growth of the selected microbial community. This could be due to the detected radiolytic degradation dynamics of the phenolic acids (the radiolytic by-products for syringic and vanillic acids are protocatechuic and gallic acid), considering the antimicrobial activity of these compounds. The antimicrobial activity of phenolic acids has been demonstrated against to a wide range of microorganisms [14.22]. As so, the initial hypothesis that the ionizing radiation would turn these recalcitrant compounds into simpler ones, more biodegradable, was not confirmed to be completely correct for the tested conditions. Although, must be noticed that microbial consortium (or part of) was maintained viable (with countable colonies) in phenolic acids cultures until the end of the experiments. The morphological characterization of the isolated colonies indicated a microbial population dynamics along incubation time, with the predominance of two morphotypes at the end of experiments for 0 kGy samples, and only one type for 100 kGy samples (Table 14.2).

TABLE 14.2 MICROBIAL POPULATION DYNAMICS FOR NON-IRRADIATED (0 KGY) AND IRRADIATED (100 KGY) CULTURE ASSAYS DURING INCUBATION TIME.

| | | Phenolic acids cultures | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 kGy | | | | | | | | 100 kGy | | | | | | | |
| | | Incubation time [days] | | | | | | | | Incubation time [days] | | | | | | | |
| Strain | Morphotype | 0 | 3 | 9 | 14 | 24 | 36 | 42 | 46 | 0 | 3 | 9 | 14 | 24 | 36 | 42 | 46 |
| A | Gram-positive, oxidase-negative, rods | + | + | - | - | - | - | - | - | + | + | - | - | + | - | - | - |
| B | Gram-negative, catalase-positive, cocci | + | - | - | - | + | + | + | + | + | - | - | - | - | - | - | - |
| C | Gram-positive, oxidase negative, rods | + | - | - | - | - | - | - | - | + | - | - | - | - | - | - | - |
| D | Gram-negative, Catalase-positive cocci | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |

## 14.5. FINAL REMARKS

An effective risk assessment of radiation control of biohazardous contaminants should be based on an integrated approach that encompasses multidisciplinary work based on the evaluation of the type, sources and routes of transmission of biohazards, bio detection methods, substrate chemical characterization, and radiation treatment conditions (e.g. temperature, irradiation atmosphere, dose rate).

To our knowledge, this study represents the unique approach that tries to associate the metabolic capacities of cork wastewater microbial consortium along with a radiolytic process, in order to promote the recalcitrant compounds degradation. Further work includes the study of extraction of phenolic compounds from cork wastewater by adsorption onto activated carbon, improving its selectivity through modification of carbon surface by ionizing radiation.

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# 15. ELECTRON BEAM TECHNOLOGY FOR WASTEWATER TREATMENT

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**Abstract**

The short information of JSC “NIITFA", its researches and developments conducted in the field of radiation technology is presented. Among them: radiation technologies and equipment, radionuclide energy sources, radiation means for non-destructive testing, radiation instruments for process monitoring and analysis of the substances composition, equipment for nuclear medicine, gas-discharge detectors of radiation, decommissioning of radiation equipment, etc.

In these studies the use of radiation technologies for environmental purposes keeps a significant place. The results of works on the use of electron accelerators for decomposition of hazardous environmental pollutions resulting from human activities are presented. It is an industrial, communal and other waste. The comparison of radiation and other methods of waste treatment and some economic characteristics of radiation technologies are given.

## 15.1. INTRODUCTION

JSC “NIITFA" was founded in 1960 under the name All-Union Research Institute of Radiation Technology (VNIIRT) as a head organization for development and implementation of radiation technology in the USSR. Over the years, the subject and the fields of activity of VNIIRT have significantly increased, and in 1989 the Institute was named as the National Technical Physics and Automation Research Institute.

The main directions of our activity as presented in Fig. 15.1 can be summarized as follows:

- Development of methods and means of radiation treatment on substances in order to modify their properties, for radiation sterilization or pasteurization of products
- Development of equipment complexes for contact radiation therapy and radioisotope diagnostic of various deceases, including cancer.
- Development of radioisotope sources of electrical energy of various powers for autonomous objects power supply.
- Development of instruments and devices that use the ionizing radiation for non-destructive testing and for analysis of materials and products, as well as automatic monitoring of technological processes.
- Development and serial production of gas-discharge detectors of ionizing radiation.

But radiation technology today also keeps the leading positions in JSC “NIITFA". One of the main objectives of the Institute has always been the development and practical application of radiation technologies for modification of the substances properties, food processing, sterilization of medical products, processing of wastes of production and consumption, and the treatment of wastewater and gas emissions. The other objective of radiation technologies is radiation therapy and radionuclide diagnostics of human diseases.

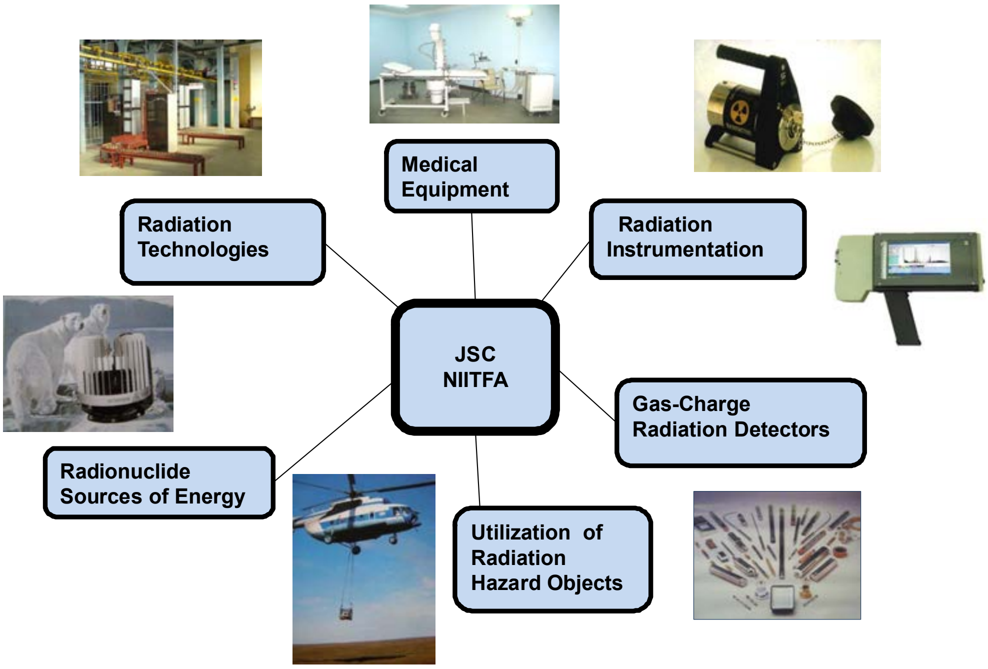

*FIG.15.1 Main directions of Institute activity*

Radiation equipment and instruments, created in JSC NIITFA", were delivered to customers in more than two dozen countries, including radiation facilities which were constructed in Peru and Vietnam, Bangladesh and Portugal, Cuba, Egypt, Syria, etc.

## 15.2. RADIATIION WASTEWATER TREATMENT

Problem of wastewater treatment brought to the attention of the Russian Government developed important documents:

- Water strategy of the Russian Federation for the period till 2020
- The Federal target program "Clean water for 2011-2017”

There is quite a wide international experience in use of such technologies: Austria, Brazil, and Ecuador, Bulgaria, Jordan, Korea, Poland, Portugal, Turkey, USA and some other countries.

The radiation technology is intended for the effective destruction in wastewater organic pollutants, such as nekal (naphthalene sulfonate), phenol, and hydrocarbon compounds. Their treatment of accelerated electrons in the reaction chamber leads to the decomposition of the substances into simple compounds (water, carbon dioxide and other) or turns pollution in easily removable subsequent after treatment components. (Fig 15.2)

TABLE 15.1. RADIATION TREATMENT OF WASTEWATER. THE COMPARATIVE CHARACTERISTICS

| Indicator | Chlorination | Ozone Treatment | UV treatment | Electron Accelerators | Notes |
|---|---|---|---|---|---|
| | 100 | 147 | 26 | 20 | Relative indicators calculated on the performance of 1 $m^3$/day |
| Power consumption W•hours/$m^3$ | 2 | 50-75 | 25 | 100 | For 1$m^3$ |
| Requirements for treated water in the mode of disinfection | Mechanical and biochemical purification and clarification | | Mechanical and biochemical purification and clarification, filtering through quartz filters or sand, high transparency | Mechanical and biochemical purification | |
| The need for reagents | Yes | Yes | No | No | |
| Side effects (ecological purity) | Formation of dioxins, pipeline corrosion, atmospheric pollution $Cl_2$, refers to dangerous objects, hard to control emissions. | Fire risk, pipeline corrosion, the formation of formaldehyde | The problem of recycling of lamps containing mercury | No | |
| Main contribution to the cost of processing of water is brought | Chlorine and reagents | Electric power and ozonizers | Electric power and UV lamps | EA and Power | |

In our country there was created one of the world's first industrial radiation effluent treatment at the petrochemical industries plant. (in Voronezh, Fig 15.3). Table 15.2 presents data on developed installations on the basis of electron accelerator for wastewater treatment.

TABLE 15.2 ELECTRON BEAM INSTALLATIONS ON THE BASIS OF ELECTRON ACCELERATOR

|  | Name of Installation | Treatment Results | EA Model | Year and Place |
|---|---|---|---|---|
| 1. | The electron beam technology for pretreatment of groundwater with biologically not degradable substances | Biodegradable substances in groundwater | EA-ELV-2<br>(20 kW, 0,8 MeV)<br>UE-ELV-3<br>(30 kW, 1,2 MeV | 1984 г.<br>Voronezh |
| 2. | The electron beam technology for wastewater treatment Petrodvorets aeration station | Non-toxic Wastewaters | EA «Electron»<br>(10kW, 0,6 MeV) | 1991 г.<br>Leningrad Region |
| 3 | Demonstration of electron-beam installation for testing radiation disinfection of water | Disinfected water | EA «Electronika- U003»<br>(3,5 kW, 5 MeV) | 2010 г.<br>Moscow |

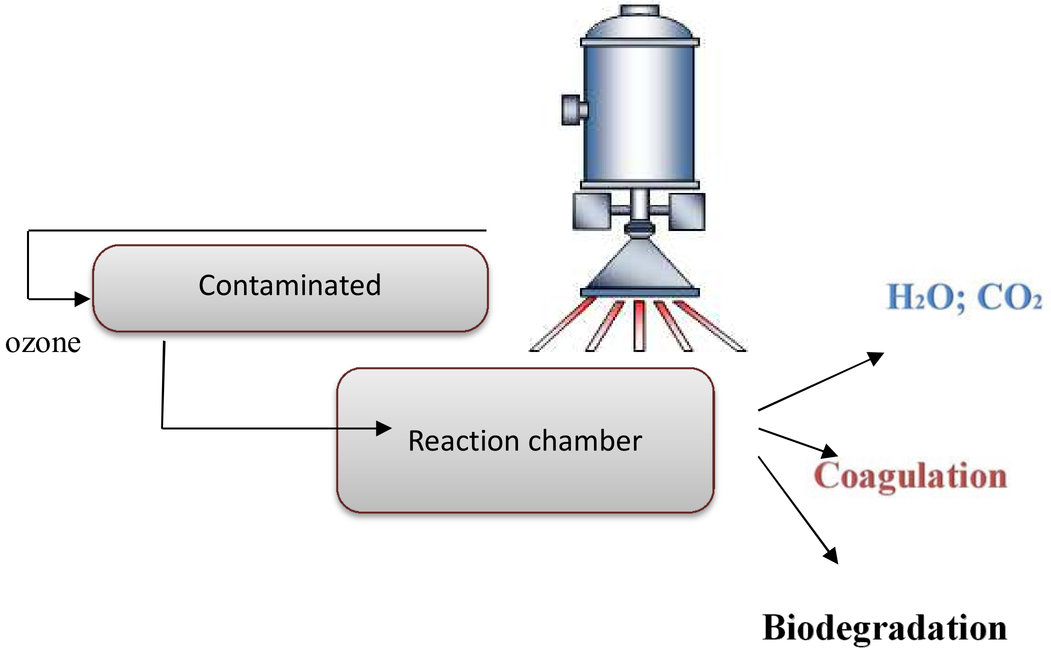

*FIG. 15.2. Radiation treatment of contaminated wastewater*

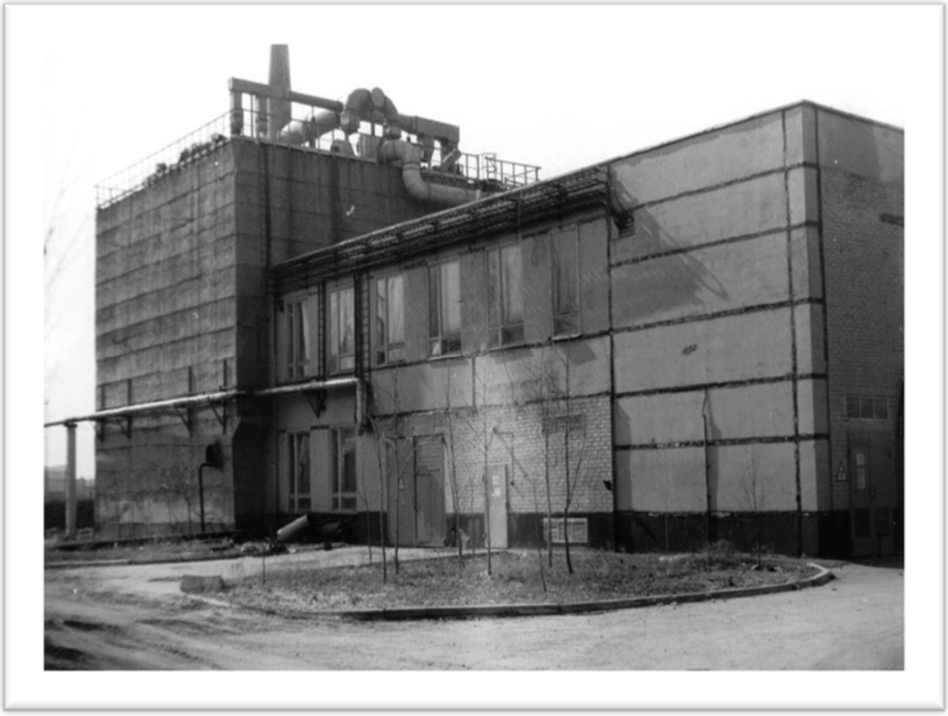

*FIG. 15.3 The first industrial radiation effluent treatment at the petrochemical industries plant (in Voronezh).*

## 15.3. THE PROBLEM OF WORK - TREATMENT OF WASTEWATER FROM HORMONAL COMPOUNDS

In connection with a rather wide spread consumption of hormonal drugs that after removal from the body is not fully decomposed by treatment facilities. Once the drugs are excreted from the human body and get into the river water, they resume their effects in fish. This raises significant changes in aquatic organisms. So, for example, carp on the French part of river Dora Riparia soaked hormonal contraceptive means, have lost their sexual identity so, there is the problem of sewage treatment for purification from hormonal compounds. The experimental investigations were carried out on the use of radiation treatment hormonal compounds, the results of which are shown in table 15.3

TABLE 15.3 THE RESULTS OF PRELIMINARY EXPERIMENTS IN PROCESSING HORMONAL COMPOUNDS SAMPLE NUMBER

| | Absorbed Dose, kGy | Results of analysis on hormonal products presence | Notes |
|---|---|---|---|
| 1 | 3 | Don’t identified | Measurement Limit 10 mcg/l |
| 2 | 1 | Don’t identified | Measurement Limit 10 mcg/l |
| 3 | 0.5 | 56mcg/l | Measurement Limit 10 mcg/l |
| 4 | 0 | 3,5 mg/l | Measurement Limit 10 mcg/l |

These studies were conducted on the pilot plant, scheme of that is shown on the figure 15.4. In parallel conducted experiments on deworming.

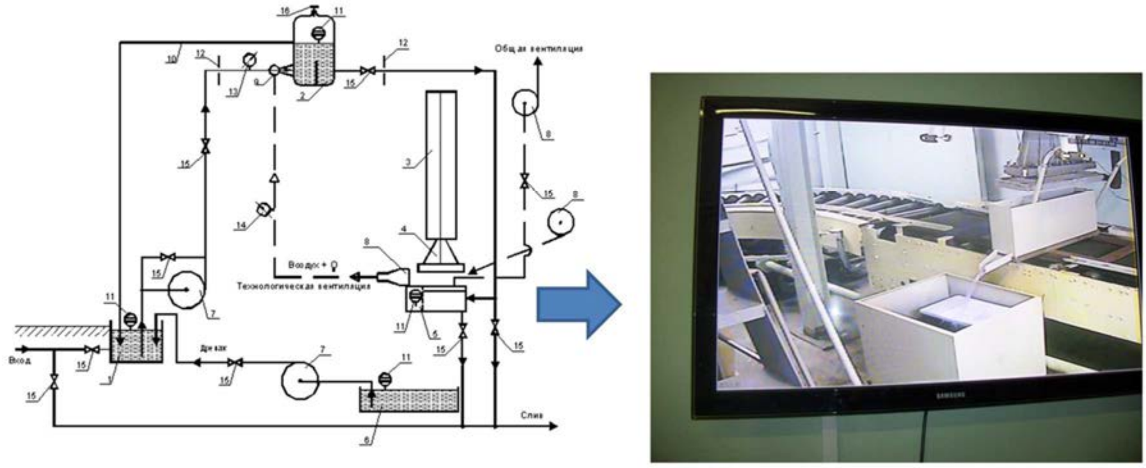

*FIG 15.4. 1-Reception Vessel, 2-Pressure Vessel, 3-Electron Accelerator, 4-Scanner Device, 5-Reaction Chamber 6-Drainage Collector, 7-Pump, 8-Ventilator, 9-Ejector, 10-Plums, 11-Level Gauge, 12-Flow Meter, 13-Pressure Gauge, 14-Vacuum Gauge 15-Valve, 16-Safety Valve*

TABLE 15.4 SHOWS THE TECHNICAL CHARACTERISTICS OF ELECTRON-BEAM TECHNOLOGIES OF WATER TREATMENT

| **Characteristics** | **Unit of measure** | **Value** |
|---|---|---|
| Performance at lower Coli-index by $10^5$ | $m^3/h$ | 1500 |
| Performance mode deworming | $m^3/h$ | 250 - 400 |
| Power beam of accelerated electrons | kW | 150 |
| The energy of accelerated electrons | MeV | 2,5 |
| Energy consumption at the Coli-index by $10^5$ | $kW\text{-}h/m^3$ | 0,3 - 0,4 |
| Energy consumption in deworming | $kW\text{-}h/m^3$ | 1,8 – 2,0 |
| The number of working hours in a year | h | 750 |

Some economic assessment the use of electron-beam treatment of wastewater is given in table 15.5.

TABLE 15.5 ECONOMIC ASSESSMENTS

| Characteristics | Price, rubles | Quantity, Pcs | Cost, rubles | Share, % |
|---|---|---|---|---|
| Electron Accelerator1,5-2.0 MeV power up150 kW | ~ 50 000 000 | 2 | 100 000 000 | 55,2 |
| Technological equipment, automatic control systems and control | 20 000 000 | 1 | 20 000 000 | 11,0 |
| The project site electronic processing (manufacturing and construction). Construction costs (materials and work, including ventilation) | 40 000 000 | 1 | 40 000 000 | 22,0 |
| System locks and alarm | 2 000 000 | 2 | 4 000 000 | 2,2 |
| Dosimetry Systems | 1 300 000 | 2 | 2 600 000 | 1,5 |
| Technical documentation for production | 1 000 000 | 2 | 2 000 000 | 1,1 |

| | | | | |
|---|---|---|---|---|
| Installation and adjustment of equipment | | | 10 000 000 | 5,5 |
| The quality management system | 2 500 000 | 1 | 2 500 000 | 1,5 |
| | In total: | | 181 100 000 | 100,0 |

The presented data show the possibilities and the results obtained radiation techniques including electron-beam treatment of wastewater.

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# 16. POTENTIAL USE OF RADIATION TECHNOLOGY FOR ENVIRONMENTAL REMEDIATION

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**Abstract**

The increasing amounts of organic and inorganic pollutants in environment discharged by various industries, agriculture activities as well as urban activities are causing serious global environmental problems and leading to lower water and air quality which increase risks to health of the living being. These pollutants include a wide range of persistent organic chemicals, such as pharmaceuticals, pesticides, polychlorobiphenyls and endocrine disruptors. Further, the presence of new pollutants called 'Emerging Compounds' in aquatic environments, wastewater and water in low concentration is being reported. Conventional water and wastewater treatments are inefficient for substantial elimination of these pollutants. Therefore, it is essential that research focus on the investigation of appropriate treatment which can be integrated into water and wastewater treatment plants to prevent the discharge of these emerging pollutants into the aquatic environments. In this regard, ionizing radiation is a promising technology for water and wastewater treatment as it offers many advantages over conventional and other advanced processes options. Traditional biological treatment and physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation, and ion exchange) have been used for the removal of certain pollutants (organic or inorganic). Generally, these methods succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. Microbiological or enzymatic decomposition, biodegradation and advanced oxidation processes (AOPs) that generate reactive species *vis-a-vis* organic contaminants as the hydroxyl radical ($^{\bullet}OH$) have also been used for organic pollutants removal from water and wastewaters for purification or reuse, but these methods are still either ineffective or expensive in large scale application. Remarkable enhancement of wastewater quality and water treatment processes is achieved when these processes are combined by adding a chemical agent ($H_2O_2$, $S_2O_8^{--}$, and TiO2). Among these processes, irradiations by electron beam or gamma radiation are emerging and promising methods used in water remediation as well as gas and sludge remediation.

## 16.1. OBJECTIVE OF THE RESEARCH

The objectives of this work were to explain and discuss the ability to deploy ionizing radiation as an emerging technology for environmental remediation, to restate the concept of water radiolysis by ionizing radiation, to illustrate the positive effect of the combination of a non-hazardous chemical agent with ionizing radiation, to establish and assist technical cooperation and to participate in coordinated research program with the member state through IAEA.

## 16.2. INTRODUCTION

Human being plays a fundamental role on the issue of pollutants in aquatic and atmospheric environment beside industries and agricultural activities. Wastewater from industrial and agricultural activities contain chemical pollutants such as phenols, sulfonated halogenated compounds, aromatic derivatives, heavy metals, petrochemical residues, endocrine disruptors, dyes, pesticides, pharmaceuticals and detergents. In addition, the discharge of sewage and sludge gives rise to the microbiological contamination of water [16.1-16.3]. Advanced Oxidation Processes (AOPs) such as ozonation, photolysis, Fenton process that generate reactive species *vis-a-vis* organic contaminants as the hydroxyl radical ($^{\bullet}OH$) are being investigated to treat effluents, particularly from industry. The most important advanced processes used in water treatment are presented in Table 16.1.

Ionizing radiations stemming from electron beam accelerator or Co-60 are part of advanced oxidation processes adequate and could be considered to address to wastewater treatment. Active species (radicals) formed by the penetration of high energy radiation in the contaminated aqueous medium can effectively remove organic pollutants and turn them into relatively less toxic or readily biodegradable substances. Moreover, the reduction of microorganisms and pathogens (disinfection) is achievable with this technology [16.3, 16.4].

TABLE 16.1. MAIN ADVANCED OXIDATION PROCESSES (AOPS) FOR WASTEWATER PURIFICATION

| | **Phase** | |
|---|---|---|
| | **Homogeneous** | **Heterogeneous** |
| **Process** | $H_2O_2/Fe^{++}$ (Fenton reagent) | $TiO_2$/UV (Photocatalysis) |
| | $Fe^{++}$/ $H_2O_2$/UV (Photo Fenton) | $TiO_2$/UV/$H_2O_2$ |
| | $H_2O_2/O_3$ | $TiO_2$/UV/$O_3$ |
| | $H_2O_2$/UV | $O_3$/Catalyst |
| | $O_3$/UV | |
| | Sonochimic | |
| | Electrochimic | |
| | Ionizing radiation | |

### 16.2.1. Water radiolysis

Ionizing of water by high energy radiation produces instantaneous radiolytic transformation through energy transfer from high energy photons or accelerated electrons to the orbital electrons of water molecules. Consequently, three reactive species, hydroxyl radical ($^{\bullet}OH$); hydrated electron ($e^-_{aq}$) which gives the featured of this process and hydrogen atoms ($^{\bullet}H$) are formed as well as les reactive species hydrogen peroxide ($H_2O_2$), hydronium ion ($H_3O^+$), and hydrogen ($H_2$)[16.5]. The most benefits of water radiolysis (in the case of pure water) are the simultaneous formation of approximately equal amounts of $G_{values}$ (0.28 µmol/joule) of hydroxyl radical ($^{\bullet}OH$, a powerful oxidizing species) and solvated electron ($e^-_{aq}$, a powerful reducing species) species.

### 16.2.2. Combination of ionizing radiation with reactive agent/oxidant to enhance degradation

#### *16.2.2.1. Nitrous oxide ($N_2O$)*

The saturation of the solution to be irradiated by the nitrous oxide ($N_2O$) increases the production of hydroxyl radical. Furthermore, nitrous oxide is inert *vis-a-vis* the hydroxyl radical [16.6, 16.7]. Studies have been conducted on the radiolytic degradation of organic compounds in the presence of $N_2O$ to evaluate the degradation and mineralization of 2, 4, 6-trinitrotoluene ($C_7H_5N_3O_6$, TNT) by gamma irradiation [16.8]. The results obtained show a significant improvement in the efficiency of the reaction system when the nitrogen oxide is introduced into the system [16.8].

Similarly, the almost total degradation of perchlorethylene ($C_2Cl_4$, PCE) by electron beam irradiation and gamma irradiation in the presence of $N_2O$ was investigated by Gehringer and Eschweiler, 2002 [16.7],. The addition of nitrous oxide allows a better elimination of atrazine relative to the introduction of dissolved oxygen (Karpel Vel Leitner et al. 1999 [16.9]).

### *16.2.2.2. Dissolved Oxygen*

In the presence of dissolved oxygen ($O_2$) in the solution to be irradiated, the reducing radicals ($e^-_{aq}$ and $H^\bullet$) are converted into oxidizing species hydroperoxyl radical ($HO^\bullet_2$) and superoxide radical ($O_2^{-\bullet}$), reactions (1-4). These species have low reactivity to many organic compounds, such as phenols and aliphatic acids [16.2,16.5]).

$$O_2 + e^-_{aq} \longrightarrow O_2^{-\bullet} \qquad (1)$$

$$O_2 + H^\bullet \longrightarrow HO^\bullet_2 \qquad (2)$$

$$HO^\bullet_2 \longleftrightarrow O_2^{-\bullet} + H^+ \qquad pKa = 4.8 \qquad (3)$$

$$HO^\bullet_2 + O_2^{-\bullet} \longrightarrow HO_2^- + O_2 \qquad (4)$$

The dissolved oxygen ($O_2$) may be involved in reactions with the organic radicals ($R^\bullet$) formed from the degradation of organic pollutants to give peroxides' radical ($RO^\bullet_2$) which is the key element for further mineralization [16.10].

$$RH + {}^\bullet OH \longrightarrow R^\bullet + H_2O \qquad (5)$$

$$R^\bullet + O_2 \longrightarrow ROO^\bullet \qquad (6)$$

$$ROO^\bullet + n\,({}^\bullet OH/O_2) \longrightarrow x\,CO_2 + y\,H_2O \qquad (7)$$

The decomposition and mineralization of 2.4-dichlorophenoxyacetic acid ($C_8H_6Cl_2O_3$) have been improved by the addition of dissolved oxygen in the ionization system [16.11]). Most often, the addition of dissolved oxygen increases the oxidation yields of solute. However, it may sometimes decrease the oxidation by playing a protective role as in the case of formic acid and ethanol [16.12, 16.13]. Also, the radiolytic degradation of atrazine was not favored by the addition of dissolved oxygen [16.9].

### *16.2.2.3. Ozone ($O_3$)*

Getoff in 1996 [16.14] proposed use of electron accelerators which the introduction of the ozone/air during the treatment. The combination of ozone ($O_3$) before or during the electron beam irradiation can increase the concentration of hydroxyl radical [16.15]). This coupling ($O_3$/E.B.) was designed to demonstrate the efficacy. Kubesch et al. [16.16]) studied the degradation of catechol ($C_6H_6O_2$) by ionizing radiation (E.B.), ozone alone and coupling ($O_3$/E.B.), this coupling has been beneficial on the effectiveness of catechol elimination. Similarly, the introduction of ozone in the radiolytic decomposition of 2,4-dichlorophenoxyacetic acid ($C_8H_6Cl_2O_3$) leads to increase the degradation of this organic pollutant [16.17]). The effectiveness of the addition or increase of the ozone concentration in the reaction medium, in particular for the decomposition of trichlorethylene ($C_2HCl_3$) [16.18]) or perochloroethylene ($C_2Cl_4$) (Gehringer and Eschweiler, 2002[7]) was also demonstrated. The addition of ozone also leads to an increase in the yield of radiolytic degradation of atrazine ($C_8H_{14}ClN_5$) [16.9]). The major advantage of this coupling lies in conversion of less active species (radicals $O_2^{\bullet-}$) into ${}^\bullet OH$ radicals.

#### *16.2.2.4. Persulfate ion ($S_2O_8^{--}$)*

The irradiation by ionizing radiation of persulfate ion ($S_2O_8^{-}$) in an aqueous solution leads to the formation of sulphate radicals ($SO_4^{\bullet-}$, E° = 2.6 V) [16.20, 16.21]) by reaction with the hydrated electron ($e^-_{aq}$) reaction 10 [16.5].

$$S_2O_8^{--} + e^-_{aq} \longrightarrow SO_4^{\bullet-} + SO_4^{--} \qquad k=1{,}1\text{x}10^{10}\ M^{-1}s^{-1} \qquad (8)$$

From the results obtained by Boukari et al. [16.22], the addition of persulfate ion improves dramatically the efficiency of phenol ($C_6H_6O$) degradation by electron beam. Also, when the concentration of persulfate ion increases, the elimination of benzotriazole ($C_6H_5N_3$) by electron beam increases [16.23]). The enhancement of citric acid removal and mineralization by electron beam irradiation was enhancing by adding persulfate ion [16.24].

#### *16.2.2.5. Hydrogen peroxide ($H_2O_2$)*

When hydrogen peroxide (electron acceptor) is combined with ionizing radiation, hydrogen peroxide can react with reducing entities, such as the hydrogen atom ($H^\bullet$), and/or hydrated electron ($e^-_{aq}$) which are produced by the radiolysis of water [16.5] . This leads to the formation of $^\bullet OH$ radicals as per reactions (11-14) [16.29, 16.5]. Therefore, it appears appropriate to combine $H_2O_2$ with ionizing radiation in the radiolytic decomposition of organic pollutants [16.25-16.27]. However, an excess of hydrogen peroxide constitutes a trap for the $^\bullet OH$ radical to form the perhydroxyl radical ($HO_2^\bullet$) [16.5, 16.28].

The elimination and mineralization of a persistent toxic organic compound, alachlor ($C_{14}H_{20}ClNO_2$), by gamma irradiation has been improved by the addition of hydrogen peroxide [16.28].

These combinations of oxidants with ionizing radiation could beneficially improve the remediation of wastewater. So, continuous operation and adaptation of this technology in large scale show the capability of ionizing radiation towards enhancement of wastewater remediation and resulted in more significant elimination of TOC which is the ultimate step required at the final stage of water purification by the advanced oxidation processes (POAs), COD, color and $BOD_5$. However, the effectiveness of these processes can be influenced by many parameters, such as load of organic and inorganic pollutants present in the medium to be treated, the oxidant concentration, pH, temperature.

### 16.2.3. Emerging Pollutants

Many researches in recent years have reported the presence of new chemical compounds, called "emerging pollutants" in wastewater and aquatic environments in low concentration which are chemicals without regulatory status and which impact on environment, human health and animal health are poorly unknown (US-EPA). The EU water framework directive 2000/06/CE announced in annex X a list of 33 priority substances or groups of substances which include metals, pesticides, phthalates, polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs) and endocrine disruptors (EDs). These substances must be removed within an objective of quality and preservation of good ecological status of water by 2015. Some of them are considered as carcinogenic, toxic and persistent. In this regard, by-products formed during water treatment by AOPs should be going under this category of pollutants. Despite the earlier research for the elimination of this category of pollutants, the expanding and demonstration of deployment of clean (Green) radiation technology to remove these emerging pollutants should be redone and represented for scientific community as well as governmental authority [16.1, 16.30].

### 16.2.4. Flue Gas remediation

While the presence of water pollution, logically there is also air pollution. For example, during the combustion process (coal, oil and natural gas), different pollutants are released into environment. These pollutants have major negative impacts on atmosphere, human health as well as animal health. Pollutants like sulphur dioxide ($SO_2$) and nitrogen oxides (NOx) and else are treatable before they emitted to atmosphere by ionizing radiation (electron beam accelerators). By this treatment, valuable by-products could be used or commercialized as an agricultural fertilizer (ammonium sulphate $(NH_4)_2SO_4$ and ammonium nitrate $NH_4NO_3$). The application of electron beam technology for flue gas treatment has been studied and developed from pilot laboratory scale to large industrial scale in Japan, USA, Germany, Poland, Bulgaria, China and Saudi Arabia [16.31-16.35].

### 16.2.5. Wastewater remediation

While the main purposes of wastewater treatment is removal of harmful impurities, color, odor and total elimination of organic as well as inorganic pollutants, high-energy electron beam irradiation is among the advanced oxidation processes (AOPs) which can effectively and economically achieve these purposes and removes these pollutants from solutions. Among the countries which are implemented this technology to wastewater treatment for save discharge to river, reduction of organic load or reuse in industry or irrigation in large scale, the Russian federation (for conversion of non-biodegradable plant waste into a biodegradable form from rubber industry) this facility treats up to 2000 $m^3$ [16.36]. also Republic of Korea developed this technology for treating wastewater from dyeing industry [16.37]), in United States electron beam irradiation was used in groundwater remediation, in Brazil a pilot scale for wastewater treatment plant was setup to study the efficiency of removal and degradation of toxic and refractory pollutants present in industrial wastewater (Sampa 2003 [16.38]).

### 16.2.6. Sewage sludge remediation

Wastewater treatment plant generally requires disinfection step to meet regulatory microbial limits. The sewage/sludge contains bacteria, viruses, and parasites which should be hygienized prior to reuse it as a bio-fertilizer. The ionizing radiation interacts with the microorganisms directly/indirectly causing the death of the pathogenic organism. Directly through high energy radiation on the nucleic acid (DNA) or on the protein presents in the microorganisms. Indirectly by the actives intermediates species formed during the radiolysis of water ($e^-_{aq}$, $^{\bullet}OH$). The first commercial electron treatment system for the disinfection of liquid sludge is installed in Florida by the Miaml-Dade Water and Sewer Authority [16.30]). Applications of irradiation technology for sludge disinfection are feasible, economical and alternative process [16.3, 16.39, and 16.40]. Recent research in various countries in both experimental scale and industrial scale has shown that sewage/sludge can be advantageously disinfected by gamma or electron beam irradiation technologies [16.3, 16.41]. Some of these countries are the United States, Canada, Japan, Germany, Brazil, Poland, Korea and India.

Figure 16.1 summarizes the applications of radiation technology in a variety of applications including environmental remediation.

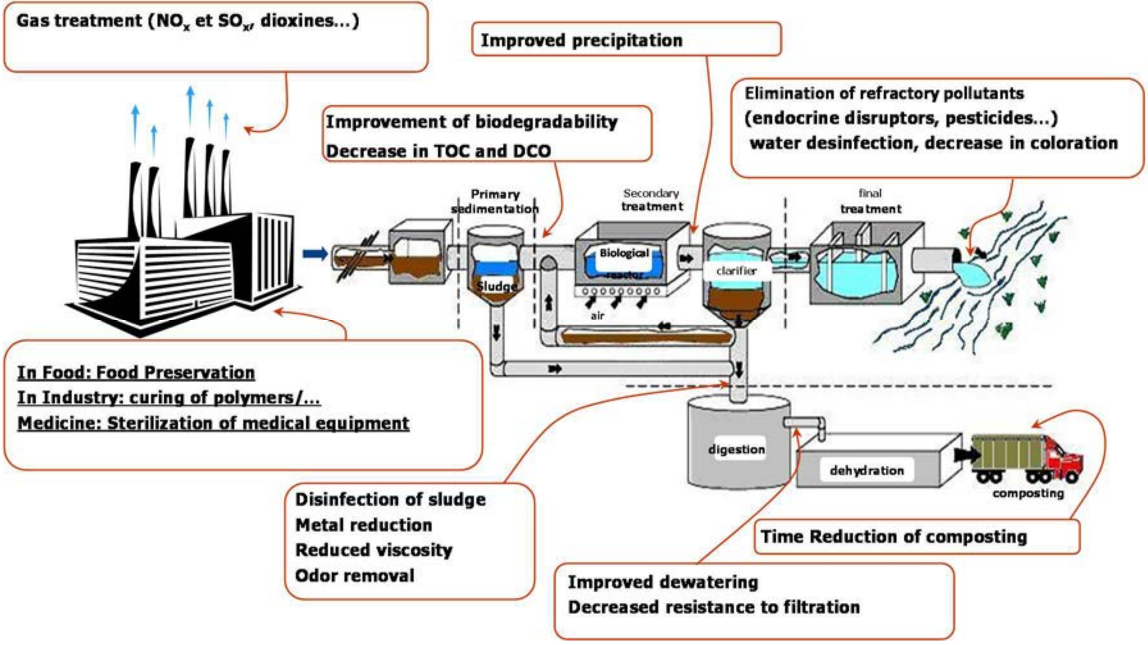

*FIG. 16.1. Schematic diagram of ionizing radiation applications*

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# 17. ACTIVITIES FOR ELECTRON BEAM REMEDATION OF ENVIRONMENT POLLUTED BY PCB

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**Abstract**

Environments in many countries, even those which have never produced PCBs have been contaminated by these substances. PCBs are persistent substances that in the environmental conditions degrade very slowly. The Slovak Republic is among the countries at high risk of harm of large group of the population (200,000) living in the contaminated district of area 40x80km$^2$. Slovak Medical University in Bratislava in collaboration with other institutes has performed a mapping of PCBs concentration in the contaminated environment, which was used in presented project for electron beam remediation of environment polluted by PCB. Based on a study, environmentally friendly methods of removing PCBs by transportable facility as most appropriate was selected radiation degradation method of PCBs. Experimental tests with real samples of sediments (PCB concentration of 100 μ g per g of sediment) showed 40% and 50% decrease PCBs concentration in the samples irradiated by dose of 100 kGy. For a period of 10 years of cleaning about 60 000 tons of sediment Strážske channel and Laborec river by the dose 350 kGy the power 100kW in the beam electron accelerator has been proposed. The transportable shielding of the accelerator producing electrons of energies from 2.5 to 10 MeV has been designed. Investment cost of 4.2 M € for an electron accelerator 2,5 MeV/100kW, transportable shielding construction, autonomous power supply, conveyor and other devices for irradiation facility operation has been estimated. The estimation of the annual cost of three-shift operation 13M € was performed.

## 17.1. OBJECTIVE OF THE RESEARCH

The goals of the work are to:

–point to environmental contamination by PCBs substances as the multiregional problem regardless of whether in the contaminated area was PCB produced or transported in products transported (i.e. electrical transformers) or in environmental compartments such as river sediments, or dust.

–justify radiation degradation of PCBs in the environment as efficient and environmentally friendly method.

–design of transportable powerful electron accelerator for radiation cleaning of environment.

## 17.2. INTRODUCTION

The Slovak Medical University (SMU) has been more than 10 years dealing with issues of occurrence and impact of PCB contaminants in the environment of eastern Slovakia. Specialists of SMU conducted studies and coordinated domestic and international projects as a solver. The projects were aimed at mapping of PCBs in the environment of eastern Slovakia, and the impact of PCBs on the health of the population living in the affected area, especially the pediatric population. Over the past years, the SMU built an analytical laboratory certified to measure PCBs in environmental samples. This laboratory is equipped with technological equipment and qualified personnel as one from leading laboratories of its kind in the EU.

Compounds such as polychlorobiphenyls (PCBs) and DDTs, in the worldwide environment have been recognized as a consequence of their extensive use [17.1–17.2]. PCBs are persistent organic substances that bio accumulate and have adverse effects on human health and the environment. Various PCB forms are responsible for numerous toxic effects, including disorders of the immune and nervous system, reproductive abnormities, behavioral abnormities, and likely carcinogenicity (they induce cancer in animals; no similar effect however could be unambiguously demonstrated in humans). Strong toxicity may even result in death. Children exposed to higher PCB levels during intrauterine development were reported to suffer from impaired visual cognition, impaired verbal memory and learning ability, lower IQ, and their ability to understand read text was delayed.

For various social and economic reasons PCBs are still in use, e.g. in electrical equipment or are in storage, mainly in developing countries and in countries with economies in transition [17.3].

Important components of the environment contaminated with PBC are transformer oils, oil in capacitors and other devices and oil in sediment streams, reservoirs and seabed. Environmental PCB contamination is widespread in many areas of the world. When choosing an appropriate method degradation of PCBs in contaminated environment the requirements for the degradation of PCBs in relatively large areas of waste, environmental protection and non-static facility were taking into account. In this way the method of radiation degradation of PCBs by mobile or transportable facility has been chosen. Mobile facility is equipped by an electron accelerator with massive shielding that is installed directly on truck chassis. The shielding may have dimensions that enable free movement of the truck on the roads. This requirement on shielding dimensions is limiting the choice of power and energy of electron beam produced by a mobile accelerator, which is disadvantage for applications in environment where large material quantity should be irradiated. Disadvantages of mobile electron accelerators may be removed by construction of transportable irradiation facility. Transportable irradiation facility consists of accelerator and modular shielding. Modular shielding is constructed from steel modular boxes that are filling by shielding material. Dimension of the modular boxes makes it possible to upload one empty box to another empty box (as “matrioška”).

Empty modular boxes and accelerator are transported by several trucks to locality of interest where the irradiation facility is built from the modules and filling by appropriate shielding material. This modular shielding can be designed with regard to beam power and electron energy produced by accelerator without any other restriction. In the present paper a transportable irradiation unit with electron accelerator of electron energies from 2.5 up to 10MeV and beam power100 kWis proposed.

By 5 MeV electron beam the effectiveness of radiation degradation of PCBs in real samples of contaminated sediment from the river Laborec was performed.

## 17.3. MATERIALS AND METHODS

With regard to PCBs, obligations for Parties under the Stockholm Convention include to eliminate the use of these substances in equipment (e.g. transformers and capacitors) by 2025 and to make determined efforts towards the environmentally sound management of PCB waste by 2028 [17.4]. The majority of vast is located in Europe (Belgium, Czech Republic, Finland, France, Germany, Italy, Poland, Russia, Slovak Republic, Switzerland, The Netherlands, UK) followed by North America, Asia, Latin America, Africa, Australia and New Zealand. Long-range transport of the PCB substances to regions where they have never been used or produced is evident [17.5].

### 17.3.1. PCB in Slovakia

In the former Czechoslovakia, PCBs had been produced at the Chemko Strážske chemical factory in the period of 1959–1984 as commercial PCB mixtures under the brand names Delor, Hydelor, and Delotherm. During the PCB production at Chemko, extensive environmental leaks occurred, in particular via wastewater discharge. As a result, the sediments of the wastewater channel of Chemko, of the River Laborec, as well as of the Zemplínska Šírava artificial lake, have become contaminated. Zemplín locality is contaminated by PCBs on area 40x80km$^2$ with about 200 000 inhabitants [17.2]. The region of Zemplín (Michalovce district) belongs to the most PCB heavily polluted areas all over the world, Fig. 17.1.

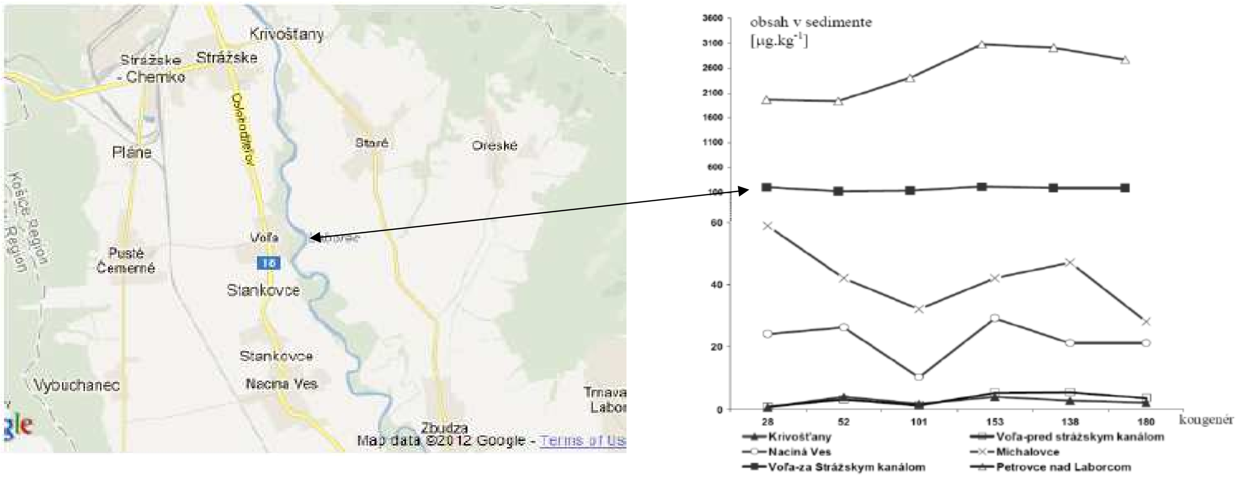

*FIG. 17.1. Distribution of PCB contaminants from Srážsky channel up to Zemplínska Šírava and Michalovce district*

Thickness of sediments contaminated by PCB of Strážsky channel and of Laborec river is between 7 up to 10 cm. Total volume of these contaminated sediments is of about 40 000 m$^3$.

### 17.3.2. Techniques for destruction of PCB

There are several techniques for destruction of PCB, but most of them are not suitable for application in environment. Incineration is the most commonly used treatment process for PCB-laden soil, sediment, and electrical insulating oils contaminated at levels greater than 500 ppm. In 1994, incineration was selected by U.S. EPA to be used at 90% of Superfund sites where PCB destruction was required. The method has two disadvantages: it incinerates the medium along with the PCBs, and it converts some of the PCBs into more toxic materials, namely, dioxins and dibenzofurans. In addition, lead, a metal commonly found in areas with PCB contamination, volatilizes at most incinerator operating temperatures. The high cost and poor public approval of incineration have created a need for alternative treatment technologies for sites contaminated with dioxins, PCBs and chlorinated pesticides. Dredging and disposal is currently considered as a cleanup method for PCB laden sediment. This method is often expensive and may temporarily increase the contamination as well as destroy wildlife habitat. Moreover, after dredging the removed sediments have to be treated or buried somewhere else, so this process transfers the problem. Other approaches include the washing of sediment with organic solvents or surfactant solutions, although the effluent resulting from the wash

processes may have to be treated or disposed of as hazardous (i.e., PCB contaminated) waste following sediment cleanup. Bioremediation is also a promising technique for the removal of PCBs from sediment. However sediment-associated PCBs are often too deeply embedded in sediment particles to be readily available for consumption by the microorganisms. The addition of activated carbon as a particulate sorbent to biological layers of contaminated sediments has also been investigated as a non-removal treatment of marine sediment contaminated with hydrophobic organic compounds. However the activated carbon must eventually be treated. Radiation degradation of PCBs and other chlorinated compounds in various matrices may overcome these disadvantages [17.6]. Ultraviolet (UV) irradiation of PCB-laden transformer oils has been shown to effectively dechlorinate PCB congeners. For example, UV-irradiation of PCB contaminated sediment in the presence of triethylamine was shown to dechlorinate PCB congeners . Dioxin-contaminated sediments were effectively treated with gamma radiation. Off-line supercritical fluid extraction of PCBs from contaminated soil followed by gamma-radiolysis has been shown to reduce a tetrachlorobiphenyl congener in association with soil. High-energy electron treatment of matrices contaminated with organic compounds can effectively destroy contaminating compounds. Research performed has demonstrated that ionizing radiation produced by high-energy electrons is remarkably effective in transforming PCBs into less problematic species. The PCBs may be reduced to inorganic chloride and biphenyl (both of which are environmentally acceptable), while the organic solvent or oil may remain practically unchanged and can be recycled.

Radiolysis has been shown to effectively dechlorinate PCBs in water, aqueous micellar systems, alcohols, and transformer oil.Similarly, the extraction of PCBs from soil followed by the flotation of the solvent and subsequent radiolysis of the floatant has been reported, along with the radiolysis of PCBs associated with soil. There are few studies related to the radiolytic degradation of PCBs associated with sediment. However, due to their hydrophobicity, PCBs in organic matrices such as oils and organic-rich sediments can only be effectively solubilized in water with the use of an organic cosolventor a surfactant, a necessary process for effective radiolysis.

### 17.3.3. Experiments

Experiments with samples of sediments from Laborec river have been performed for testing of PCB radiation degradation efficiency with regard to treatment of PCB contamined sediments and aplied irradiation dose.

The commercial PCBs Delor 103 and Delor 106, produced in Chemko Strážske, are mixtures of about 40 to 80 PCB various chlorinated congeners with chlorine substituent numbers 1–10. Samples for verification of PCB radiation degradation were collected from stream channel of Laborec river at the village Voľa. The average PCB concentration in the sediment of the river Laborec at Voľa village is about 100μgkg$^{-1}$.

Radiation dechlorination of PCBs in sediment samples has been tested by 5MeV/1kW electron beam. Description of sample chemical pre-treatment and dose of sample irradiation are given in Table 17.1.

PCB concentration in irradiated samples was based on determination of congeners No.111, 124, 144 and 146 in samples No. 1 to 10. In comparison to the sample No.10, the average PCB concentration in the samples No. 2, 8 and 9 was decreased by 40%. In the sample No.4 the PCB concentration was reduced by 50%.

TABLE 17.1. DESCRIPTION OF SAMPLE CHEMICAL PRE-TREATMENT AND DOSE OF SAMPLE IRRADIATION

| No. | Sample description | Dose | Notice |
|---|---|---|---|
| 1. | 20g sediment + 2g $K_2CO_3$ + 1ml $H_2O_2$ (30%) | 100 kGy | |
| 2. | 20g sediment + 2g $K_2CO_3$ + 1g charcoal | 100 kGy | |
| 3. | 20g sediment + 2g $K_2CO_33$ + 0.5 g detergent | 100 kGy | |
| 4. | 20g sediment + 2g $K_2CO_3$ + 1g CuSO4.5$H_2O$ | 100 kGy | |
| 5. | 20g sediment + 2g $K_2CO_3$ | 100 kGy | |
| 6. | 20g sediment + 2g $K_2CO_3$ | 100 kGy | 50ºC |
| 7. | 20g sediment + 1g $K_2CO_3$ | 100 kGy | |
| 8. | 20g sediment + 2g $K_2CO_3$ | 100 kGy | |
| 9. | 20g sediment + 3g $K_2CO_3$ | 100 kGy | |
| 10. | 20g sediment | 0 kGy | reference |

### 17.3.4. Transportable facility for electron beam remediation of environment polluted by PCB

The EB irradiation facility is technology with no secondary waste generation, no catalysts, no heating and is easy for automation. These characteristics are in agreement with basic technological requirements formulated by inhabitants of contaminated districts. We have prepared a pilot project funded by our country with aims:

- construction the prototype plant with properties clean (green) technologies to restoring the environment,
- development of environmentally friendly nuclear method for removal of PCB,
- reducing the concentration of PCB contaminants in the environment to create the conditions for long-term improvement in the health status of the population in the district of Michalovce,
- cleaning of sediment in Zemplínska Šírava, which will intensify a development of tourism and industrial exploitation of the whole area, including fishing permits, allowing the creation of new jobs in an area with a high percentage of unemployment.

The project proposes a technical design of transportable devices for radiation remediation of locality Strážske from PCB pollutant that demonstrates negligible environmental impact and ensures that once the necessary action is over it moves to another site environment

The power of electron beam (thereinafter accelerator power) for the volume of sediments with PCB 40 000$m^3$ with density about 1,5$gcm^{-3}$, irradiation dose 350kGy and acceptable irradiation time 10 years of the contaminated sediments is calculated:

$$P(kW)=D(kGy)\ .\ M(kg\ s^{-1})\ /\ \varepsilon$$

Where : D - absorbed dose (350kGy)

M - mass of irradiated material (40 000$m^3$.1,5$tm^{-3}$/80 000h/10y=0,75$th^{-1}$)

ε efficiency of the process (0,7)

D irradiation dose (350kGy),

40 000t/10 years of operation (750$kgh^{-1}$) and efficiency of the process $\varepsilon$ =0,7

Desired EB power: P(kW)=350kGy . 750kg/3600/0,7=104 kW

Parameters and properties EB irradiation unit

The transportable electron beam system for application in environment with following parameters and properties:

- high reliability
- high efficiency 50-95%
- power 100kW
- electron energy 2,0-5 MeV
- electron accelerator cost ≤2M€
- not large
- continuous operation (over 8000 hours per year)

Advantages of transformer accelerators: high effectiveness and high reliability make this type of accelerators atractive for using in environment. Disadvantage of the transformer accelerators is low energy, see Table 17.3.

TABLE 17.2. CAPABILITY OF D.C. POWER SUPPLY FOR TRANSFORMER ACCELERATORS

| Accelerator | Power line transformer | Cockckroft-Walton | HF Transformer | Dynamitron |
|---|---|---|---|---|
| Ratings | 150-1000kV<br>10-1000 mA | 300-5000 kV<br>30-1000 mA | 500-1000 kV<br>30 mA | 500-5000 kV<br>1-70 mA |
| Frequency | 50/60 Hz | 1-3 kHz | 20-50 kHz | 50-100 kHz |
| Insulation | Oil/SF6 | SF6 | SF6 | SF6 |
| Efficiency | >90 % | 70-80 % | 85 % | 30-60 % |
| Remarks | Low energy<br>High power | High energy<br>High power<br>Large | High energy<br>Low power<br>Compact | High energy<br>Low eff. |

### Transportable irradiation facility with electron accelerator

Transportable irradiation facility is basedon construction of modular shielding transportable by truck.

Shielding modules are transported empty and are filling by shielding material at the place where PCB contamination should be degradated.

Design of transportable irradiation unit for acelerator of electron energies from 2.5 up to 10MeV and beam power100kW is shown in Fig. 17.2.

Material composition of shielding material is chosen with regard to energy and intensity of electron beam. The composition of shielding material is calculated by the Monte Carlo code MCNPX. Thus the modular shielding can be used for various electron accelerators and various application of radiation processing. On the other hand in this case a new licensing for acelerator operation should be approved.

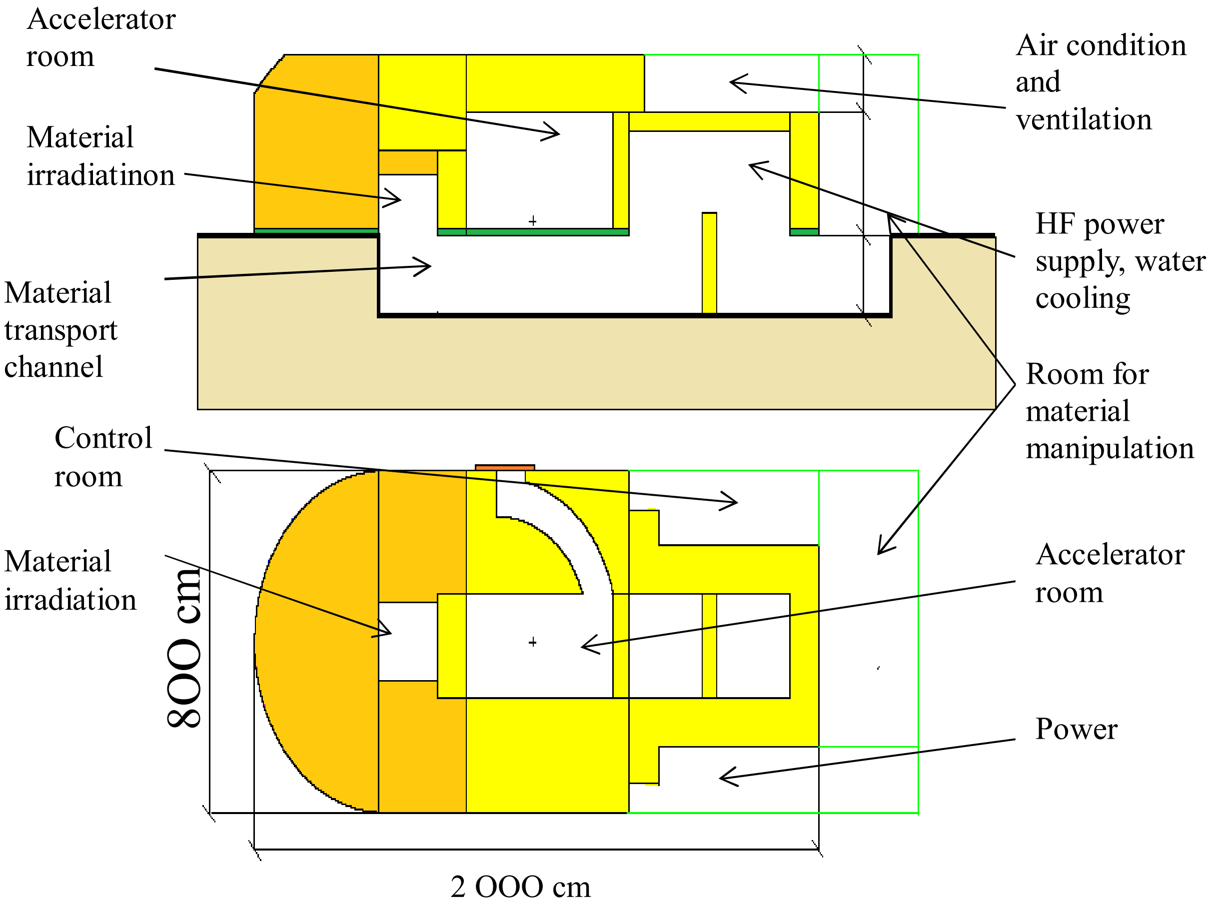

*FIG. 17.2. Design of transportable irradiation unit for acelerator of electron energie from 2,5 MeV up to 10MeV and beam power100kW*

As shielding materia for accelerator 2,5MeV/100kW can be used ordinary sand.

Annual operation costs for degradation of PCB in river sediments by irradiation unit with electron accelerator 2,5MeV/100kW is given in Table 17.3.

TABLE 17.3. ANNUAL OPERATION COSTS FOR DEGRADATIONOF PCB IN RIVER SEDIMENTS

| Items | | | Cost* [k€] | Remarks |
|---|---|---|---|---|
| Operation cost | Fixed | Investment | (4 200) | |
| | | Interest | 336 | 8% |
| | | Depreciation | 210 | 20 years |
| | Variable | Electricity | 342 | 350 kW |
| | | Labour | 300 | 3 shifts |
| | | Maintenance, etc. | 112 | 2% |
| Total cost | | | 1300 | E-beam |

*Accelerator DC/2-5MeV/100kW, transportable modular shielding, diesel aggregate, conveyor, etc.

Operation cost for degradation of PCB in 1 kg of sediment irradiated by EB/350kGy
1,300k€ /year/15,000 kg/20h(day) /300days/year ≈ 0,3€ per kg

## 17.4. CONCLUSIONS

Technical solution of modular transportable electron beam irradiator for treatment of environment contaminated by PCBs was proposed.

The modular shielding of the transportable electron beam irradiator can be used for various electron accelerators and various application of radiation processing.

Annual operation costs for degradation of PCB in river sediments with 100kW electron accelerator was presented.

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# 18. RADIATION PROCESSING OF POLYMERIC MATERIALS FOR INDUSTRIAL APPLICATIONS AND ENVIRONMENTAL PRESERVATION: THAILAND CONTRIBUTION

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**Abstract**

In the first part, radiation-induced crosslinking of PLA was investigated. Results showed that the presence of a suitable crosslinking agent (TAIC) enables PLA to undergo crosslinking induced by gamma radiation. The optimum condition for radiation-induced crosslinking of PLA was determined. TMA results revealed that PLA cross-linked by gamma radiation has higher thermal stability, compared to unirradiated PLA. In the second part, unmodified silica, silica modified with Si69, silica modified by thermal admicellar polymerization and silica modified by radiation-induced admicellar polymerization were applied as rubber reinforcement. The results revealed that the mechanical properties of rubber reinforced with silica modified by admicellar polymerization were superior to those reinforced with unmodified silica or silica modified with Si69. In the third part, metal adsorbent containing hydroxamic acid groups was successfully synthesized by radiation-induced graft copolymerization of methyl acrylate (MA) onto cassava starch. The maximum percentage conversion of the ester groups of the grafted copolymer, % Dg = 191 (7.63 mmol/g of MA), into the hydroxamic groups was 70% (5.35 mmol/g of MA) at the optimum condition. The adsorbent of 191 %Dg had total adsorption capacities of 2.6, 1.46, 1.36, 1.15, and 1.6 mmol/g-adsorbent for $Cd^{2+}$, $Al^{3+}$, $UO_2^{2+}$, $V^{5+}$ and $Pb^{2+}$, respectively, in the batch mode adsorption.

## 18.1. OBJECTIVE OF THE RESEARCH

Our objective focuses on the use of radiation processing to modify properties of polymeric materials. In the first part, radiation-induced crosslinking was applied to improve mechanical and thermo mechanical properties of PLA. In the second part, radiation-induced admicellar polymerization was used to render silica surface more compatible with natural rubber. In the third part, metal adsorbent was prepared by radiation-induced grafting copolymerization of methyl acrylate (MA) onto cassava starch.

## 18.2. INTRODUCTION

Poly (lactic acid) or polylactide (PLA) is a compostable thermoplastic obtained by ring-opening polymerization of lactide monomers which can be derived from renewable resources [18.1], such as starch or sugarcanes. In recent years, PLA has been receiving a great deal of attention, essentially due to its degradability. For this environmental-friendly profile, along with a highly transparent appearance, similar to that of polyethylene terephthalate (PET), PLA has undoubtedly become one of the most promising alternatives to non-biodegradable synthetic polymers conventionally derived from petroleum-based chemicals. Nonetheless, two of the most important factors that prevent PLA from being commercially and widely used are its low thermal stability [18.2–18.3] and high cost, compared to commercial plastics such as polyethylene (PE) or PET commonly used in packaging materials. This work intends to utilize radiation processing as a means to overcome the aforementioned shortcomings associated with PLA, by using radiation-induced cross-linking to improve its thermal stability.

Applications of natural rubber as everyday products are continuously increasing. Fillers are normally added to rubber to achieve desired properties suitable for specific applications. Silica is well-known as one of the most common fillers in the rubber industry. Nevertheless, adhesion between the surfaces of silica and rubber is rather poor, since the silica surface is hydrophilic, while the rubber surface is hydrophobic. This weak adhesion can result in detachment of silica particles from the rubber matrix. A number of research groups modified the silica surface by a technique called admicellar polymerization to form a thin polymeric film on the silica surface, in order to enhance the adhesion between the surfaces of silica and rubber [18.4–18.6]. Admicellar polymerization was initially introduced by Wu et al. in 1987 [18.7]. The technique comprises of a 4-step process; admicelle formation on the surface, monomer adsolubilization, polymerization of monomers dissolved in admicelles and surfactant removal to expose the formed polymer film. A number of researches have applied admicellar polymerization to modify the silica surface and analyzed the mechanical properties of rubber reinforced with the modified silica. This research aims to apply silica modified by radiation-induced admicellar polymerization as fillers for natural rubber and investigating the mechanical properties of the reinforced natural rubber.

Polymeric chelating resins containing hydroxamic acid group have been used for extraction and separation of metal ions due to the ability of hydroxamic acid group to form complexes with various metal ions [18.8] (Mendez and Pillai, 1990). Poly (hydroxamic acid) chelating resins can be synthesized from several polymers such as poly (styrene-co-maleic acid) and poly (methacrylate). Starch is a natural polymer that can be chemically modified to give novel properties for different purposes. A number of studies investigated graft copolymerization of vinyl monomers on starch [18.9] and discovered that chemical modification can expand the range of its utilization. The main objective of this research is to convert cassava starch into useful product for environmental application. In the present work, an adsorbent containing hydroxamic acid groups was synthesized by radiation-induced graft copolymerization of MA onto cassava starch.

## 18.3. MATERIALS AND METHODS

### 18.3.1. Radiation-induced crosslinking of PLA

#### *18.3.1.1. Materials*

Polylactic acid (PLA 2002D) was purchased from Nature Works® (USA). Triallyl isocyanurate (TAIC) was supplied by Aldrich (USA). Chloroform (Lab Scan) was used as received.

#### *18.3.1.2. Sample Preparation and Irradiation*

PLA pellets were dried in a vacuum oven at 75°C for 24 h. A co-current twin-screw extruder (Lab Tech, LTE16-40, Thailand), equipped with segmented screw of diameters of 16 mm and L/D ratio of 40, was used to mix PLA with TAIC at different concentrations: 0, 1, 3 and 5 phr (hereafter referred to as T0, T1, T3 and T5, respectively). The temperatures of barrel heating zone I, II, III, IV and of the die of the extruder were set to 155, 175, 185, 195, and 200°C, respectively. The TAIC-containing PLA pellets were then compressed by a compression molder (Lab Tech, Thailand) to form 150 mm x 150 mm x 0.2 mm films. The pellets were pre-pressed and full-pressed at 200°C for 8 and 2 min, respectively, followed by cold-pressing at room temperature for 2 min.

The film samples were irradiated at the Office of atoms for Peace (OAP) using a Co-60 gamma irradiator (GammaCell® 220 Excel, Nordion, Candida) at 20, 40, 60, 80 and 100 kGy, under vacuum.

#### *18.3.1.3. Mechanical Properties*

The mechanical properties were measured at room temperature on a tensile tester (AG-100kNG, Shimadzu, Japan) at a crosshead speed of 10 mm/min. Sample preparation was done using a SD-type lever-controlled sample cutter (SDL-100, Dumbbell Co., Ltd., Japan) and a super dumbbell cutter (SDMK-1000-D, Dumbbell Co., Ltd., Japan), according to the ASTMD-638-IV. For each blend composition at each condition, ten samples were tested and the results were averaged. A thermomechanical analyzer (Mettler Toledo, TMA/SDTA 841$^e$) was used to study the thermo mechanical properties of the samples. Sample films (thickness 0.2mm) was fixed to the sample holder under a constant load of 0.5 g (0.004 Newton) and heated from 0°C to 260°C at a heating rate of 10°C/min. The deformation (%) was recorded against the temperature.

### 18.3.2. Radiation-induced admicellar polymerization of isoprene on silica

#### *18.3.2.1. Materials*

Natural rubber (STR 5L) and silane coupling agent (Si69) were obtained from Bangkok Rubber Co., Ltd. (Bangkok, Thailand). Silica Hi-Sil®233 (Siam Silica Co., Ltd., Thailand), dodecyltrimethylammonium bromide ($[CH_3(CH_2)_{11}N(CH_3)_3]Br$, or DTAB) (98.0%, Fluka, Switzerland), tetradecyltrimethylammonium bromide ($[CH_3(CH_2)_{13}N(CH_3)_3]Br$ or TTAB) (99%, Acros, Belgium), Cetyltrimethylammonium bromide ($[CH_3(CH_2)_{15}N(CH_3)_3]Br$ or CTAB) (98%, Fluka, Switzerland), isoprene (98%, Fluka, Switzerland), potassium persulfate ($K_2S_2O_8$, Fluka, Switzerland), and tetrahydrofuran (Fisher Scientific, USA) were used as received. Gamma irradiator used was a Gammacell 220 Excel from MDS Nordion, Canada.

#### *18.3.2.2. Thermal admicellar polymerization*

The surfactant was dissolved in 100 ml of distilled water. The amounts of surfactants used were 2.5, 1.5 and 1 mmole for DTAB, TTAB and CTAB, respectively. The solution was adjusted to pH 8 by sodium hydroxide. Then 2.5g of silica was added into the mixture. The mixture was continuously stirred for 24 h. Ethanol, potassium persulfate and isoprene were afterward added. The molar ratio of the surfactant to ethanol was 1:43, while that of the monomer to potassium persulfate was 10:1. The molar ratio of the surfactant to the monomer was varied (1:2, 1:4, 1:6, 1:8, 1:10, 1:12 and 1:14) to determine the optimum condition. The mixture was then gradually stirred and heated to 80°C, where the temperature was held for 3 hours to induce the polymerization. The silica samples were subsequently filtered and washed many times with distilled water until the redundant surfactant and the upper layers of admicelle formed on silica surface were completely removed. After the washing steps have been thoroughly done, the washing water was analyzed by UV to see whether there is some remaining outer-layered surfactant. We further confirmed the removal of the outer-layered surfactant by floating test. Once the outer-layered surfactant has been removed, the surface will be hydrophobic and therefore the samples will be floating on the water surface. On contrary, if there is some remaining outer-layered surfactant, the surface will still be hydrophilic and the samples will be sinking down at the bottom. The silica samples were later dried in an oven at 40°C for 3 days, before the characterization.

#### *18.3.2.3. Radiation-induced admicellar polymerization*

The experiment was mostly done the same way as in the thermal process, except that there was no addition of potassium persulfate and gamma radiation was used instead of heat. The amount of surfactant used was 2.5, 1.5 and 2.5 mmole for DTAB, TTAB and CTAB, correspondingly. The molar ratio of the surfactant to ethanol was 1:43, whereas that of the surfactant to the monomer was 1:6. To determine the optimum dose, the mixture was irradiated at the total dose of 5, 6, 7, 8, 9, 10, 11, 12 and 13 kGy, at the dose rate of 0.17 kGy/min. The washing and drying processed were done precisely the same way.

#### *18.3.2.4. Rubber mastication, compounding and vulcanization*

Rubber (STR 5L, 600g) was masticated in an Internal Mixer (Lab Tech Engineering Co., Ltd., Bangkok, Thailand) at 60 °C. After masticating the rubber for 3 min to reduce its viscosity, the ingredients according to the formulation of the rubber compound, shown in Table 18.1, were added, gradually and respectively. The first two compounds added were activators (zinc oxide and stearic acid, in that order) and the mixture was masticated for 2 min. Next, the filler (unmodified or modified silica) was put in and the mastication continued for another 2 min. After that, processing aids (PEG 400, Shellflex oil and wax) were correspondingly added. Then, antioxidation reagent (22CP46) was added and the mixture was thoroughly masticated. Subsequently, accelerators (mercaptobenzothiazole (MBT), mercapto benzothiazyl disulphide (MBTS) and tetramethylthiuram monosulfide (TMTM), respectively) were added and the mastication was maintained for another 2 min. Finally, sulfur was added as a vulcanizing agent. The rubber compound was thoroughly masticated to ensure that all ingredients were fully mixed. After mastication, a Rheometer (EK 100H, EEKON) was used to determine cure time. The rubber compound was compression molded with a Compression Mold (DAH TYAN Industrial Co., Ltd.) at 160 kg/cm$^2$ at a 160 °C cure temperature. The vulcanized rubber was left intact for 24 h, before it was subjected to mechanical tests.

#### *18.3.2.5. Characterization*

Scanning electron microscope (SEM) by JEOL (Model JSM-5410LV) was used to study surface morphology and elemental analysis. The silica sample was put on carbon tape attached to a brass plate. Sample thicknesses were determined using a Gauge from Teclock Corporation. Sample preparations were done using a Cutting Board and Machine from CEAST. Abrasion tests were performed using an Abrasion Tester from FRANK. The universal testing machine used for this study was a Tensile Tester (5565) from Instron.

### 18.3.3. Preparation of metal adsorbent from poly(melthyl acrylate)-grafted-cassava starch

#### *18.3.3.1. Materials*

Commercial cassava starch was obtained from Siam Ouality Starch Co., Ltd. Methyl acrylate was purchased from Aldrich and was used as received. Hydroxylamine hydrochloride was obtained from Fluka. All other chemicals and solvents were also used without further purification.

### *18.3.3.2. Radiation-induced graft polymerization*

In a gelatinization reactor, 20 g of cassava starch was mixed with 190 ml of distilled water. The mixture was continuously stirred using a mechanical stirrer under nitrogen atmosphere. The mixture was gradually heated to 80°C and held at this temperature for 1 hr. The mixture was left to cool down to yield gelatinized starch. The obtained gelatinized starch was mixed with 45 ml of methyl acrylate. The mixture was stirred under $N_2$ atmosphere for 1 hour to form a homogeneous mixture. The mixture was transferred into the glass bottle and purged with $N_2$ gas for 5 min. The bottle was tightly closed with cap and irradiated by gamma radiation using a Gammacell 220 Excel (Co-60 source) at a dose rate of 0.14 kGy/min and total dose of 5.5, 6, 6.5, 7, 7.5, 8 and 8.5 kGy. The maximum degree of grafting was obtained at the absorbed dose of 7.5 kGy. After irradiation, the crude product was precipitated in methanol, filtered and dried at 50°C in a vacuum oven. Poly (methyl acrylate) (PMA) homopolymer formed during the graft copolymerization was separated from the grafted copolymer by washing several times with methanol: water (4:1). The product was dried in vacuum oven at 50°C. The degree of grafting was determined by the following equation:

$$Dg\ (\%) = 100\ [(W_2-W_1)/W_1]$$

Where $W_1$ and $W_2$ are the weights of cassava starch and graft copolymer, respectively.

### *18.3.3.3. Preparation of hydroxylamine ($NH_2OH$) solution and modification of graft copolymer*

Hydroxylamine hydrochloride ($NH_2OH.HCl$) 20% (w/v) were dissolved in a 300 ml methanolic solution. The HCl was neutralized by NaOH pallet. The precipitated NaCl was separated by filtration. The pH of the reagent was adjusted to pH 13 by adding NaOH pallet. 20 g of graft copolymer was placed in a reactor equipped with a mechanical stirrer and condenser and the hydroxylamine solution was added. The reaction was carried at 75°C for 2 hr. After completion of the reaction, the modified graft copolymer was washed several times with a methanolic solution. Then, it was dried in vacuum oven at 50°C overnight. The modified graft copolymer was treated with 100 ml of methanolic HCl solution (0.2 M) for 10 min, washed several times with the methanolic solution and dried in vacuum oven at 50°C.

### *18.3.3.4. Characterization and metal adsorption*

Fourier transform infrared (FTIR) spectra were recorded by FTIR spectrometer (Tensor 27, BRUKER) using the KBr disc technique at a resolution of 4 $cm^{-1}$ and 16 co-added scans. The spectral scan range was 4000-500 $cm^{-1}$. Elemental analysis was used to provide accurate information of the conversion of poly (methylacrylate ester) into poly (hydroxamic acid) via treatment with hydroxylamine in an alkaline medium. It can be used to determine the conversion of poly (methylacrylate ester) into poly (hydroxamic acid) since the modified graft copolymer has nitrogen atoms in its molecular structure, whereas unmodified graft copolymer does not. Elemental analysis of the modified copolymer was carried out with a CHNS/O 2400 Series II element analyzer (Perkin Elmer). The percent conversion of poly (methylacrylate ester) into poly (hydroxamic acid) was calculated as follows:

$$\text{Amount of hydroxamic acid groups (X)} = \left(\frac{W_s.N}{100}\right)/14x10^3$$

$$\text{Density of hydroxamic acid group (Y)} = \frac{X}{W_s}$$

$$Z = \left( \frac{W_1 - W_0}{86.09} \right) / W_1$$

$$\% \text{ Conversion} = \frac{Y}{Z} x 100$$

Where $W_s$ denotes the weight of sample, and $N$ denotes the percentage of nitrogen, and $W_0$ and $W_1$ are the weights of cassava starch and PMA-grafted copolymer, respectively. The factor 86.09 corresponds to the molecular weight of MA. For the metal adsorption study, 0.5 g of adsorbent was soaked into metal solution and shaken using a rotary shaker at room temperature. After equilibration was completed, a 5 ml supernatant was collected for metal ion determination. The initial and final metal concentrations were determined by an inductively coupled plasma mass spectroscopy (ICP-MS, 4500 Series, Hewlett Packard).

## 18.4. RESULTS AND DISCUSSION

### 18.4.1. Radiation-induced crosslinking of PLA

Figure 18.1. shows the tensile strength and elongation at break of PLA samples irradiated under vacuum as a function of crosslinking agent content and dose. Tensile strength of T0 drastically decreased with dose, especially after 60 kGy, while T1 remained roughly the same from 0 to 80 kGy. T3 slightly increased with dose, whereas T5 obviously increased with dose. Similar trends were observed for elongation at break of PLA samples. The results showed that, with optimum amount of crosslinking agent, irradiation under vacuum brought about enhancement in mechanical properties of PLA samples.

Figure 18.2. shows the TMA thermograms of T3 samples irradiated at 0, 40, 60 and 80 kGy. Unirradiated T3 sample started its initial elongation slightly after 60°C, continued its gradual elongation to higher temperatures and showed its drastic deformation at approximately 100°C, after which it finally fractured. The significant elongation reflects the softening of the sample. All T3 samples irradiated in vacuum at 40, 60 and 80 kGy also showed initial elongation at around 70°C and continued to show their gradual deformation to higher temperatures. All T3 samples were thermally stable even after 200°C and showed approximately less than 15% of deformation even at 250 °C, without breaking. These results hence, once again, confirmed the radiation-induced of PLA samples irradiated as well as their higher thermal stability.

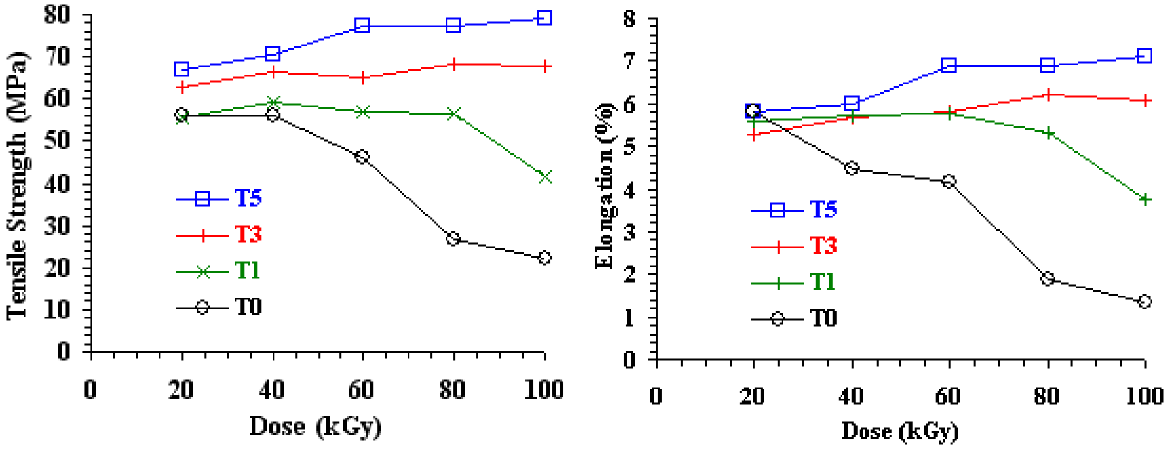

*FIG.18.1. Tensile strength (left) and elongation at break (right) of PLA sample irradiated at different contents of crosslinking agent and doses.*

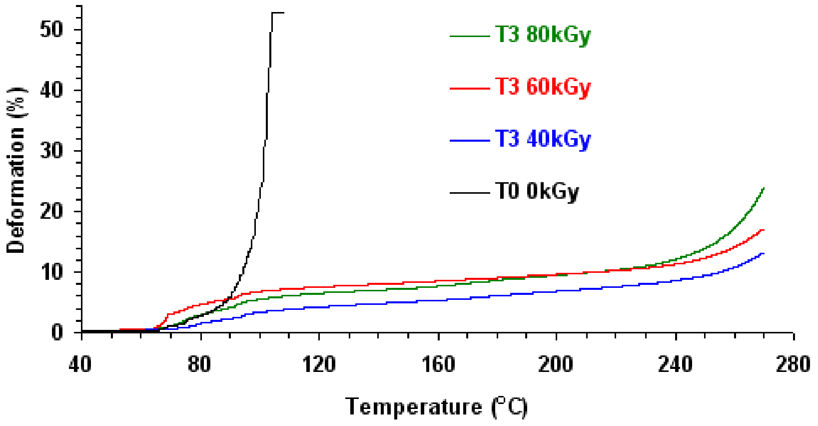

*FIG. 18.2. TMA thermograms of P100 T3 samples irradiated at different dose under vacuum.*

### 18.4.2. Radiation- induced admicellar polymerization of isoprene on silica

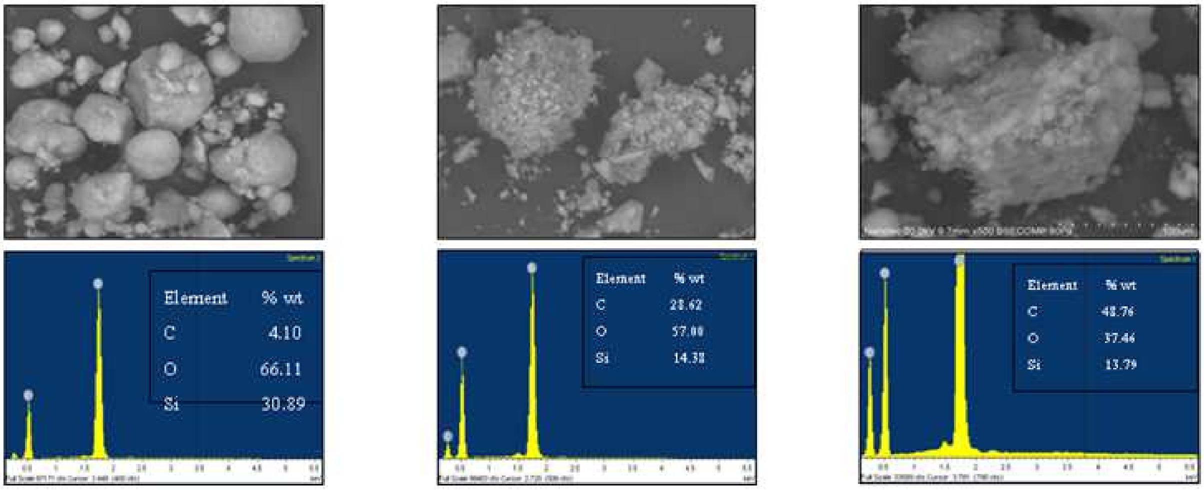

*FIG. 18.3. SEM images and elemental analysis of unmodified silica (left), silica modified with thermal admicellar polymerization using CTAB (middle) and silica modified with radiation-induced admicellar polymerization using CTAB (right).*

SEM was used to compare the surface morphology and the elemental analysis of the unmodified silica and the silica samples modified via both thermal and radiation processes. Figure 18.3 (left) shows relatively smooth surface of the unmodified silica. However, these particles tend to congregate into clusters. On the contrary, Figure 18.3 (middle) and (right) expose a comparatively rough surface and dispersed particles of the silica modified by both thermal and radiation method. A better dispersion of the modified silica is a result of the polyisoprene film formation of the silica surface. The elemental analysis reveals that the carbon content of the unmodified silica is approximately 4%, while that of the silica samples modified via both methods is much higher, varying from 20–40%. The increase of the carbon content stems from the fact that carbon is one of the major components of polyisoprene film coated on the silica surface.

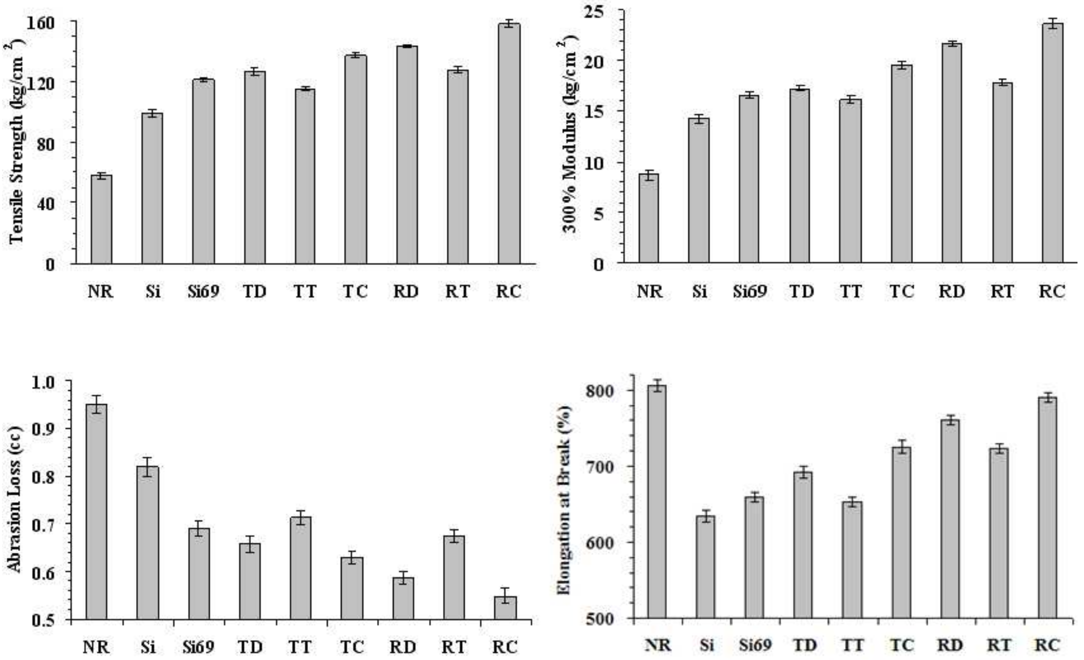

*FIG. 18.4. Mechanical properties of natural rubber (NR), natural rubber reinforced with unmodified silica (Si), natural rubber reinforced with silica modified with Si69 (Si69), natural rubber reinforced with silica modified with DTAB, TTAB and CTAB via thermal admicellar polymerization (TD, TT and TC, respectively) and natural rubber reinforced with silica modified with DTAB, TTAB and CTAB via radiation-induced admicellar polymerization (RD, RT and RC, respectively).*

The mechanical properties of natural rubber and natural rubber reinforced with unmodified silica as well as silica modified via different conditions were tested. The results are shown in Figure 18.4. The pure natural rubber has the highest abrasion loss, i.e. the lowest abrasion resistance. In contrast, the rubber reinforced with silica has higher abrasion resistance and therefore lower abrasion loss. This is owing to the fact that silica embedded in the rubber latex is able to withstand high abrasion. The silica modified with CTAB by radiation method had the lowest abrasion loss. Figure 18.4. indicates the higher moduli of natural rubbers reinforced with surface-modified silica, compared with neat natural rubber and natural rubber reinforced with unmodified silica. Higher torques required to pull the samples to 300% of their original lengths once again confirms the improved mechanical properties of natural rubber strengthened with surface-modified silica. The sample with the highest 300% modulus was natural rubber reinforced with silica modified by CTAB via radiation-induced method. Figure 18.4. clearly displays that natural rubber reinforced with silica modified via both thermal and radiation-induced admicellar polymerization has higher tensile strengths than pure natural rubber or natural rubber reinforced with unmodified silica. Unlike unmodified silica, the modified silica has better attachment to the rubber matrix. The reinforcement imparted by the modified silica subsequently enhances the tensile strength of natural rubber. Once more, the natural rubber with the highest tensile strength was also reinforced with silica modified by CTAB via radiation-induced method. Figure 18.4. also shows elongation at break of these nine different samples. The unmodified natural rubber has higher elongation at break, compared with natural rubber treated with silica. However, the elongation at break of the natural rubber reinforced with modified silica is higher than that of the ones reinforced with unmodified silica. This is due to better adhesion between the surfaces of the modified silica and the natural rubber.

With poor adhesion, the unmodified silica is inclined to detach from the rubber matrix. This detachment creates cavities, hence resulting in poor elongation at break of the rubber.

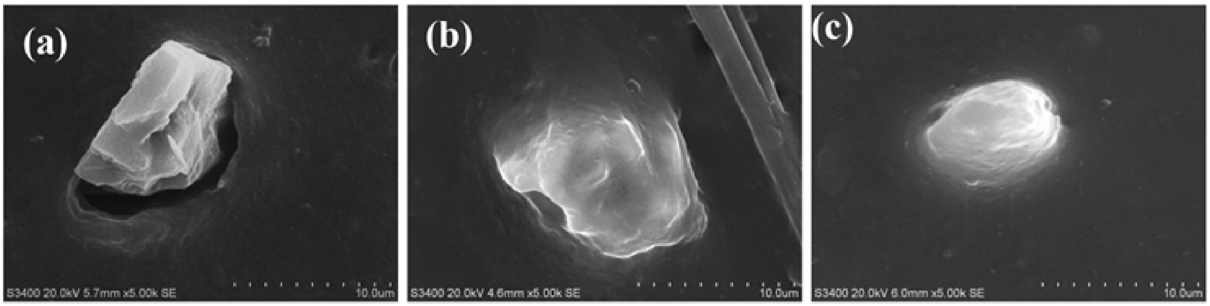

*FIG. 18.5. SEM images of natural rubber (before tensile tests) reinforced with (a) unmodified silica, (b) silica modified with CTAB via thermal method and (C) silica modified with CTAB via radiation-induced method.*

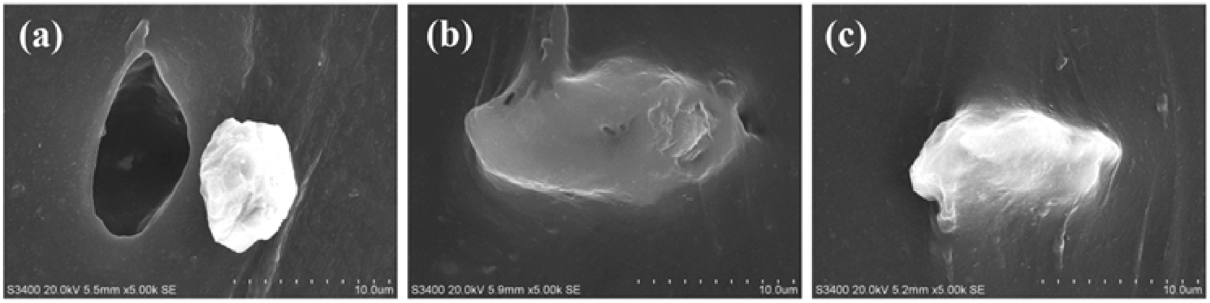

*FIG.18.6. SEM images of natural rubber (after tensile tests) reinforced with (a) unmodified silica, (b) silica modified with CTAB via thermal method and (C) silica modified with CTAB via radiation-induced method.*

To analyze the adhesion between the interfaces of natural rubber and silica modified via admicellar polymerization, SEM micrographs of natural rubber reinforced with unmodified silica, silica modified with CTAB via both thermal and radiation-induced admicellar polymerization, before and after mechanical testing, were taken and shown in Figures 18.5. and 18.6, respectively. Figure 18.5.(a) illustrates that there is a cavity between the surfaces of natural rubber and unmodified silica. This can simply be explained from the fact that the surface of unmodified silica is polar or hydrophilic, while that of natural rubber is non-polar or hydrophobic. This, hence results in very poor adhesion. On contrast, natural rubber reinforced with silica modified by CTAB via both thermal and radiation methods showed no void between the surfaces of natural rubber and modified silica, since the silica surface is coated with polyisoprene film. The modified silica, consequently, adheres to natural rubber much better than the unmodified silica. After the mechanical tests, the SEM photographs of the tested samples were taken to analyze the fracture surfaces, as seen in Figure 18.6. Figure 18.6(a) clearly shows the detachment of a silica particle from the rubber matrix, whereas Figures 18.6(b) and 18.6(c) once more show no separation of the silica particle from the rubber matrix, even after the mechanical tests.

These results clearly validate the improved adhesion between natural rubber and modified silica, as well as strongly confirm the effectiveness of surface modification of silica through radiation-induced admicellar polymerization.

### 18.4.3. Preparation of metal adsorbent from poly(melthyl acrylate)-grafted-cassava starch

Figure 18.7. represents the effect of total dose on degree of grafting. The degree of grafting increased with increasing dose up to 7.5 kGy, after which it started decreasing. The increase in the total dose enhances the formation of radicals, resulting in high degree of grafting. The degree of grafting reached about 135% at the absorbed dose of 7.5 kGy. At the absorbed dose higher than 7.5 kGy, the degree of grafting decreased, which may be due to the degradation of cassava starch. The ester group of the PMA-grafted copolymer was converted into the hydroxamic acid group by treatment of an ester with hydroxylamine in an alkaline solution. Modification parameters were determined in relation to % nitrogen. The maximum percentage of conversion 70% (5.35 mmol/g of hydroxamic acid groups) was observed at 20% (MeOH: H2O = 5:1). The % conversion increased with increasing reaction time up to 2 hr. and pH 13 respectively, which gave the maximum % conversion.

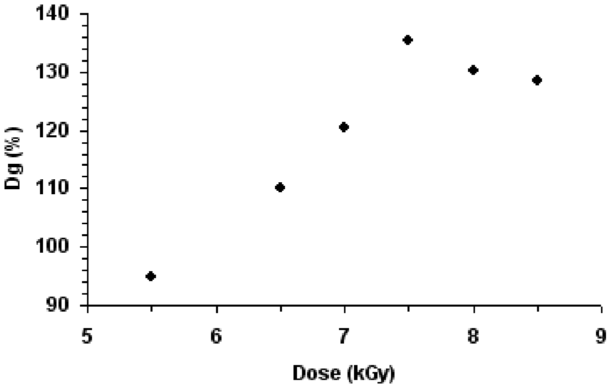

*FIG. 18.7. Effect of total dose on degree of grafting.*

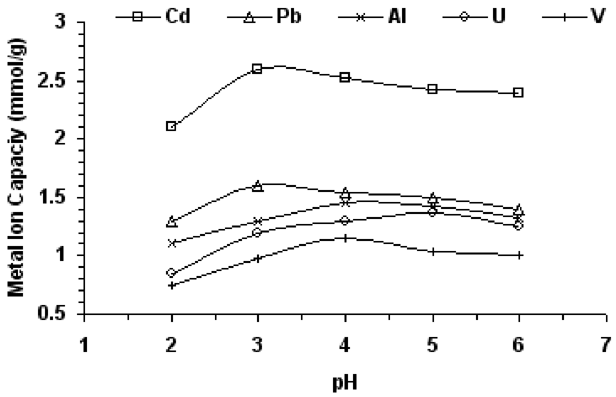

*FIG.18.8. Metal ion capacities of adsorbent containing hydroxamic acid groups as a function of pH.*

Figure 18.8. shows the metal ion capacities of the adsorbent as a function of pH. The adsorption behavior of the adsorbent containing hydroxamic acid groups toward metal ions was investigated by the study of resin binding of $Cd^{2+}$, $Al^{3+}$, $UO_2^{2+}$, $V^{5+}$ and $Pb^{2+}$ ions in aqueous solutions. The binding capacities of $Cd^{2+}$, $Al^{3+}$, $UO_2^{2+}$, $V^{5+}$ and $Pb^{2+}$ ions were pH dependent and their selectivity toward these metal ions is in the following order: $Cd^{2+}>Pb^{2+}>Al^{3+}>UO_2^{2+} > V^{5+}$. The binding capacities depend on the type of metal ion and the condition. Different metals have different chelating behaviors with the adsorbent. The dissolution of each metal in the solution is different. In addition, each ligand has different selectivity, exchange rate and stability constant for each metal. The adsorbent exhibited a remarkable % adsorption for $Cd^{2+}$, $Al^{3+}$, $UO_2{}^{2+}$, $V^{5+}$ and $Pb^{2+}$ at pH 3, 4, 5, 4, and 3, respectively. The adsorbent of 191 %Dg had total adsorption capacities of 2.6, 1.46, 1.36, 1.15, and 1.6 mmol/g.adsorbent for $Cd^{2+}$, $Al^{3+}$, $UO_2^{2+}$, $V^{5+}$ and $Pb^{2+}$, respectively, in the batch mode adsorption.

## 18.5. CONCLUSION

Radiation-induced crosslinking of PLA was investigated. Results showed that the presence of a suitable crosslinking agent (TAIC) enables PLA to undergo crosslinking induced by gamma radiation. The optimum condition for radiation-induced crosslinking of PLA was determined.

Silica modified by radiation-induced admicellar polymerization was applied as filler for natural rubber. Mechanical properties of natural rubber reinforced with silica modified by radiation-induced admicellar polymerization were analyzed and compared with those of neat natural rubber, natural rubber reinforced with unmodified silica, natural rubber reinforced with silica modified with Si69 and natural rubber reinforced with silica modified by thermal admicellar polymerization. The results showed that the mechanical properties of rubber reinforced with silica modified by admicellar polymerization were superior to those reinforced with unmodified silica or silica modified with Si69. For natural rubber reinforced with silica modified by admicellar polymerization, the results further indicated that CTAB proved to be the most efficient surfactant to enhance the mechanical properties of natural rubber, both for thermal and radiation-induced admicellar polymerization. Adsorbent containing hydroxamic acid groups was successfully prepared by radiation grafting of methyl acrylate onto cassava starch followed by treatment with hydroxylamine. The adsorbent exhibited a remarkable % adsorption for $Cd^{2+}$, $Al^{3+}$, $UO_2{}^{2+}$, $V^{5+}$ and $Pb^{2+}$ at pH 3, 4, 5, 4 and 3, respectively. The selectivity of adsorbent towards the metal ions used is in the following order: $Cd^{2+} > Pb^{2+} > Al^{3+} > UO_2^{2+} > V^{5+}$.

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# 19. ACCELERATORS FOR ENERGY AND ENVIRONMENT AT THE ILLINOIS ACCELERATOR RESEARCH CENTER

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**Abstract**

Particle accelerators are an enabling technology not only utilized in their traditional role for fundamental research, but also in such diverse fields as medicine, industrial processes, and national security and defense. In recognition of this large impact on the US economy, the Fermi National Accelerator Laboratory (FNAL) has partnered with the Illinois Department of Commerce and Economic Opportunity (DCEO) and the Department of Energy's Office of High Energy Physics (DOE/OHEP) to build the Illinois Accelerator Research Center (IARC). Located on the Fermilab campus, this facility will house office, technical, and educational space in a state-of-the-art facility for research and development of, education in and industrialization of particle accelerator technology. Key to the success of IARC will be DOE support of the idea that translational technology, namely developing ideas from the laboratory into commercial practice, only happens when the proper environment is cultivated. The proper environment promotes friendly, flexible collaboration with industry and universities and provides sufficient seed resources such that non-traditional and multi-disciplinary efforts can flourish. A key concept for the IARC program is that it serves as a portal to allow industrial access not just to the IARC physical plant but rather to the facilities and expertise of the entire laboratory. A successful program at IARC will lower barriers for Laboratory – Industry cooperation on accelerator technology and applications and enable an entire new class of projects to be undertaken as Government-Industry partnerships. In this paper Fermi National Accelerator Laboratory (Fermilab) is pleased to present a list of high impact application areas that provide opportunities for research and development of accelerator technologies to address national challenges in energy and the environment. Fermilab and its partners and collaborators are well positioned to undertake successful research and development programs on these technologies. The majority of the high-impact application areas described herein involve the use of electron-driven chemistry. An accelerator-generated electron beam can drive chemical reactions that would otherwise take place only at high temperatures and/or under the influence of catalysts. The resultant electron beam process may have a smaller carbon footprint due to its reduced energy consumption. Electron beams are also unique in that they can simultaneously drive both oxidation and reduction reactions in aqueous solutions, allowing the efficient destruction of harmful waterborne organic pollutants. The ability of ionizing radiation to crosslink materials altering their materials properties provides additional opportunities. Although we present a number of specific examples that represent high value opportunities to improve energy efficiency, reduce pollutants from energy production, clean up water, and reduce environmental toxins, it is likely that many additional potential applications will emerge as the technology is further developed. Other applications of accelerator technologies described in this document include accelerator-generated neutrons to produce energy and to treat nuclear waste and the use of superconducting magnet technology developed for accelerators to allow the construction of smaller, more compact and efficient generators for wind turbines.

## 19.1. IARC FACILITY

Fermilab foresees that many of the accelerator technologies described herein will be developed at the Illinois Accelerator Research Center (IARC), a new accelerator research and development facility being built at Fermilab. Located on the Fermilab campus, this 83,000 square foot, state-of-the-art facility will house offices, workshop, laboratory, and educational space to design and develop cutting-edge accelerator technologies. IARC's close proximity to the Fermilab Industrial complex also provides excellent access to the technical expertise and facilities of Fermilab

IARC was conceived and proposed by Fermilab and the US Department of Energy (DOE) to the State of Illinois in 2007. The need for a US facility like IARC was recognized at the Accelerators for America's Future symposium held in Washington DC in Oct 2009. The 2010 report from this symposium contains a wealth of information on the basic justification for investment in accelerator applications as well as the opportunities for new accelerator applications for a facility like IARC. Following the lead of this symposium, the 2012 Senate Water and Energy Bill encouraged DOE to pursue the development of accelerator applications more aggressively. It requested DOE Office of High Energy Physics (OHEP) provide a plan to address the opportunities made evident in the Accelerators for America's Future symposium. In 2011, OHEP convened an Accelerator R&D Task Force to offer advice on the creation of such a plan. An interim report from this committee was presented at the High Energy Physics Advisory Panel (HEPAP) meeting in March 2012. The final report to the House and Senate Appropriations Subcommittees was completed in September 2012. Through this request by Congress, OHEP is now the designated steward of accelerator science and technology within the DOE Office of Science complex, with a new thrust toward applied technology. In 2014 the Accelerator Stewardship Program issued a Request for Information targeted at accelerator applications for Energy and Environment. A funding announcement to support new projects in this area is expected in 2015. It is anticipated that many of the new applications described in this paper will be funded by HEP via the Accelerator Stewardship Program.

Unlike other smaller EB test facilities worldwide, IARC is designed to house high power (hundreds of KW), low energy (<10 MeV) electron accelerators needed to make many future applications for energy and environment practical. In addition to the ready availability of the staff and technical resources of a world-class accelerator laboratory, one goal of IARC is to provide high power electron accelerator test platforms that can serve both as a test beds for industrial process development and at the same time allow accelerator cost and reliability optimization. Development of a compact megawatt class mobile electron accelerator is another IARC objective that could enable in-situ demonstration and validation of many proposed future accelerator applications.

Construction of IARC is in progress. The State of Illinois, Department of Commerce and Economic Opportunity (DCEO) provided a $20M grant for the construction of a new building addition next to an existing heavy assembly building on the Fermilab site. The shell of this addition was completed in May 2014. See figure 19.1. DOE/OHEP committed $13M for site prep and to outfit the new space (networks, partitions, furniture, etc.) This work is in progress with first occupants expected in the fall of 2014. In parallel, an adjacent existing Heavy Assembly Building (HAB) valued at $38M is being refurbished by DOE. Together these will create a $70M complex to enable the IARC mission. We envision accommodating the first industrial partners and launching the program at IARC in 2015.

*FIG 19.1, IARC: State funded addition (white) next to existing Heavy Assembly building*

## 19.2. HIGH IMPACT OPPORTUNITIES IN ENERGY AND ENVIRONMENT

As part of establishing the program at IARC Fermilab has identified a number of opportunities with the potential to make a large impact in the area of clean energy production and preservation of the environment. In this section we outline some of these opportunities that have been identified.

Unlike previous research efforts in some of these areas, Fermilab intends to engage industry from the beginning of each project. Prior to requesting funding and starting a development project our policy will be to require a reviewed business plan to insure that if technical objectives of the project are met the technology can and will find its way into broad use via profitable businesses. We believe this approach is key to large scale transformational change in the area of energy and environment.

### 19.2.1. Energy Produ0ction and Efficient Industrial Processes

#### *19.2.1.1. Gas to Liquids Conversion*

Large-scale Fischer–Tropsch plants exist and/or are under construction to convert natural gas to liquid hydrocarbons. However, these require extensive infrastructure due to the required high temperatures and pressures, catalysts, etc. Many of these chemical techniques cannot be applied at the well head to make use of flare gas due to the cost and scale of the required equipment. Patents also exist for alternative technologies to capture flare gas at smaller scales but no existing solution has been proven to be efficient and cost effective.

Accelerator-generated electron beams can efficiently break carbon-hydrogen bonds allowing conversion of natural gas and biogas, both of which are mainly methane, to liquids which are useful for many applications, including transportation fuels. There are multiple approaches under consideration, including direct creation of long-chain hydrocarbons via removal of protons (i.e. hydrogen) or alternative reactions in which natural gas, $CO_2$ from a power plant, and water are converted into alcohol creating valuable fuels such as alcohol while lowering overall emissions via reuse of the carbon. Possible accelerator driven reactions to create alcohol are shown in Figure 19.2. Figure 19.3. is a schematic plant.

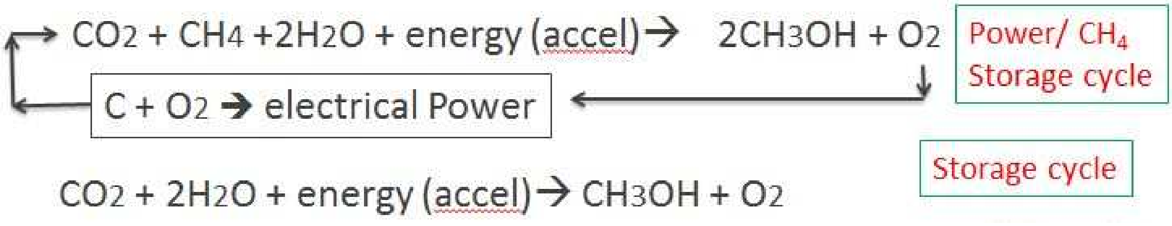

*FIG 19.2 Accelerator driven reactions for carbon reuse and renewable energy storage*

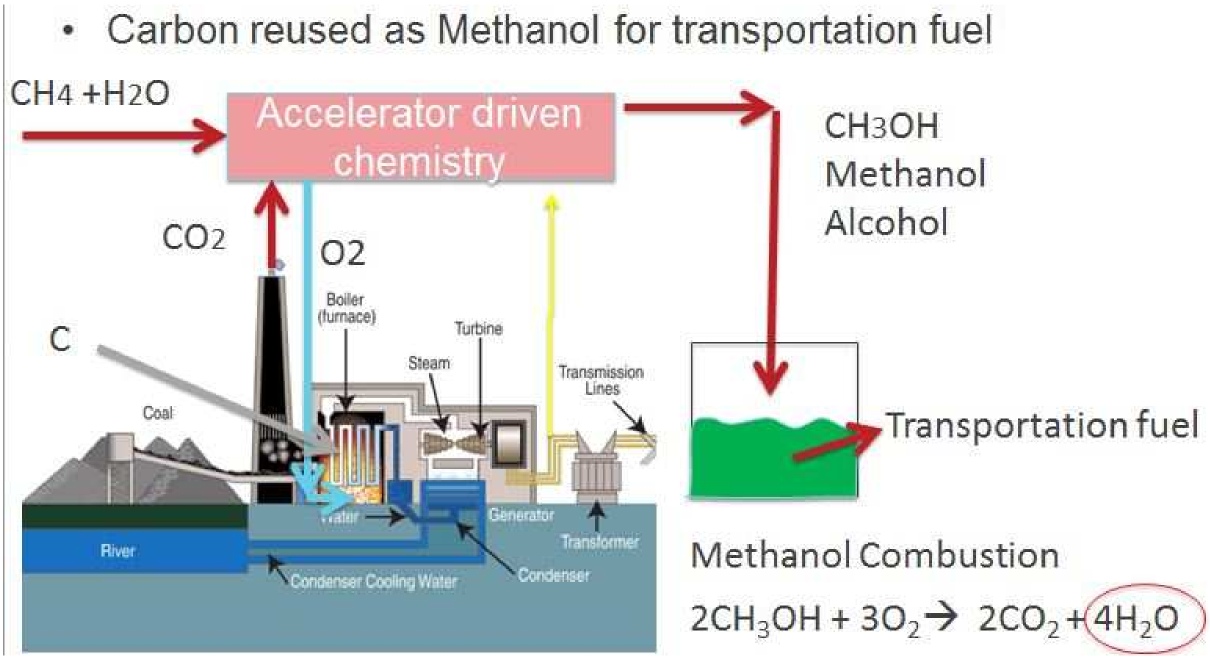

*FIG. 19.3. Plant schematic for Accelerator driven carbon reuse and energy storage*

## FLARE GAS RECOVERY

An accelerator-generated electron beam may be used to efficiently convert natural gas produced by oil wells to longer chain liquid hydrocarbons at the well head [19.**Error! Bookmark not defined.**]. At present, it is uneconomical to collect some associated gas, which is consequently flared (burned at the well head). In 2011 natural gas flared at well heads worldwide corresponded to 25% of the U.S. annual natural gas consumption with a retail value of about $30 billion. Recent widespread use of fracking technology results even more gas flared in the U.S. For example more than 30% of the gas produced by the Bakken play in North Dakota in 2012 was flared. A mobile accelerator (Figure 19.4) at the wellhead could convert natural gas to liquids, which could be collected and shipped with the oil. Aside from providing a new source of useful petroleum liquids, flare gas recovery would substantially reduce the emission of greenhouse gases.

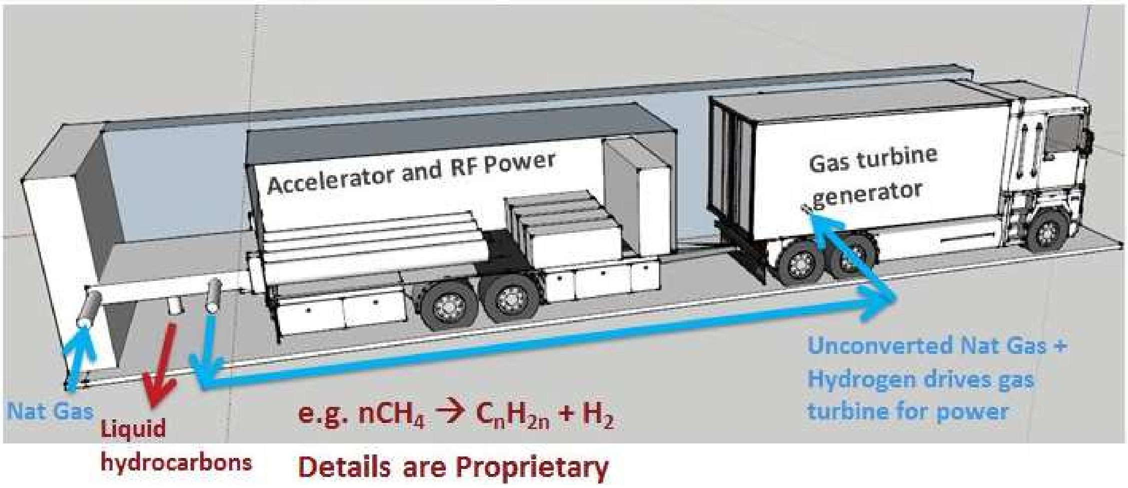

*FIG. 19.4. Accelerator driven reactions for carbon reuse and renewable energy storage*

Techniques for flare gas recovery via the use of accelerators are proprietary. It is likely that any commercially successful technique will generate large revenues so both process and accelerator IP is and will be closely guarded.

## BIOGAS RECOVERY

Biogas typically refers to a mixture of gases produced by the breakdown of organic matter in the absence of oxygen. Biogas, which consists mainly of methane, has significant potential as a renewable fuel. Conversion to liquids of biogas at landfills or anaerobic digesters may substantially improve the economics of biogas production and use as a fuel source. An accelerator-generated electron beam may be used to convert biogas to liquid hydrocarbons, which can be used as a chemical feedstock or liquid fuel [19.1]. The accelerator system would be installed at the location where the biogas is produced, typically a landfill or anaerobic digester. In addition to increasing energy production, the conversion of methane, a powerful greenhouse gas, to a useful fuel will also reduce global warming. Electron beam technology potentially allows transformation of other biologically-produced compounds, such as triglycerides or long chain lipids, into shorter-chain liquid fuels or methane.

### *19.2.1.2. Superconducting Generators for Wind Energy Capture*

The use of superconducting (SC) magnet technologies developed for high energy physics could allow smaller, more compact and efficient generators for wind turbines [19.2]. This in turn can allow the manufacture of larger capacity wind turbines, since current designs are limited by the weight of the required generator and gearbox. Elimination of gearboxes further reduces mass and complexity of large wind turbine generators thereby bringing down the cost per watt of wind power. Challenges expected with this technology include cryogenic refrigeration, AC losses in SC generator windings, reliability, controlling size of generator & refrigerator, and developing self-starting designs. Unknowns that currently prevent widespread use of this technology includes complexity and as yet undemonstrated reliability of superconducting generator system compared with conventional generators.

The basic SC coil designs and techniques developed for High Energy Physics (HEP) accelerators have direct applicability to SC generators for wind turbines and can have much higher power densities than conventional generators and gear boxes resulting in lower weigh for a given power rating. Elimination of the gear box can also improve overall turbine reliability. Ultimately these attributes can allow wind turbines of higher power output than is currently possible with conventional generators. Like a ramped HEP accelerator magnet, an AC SC generator has to control AC losses in the windings which ultimately end up in the cryogenics system. New coil designs, winding, insulation, coil heat treatment techniques, magnet protection schemes, etc. both from both NbTi and $Nb_3Sn$ based accelerator magnets are directly applicable to SC generators for wind turbines. Similarly, the extensive SC magnet expertise and infrastructure at HEP labs can be applied to the problem of low cost renewable energy. High Tc magnet and wire development in HEP is also directly applicable. The application needs high reliability and high performance SC magnets at a low cost. This is very similar to the requirements on SC magnets for a large accelerator. Use of high Tc conductors has the potential to greatly simplify the required refrigeration systems (e.g. cryogen free systems like cryocoolers) and bring down costs. However both the magnet techniques and refrigeration schemes need additional development before widespread deployment is feasible.

### *19.2.1.3. Highway Asphalt Treatment*

Asphalt is used in approximately 95% of the 2.2 million miles of roads in the US. Tens of billions of dollars are spent every year on roadway repair. We propose to use an accelerator-generated electron beam to drive a chemical reaction in the binder (modified bitumen or alternatives) after it has been applied to road surfaces to improve its material properties. Irradiation by a mobile, vehicle-mounted EB source will cause crosslinking to a depth of a few centimetres, which can improve the wear-resistance and weather-resistance of the asphalt [19.3]. This technology has the potential to save a large amount of taxpayer dollars and reduce the large carbon footprint resulting from the use of diesel-powered heavy equipment currently used in asphalt road repairs. Fermilab has filed a patent on this technology and is actively engaged in research. A schematic of such a system is shown in Figure 19.5.

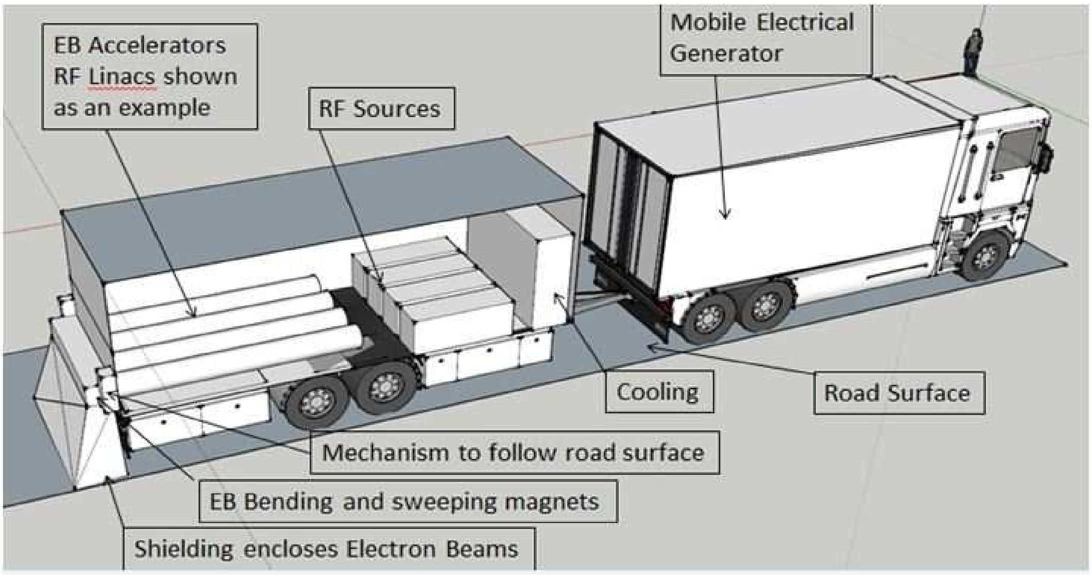

*FIG. 19.5. Schematic of a mobile accelerator to crosslink highways and other paved surfaces*

### *19.2.1.4. ADS for Energy Production and nuclear waste destruction*

Accelerator-generated neutrons may be used to maintain a fission chain reaction in a subcritical fuel assembly. This would enable a new generation of nuclear reactors, known as accelerator driven systems (ADS) that can be tuned off merely by stopping an accelerator beam, rather than by inserting control rods and rendering the fuel assembly subcritical [19.4]. Further, ADS would allow the use as a nuclear fuel of thorium-232, which is three to five times as abundant in the Earth's crust as uranium. While Fermilab is interested in this technology, the regulatory environment means new designs for nuclear industry processes are very capital intensive. The low price of natural gas in the U.S. means that industry is not vigorously pursuing new nuclear power installations. Fermilab has an extensive R&D program for a project named Proton Improvement Plan – II (PIP-II) based on an 800 MeV Superconducting Proton Linac. When completed, such a linac would be an ideal source to provide protons for an ADS test facility. Provisions in the civil construction of PIP-II are envisioned to enable a future ADS test facility if funding for this technology becomes available. Currently the technology faces serious issues of public acceptance in the U.S. following the Fukashima incident in Japan. On the positive side nuclear energy is carbon free and this may sway public options Also, as described later in this paper, ADS may be able to solve the problem that conventional nuclear power plants create very long lived nuclear waste that must be stored safely.

### 19.2.2. Environmental use of accelerator Technology

Electron beams have many potential uses for preservation of the environment. We list a few of these potential applications below. A common theme for successful widespread adoption of this technology is efficient, reliable, cost effective accelerators. In many cases a combination of technological advances and regulatory changes will be required for deployment.

#### *19.2.2.1. Environment Air: Electron Beam Flue Gas Treatment (EBFGT)*

Accelerator-generated electron beams can be used to remove pollutants in the flue gas emitted by fossil-fuel power plants and several test facilities have been build and operated [19.5, 19.6]. EBFGT can be applied to NOx and SOx, which are responsible for acid rain, and to $CO_2$, a major greenhouse gas. Using electron beams, NOx and SOx can be converted into ammonium nitrate and ammonium sulphate, which can be separated as particulates and subsequently used as fertilizers. Methane can be used in an electron-beam induced process to remove $CO_2$, resulting in the production of methanol, which can be used as a chemical feedstock. The pollutant removal processes can be applied sequentially to remove NOx and SOx, and then to remove $CO_2$. When combined with other conventional pollutant removal processes the fully treated flue gas stream is almost free of pollutants. While several pilot plants have demonstrated efficient SOx and NOx removal, EBFGT is currently not in widespread use. It has never been tried for carbon capture or reuse. New EPA requirements in the U.S. will require significant reductions in $CO_2$, NOx, and SOx from coal fired power plants. Key for widespread adoption of the technology is efficient, compact, reliable, and affordable accelerators. Fermilab is partnered with an industrial vendor to produce such an accelerator. We plan a test facility at IARC for accelerator and process optimization. Our industrial partner is funded to install EBFGT on a coal fired plant in Canada.

Techniques to combine $CH_4$, $CO_2$ and $H_2O$ into methanol and $O_2$ via the use of accelerators are proprietary. It is likely that any commercially successful technique will generate large revenues so IP is and will be closely guarded.

#### *19.2.2.2. Environment: Water*

#### DESTRUCTION OF ORGANIC MATERIALS IN INDUSTRIAL WASTEWATER

An accelerator-generated electron beam may be used to destroy organic materials, e.g. dyes, pesticides, pharmaceuticals, endocrine disruptors, etc., that would otherwise be released to the environment in a liquid or gas waste stream, or collected for treatment [19.6]. Accelerator-based destruction of organic materials is known to work. Commercially it may be more effective than conventional methods since the technique allows simultaneous creation of oxidation and reduction conditions in irradiated water. R&D on this technology is currently being pursued in Europe, Asia, and the Middle East but it is currently not in widespread use. The US had a technical lead in the mid 90's after a study at Miami-Dade, FL showed that electron-beam treatment can break down waterborne organic toxins such as halogenated hydrocarbons. However, this lead has been lost since no such projects have been funded or operated in the US for more than a decade. Both technical and regulatory obstacles remain that prevent widespread use of this technique. Cost of treatment must be reduced via reliable cost effective turn-key accelerators and reliable high power beam windows operating in harsh environments. At the same time regulatory requirements on effluents to streams and rivers must demand reduced levels of organic contaminants. The added cost of treatment system only makes sense to industry if they are constrained by regulations not to pollute water released from their site after industrial use.

### MUNICIPAL WASTE WATER TREATMENT

An accelerator-generated electron beam may be used to treat the output from municipal waste treatment plants. This treatment method will efficiently kill pathogens, remove pharmaceuticals, and remove odor [19.7]. The result will be a nutrient-rich liquid that can be used as a fertilizer. This will reduce phosphate pollution, a major contributor to eutrophication of surface waters and to algae blooms while at the same time helping to preserve limited phosphate deposits that are currently mined for fertilizer

### CONTAMINATED GROUND WATER CLEANUP

An accelerator-generated electron beam may be used to remove organic contaminants, many of which are on the EPA’s National Priorities List, such as gasoline, oil, methyl tertiary butyl ether (MTBE), pesticides, refrigerants and other chemical waste from groundwater [19.6]. Contaminated ground water would be pumped out of one or more boreholes and treated using a mobile accelerator, which would transform the organic contaminant into far less harmful substances.

## *19.2.2.3. Environment: Land*

### MUNICIPAL SEWAGE SLUDGE TREATMENT

Treating sewage sludge with an accelerator-generated electron beam, rather than disposing of it in a landfill, will provide pathogen-free fertilizer [19.7] and will also allow recycling of nitrates and phosphates, thereby saving energy and conserving phosphate reserves. This method has the potential to reduce the energy required to created conventional fertilizers and also to reduce agricultural runoff from chemical fertilizers that contaminate waterways.

### ACCELERATOR DRIVEN SYSTEMS FOR MINOR ACTINIDE DESTRUCTION

Accelerator-generated neutrons may be used to transmute minor actinides in nuclear waste into stable isotopes. The destruction of minor actinides may render the waste remaining after spent fuel reprocessing safe in decades rather than millennia [19.8]. This is may remove one major objection to the use of this carbon free energy source. At the moment this technology while promising faces a number of obstacles. Currently, the US DOE does not support ADS research. In part this may be because it is in conflict with breeder reactor IP owned by US companies. There are also technical obstacles in the feasibility of large-scale actinide destruction via ADS is unknown and it will require high power (10 MW class) and high reliability proton accelerators that are as yet undemonstrated. There are also regulatory hurdles in the U.S. as well since licensing of new class of nuclear facility is time consuming and capital intensive. Finally there are economic barriers, although there are ADS R&D efforts in Japan, India, and Belgium, the low cost of natural gas in the U.S. does not support R&D investments by the power industry, especially given the high capital investments required for new nuclear power facilities. Given cost and scope of any ADS project, public funding will be required, which means overall technology solution is likely to be developed in the public domain. However, nuclear industry has an extensive portfolio of IP, some of which may be needed for the application.

## 19.3. WHAT METRICS COULD BE USED TO ESTIMATE THE LONG-TERM IMPACT OF INVESTMENTS IN NEW “GREEN” ACCELERATOR TECHNOLOGIES?

Past research dollars spent on accelerator applications for energy and environment have yielded many technical successes. However, many of the technologies envisioned have not seen widespread deployment. Before additional investments are made it is important to establish metrics suitable for estimating the long-term impact of investments in new “green” accelerator technologies. We suggest that these metrics include:

- Existence of viable Business Plan indicating that if technical success is achieved that profitable business can and will be created to deploy the technology
- Demonstrated overall reduction in greenhouse gas emissions  sufficiently documented that decision makers can write regulations requiring use of the technology
- Estimates for decision makers of the value of healthcare savings and improved longevity due to reduced pollution and improved air and ground water quality
- Estimates of the number and value of new businesses and jobs created by adoption of the technology

## 19.4. CONCLUSIONS

Fermilab is actively engaged in accelerator R&D in support of its basic science mission. Much of the technology developed in the pursuit of science can have applications beyond High Energy Physics. With the completion of IARC, we plan to launch a large program of cooperative work with industry including but not limited to accelerator applications for Energy & Environment. Many of these applications can have transformative impacts on the way mankind generates and uses energy. They can also have very positive effects on the environment for benefit of all mankind. In addition to these goals we also believe that industrialization of these technologies can lead to create new industries and jobs stimulating the economy and creating revenues that can support sustainable development in the future.

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# 20. DECIMAL LOG REDUCTION (D-10) VALUES OF SELECTED MICROBIAL PATHOGENS AND INDICATOR ORGANISMS IN AEROBICALLY AND ANAEROBICALLY DIGESTED SEWAGE SLUDGE UNDER 10 MEV ELECTRON BEAM (EBEAM) CONDITIONS

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*This paper is an excerpt from the original publication, "Electron beam inactivation of selected microbial pathogens and indicator organisms in aerobically and anaerobically digested sewage sludge" by Praveen et al (2013) that was previously published (Bioresources TechnologyVol: 144, pages 162-167)*

**Abstract**

Microbial pathogens in municipal sewage sludges need to be inactivated prior to environmental disposal. The efficacy of high energy (10 MeV) electron beam (eBeam) irradiation to inactivate a variety of selected microbial pathogens and indicator organisms in aerobically and anaerobically digested sewage sludge was evaluated. Both bacterial and viral pathogens and indicator organisms are susceptible to eBeam irradiation. However, as expected there was a significant difference in their respective eBeam irradiation sensitivity. Somatic coliphages, bacterial endospores and enteric viruses were more resistant compared to bacterial pathogens. The current US EPA mandated 10 kGy minimum dose was capable of achieving significant reduction of both bacterial and viral pathogens. Somatic coliphages can be used as a microbial indicator for monitoring eBeam processes in terms of pathogen inactivation in sewage sludges.

## 20.1. OBJECTIVE OF THE RESEARCH

The underlying hypothesis was that high energy (10 MeV) eBeam irradiation is capable of inactivating a variety of microbial pathogens at significant levels. The experimental objective was to obtain decimal log reduction (D-10) values of selected pathogens and other target organisms in aerobically and anaerobically digested sewage sludge samples (biosolids) under 10 MeV eBeam irradiation conditions.

## 20.2. INTRODUCTION

The wastes in developed and in many developing countries are treated in centralized wastewater treatment plants. At these plants, the resulting sewage sludge is treated appropriately to reduce the potential for human infections and other public health impacts. In the United States, the land disposal of biosolids is federally regulated by the US EPA (US EPA, 1993). This regulation classifies biosolids as either Class A or Class B biosolids based on the level of treatment, pathogen loads, and their potential to attract disease vectors. Class A biosolids undergo a more complete disinfection process with the aid of specific treatment processes referred to as Processes to Further Reduce Pathogens (PFRP). The EPA approved PFRP processes are heat treatment, drying, composting, thermophilic aerobic digestion, pasteurization, and ionizing irradiation. Ionizing radiation using either cobalt-60 or electron beam (eBeam) at a minimum dose of 10 kGy is considered as an effective PFRP to produce Class A biosolids. There is however limited empirical data on the efficacy of eBeam technology to disinfect pathogens in biosolids. Given the significant differences in dose rate and energy levels between current eBeam and cobalt-60 processes there is a need to build an information base regarding the inactivation profiles of specific microbial pathogens under eBeam irradiation conditions.

## 20.3. MATERIALS AND METHODS

### 20.3.1. Biosolid samples

Biosolids samples from aerobic and anaerobic digester-based wastewater treatment plants in Texas were collected multiple days for the different irradiation trials. The samples were collected from the digester outlets in sterile containers and transported on "blue-ice". Separate collections were made for different irradiation trials. The moisture content and solids concentration (%) of the biosolid samples were determined by drying 20 ml of wet samples at 102°C for 24 h

### 20.3.2. Sample preparation for eBeam trials

The starting levels of *E. coli*, aerobic and anaerobic spore formers were analyzed immediately or within 24 hours of sample collection. The samples had significant levels of *E. coli*, aerobic and anaerobic spore formers. However, the density of other indicator organisms and specific pathogens were low. Hence, *Salmonella* Typhimurium, coliphages, and enteric viruses had to be spiked into the samples in the laboratory at sufficient titers for the inactivation studies. One set of samples were spiked with high titer of laboratory grown strains of nalidixic acid and novobiocin resistant *Salmonella enterica* serovar Typhimurium. Similarly, the samples were spiked *with E. coli* phages, ϕX174, MS- poliovirus-1 (VR- 1562) and rotavirus (SA-11). For these microorganisms, the high titers were prepared and quantified using standard protocols. Each of these microorganisms was spiked into separate samples to facilitate accurate quantification.

### 20.3.3. eBeam irradiation trials

Twenty ml of evenly mixed biosolids samples were placed (in triplicate) in Whirl-Pak® bags (Nasco, New York, NY) and heat sealed. The eBeam irradiation was performed at the National Center for Electron Beam Research's eBeam facility on the Texas A&M University campus.

Irradiation dose measurements were performed using alanine dosimetry that was validated to international standards. The dosimeters were placed at different locations within the sample (using heat-sealed pouches) to verify the delivered eBeam dose. Preliminary studies were performed to ensure that the samples could be irradiated effectively with dose-uniformity ratio (DUR) ~ 1.0. The DUR is an important criterion when performing irradiation experiments. A DUR of ~1.0 signifies that the ratio between maximum and the minimum doses anywhere within the sample bag is uniform. The dosimeters were measured using the Bruker E-scan spectrometer (Bruker, Billerica, MA). The measured dose was used for data plotting and calculation of inactivation kinetics. Each inactivation experiment was carried out with triplicates on multiple days.

The inoculated samples were subjected to different target doses of eBeam irradiation. Experiments involving *E. coli* and *S.* Typhimurium were irradiated at lower doses of eBeam ranging from 0.2- 1.0 kGy. Samples that were spiked with bacteriophages, enteric viruses and bacterial spore formers were irradiated at higher doses ranging from 1-10 kGy (due to their known intrinsic resistance to ionizing radiation). The Irradiated samples were stored at 4°C and analyzed within 2 hours post irradiation. Non-irradiated sludge samples were used as controls for each set of organism that was evaluated. The non-irradiated samples were also transferred to the eBeam irradiation facility, but were not irradiated so as to subject them to the same experimental conditions.

### 20.3.4. Microbiological Analysis

The samples were analyzed for the different target organisms under aseptic conditions as follows.

*Salmonella* Typhimurium – The samples were serially diluted in 1X PBS and dilutions were plated in Tryptic Soy Agar plates containing nalidixic acid (25 µg/ml) (Sigma, St. Louis, MO) and novobiocin (25µg/ml) (Sigma, St. Louis, MO). The plates were incubated overnight at 37°C and the characteristic *Salmonella* colonies were enumerated.

*Escherichia coli* - The samples were serially diluted, and dilutions were plated in EC-MUG media (Difco Co., Detroit, MI) and plates were incubated overnight at 37°C. The plates were read under long wave (366 nm) ultra violet light and the fluorescent colonies were enumerated.

*Aerobic spore formers*– The samples were initially exposed to 64℃ for 15 minutes to remove the vegetative cells. The heat treated samples were further serially diluted and 0.1 ml of the dilutions were plated in Tryptic Soy Agar (Difco Co., Detroit, MI) plates and incubated overnight at 37°C to enumerate aerobic spore forming bacteria.

*Anaerobic spore formers* – The samples were pre-treated for 15 minutes at 64°C (to remove vegetative cells) and serially diluted in 1X PBS. Perfringens agar base, including TSC (Tryptose Sulphite Cycloserine) and SFP (Shahadi Ferguson Perfringens) (Oxoid Limited, Basingstoke, Hampshire, England) media was prepared and m-CP selective supplement I (Fluka, Buchs, Switzerland) was added (1 vial/ 500 ml). The media was dispensed into petri plates along with 1 ml of the samples and swirled. The plates were then incubated overnight in anaerobic jars at 37°C. Black colored colonies were enumerated which indicated the presence of anaerobic spore forming bacteria mostly *Clostridium perfringens*.

*Somatic coliphages, male-specific coliphages and enteric viruses* – The viruses in the sludge sample were extracted using 3% beef extract and filtered using 0.22 µm filters (Millipore, Billerica, MA) (Murthi et al., 2012). The filtered extracts were serially diluted and the target phages and enteric viruses were enumerated. Enumeration of coliphages was carried out using Single Agar Layer method (Method 1602, US EPA, 2001) with the host bacteria *E. coli* CN- 13 for somatic coliphage and host bacteria *E. coli* $F_{amp}^{+}$ for male specific coliphage. Plaques were counted after overnight incubation at 37°C. The viral extract obtained from the sludge samples were also used for enteric virus estimation using tissue culture methods. Infectivity assay was carried out in 6 well plates using BGMK (Buffalo Green Monkey Kidney) cell lines. Around 0.2 ml of the sample as well as dilutions was used for infection of the BGMK cells and the plates were incubated at 37°C at 5% $CO_2$ atmosphere for 24 hours. Plaques were enumerated after staining the plates with 0.1% crystal violet. The rotaviruses in the sample extracts were enumerated using modified PFU method using MA-104 cell line (Espinosa et al., 2012).

### 20.3.5. Data Analysis

Based on the microbial counts obtained from the samples irradiated with different doses, a survivor curve was plotted. The plate counts were transformed into $\log_{10}$ values and were plotted against the measured e-beam doses and a linear regression analysis was performed. The $D_{10}$ value of target microorganisms was calculated by calculating the negative reciprocal of their respective regression slope using SigmaPlot 11.0, (Systat Software Inc. San Jose, CA). Student-t-tests were performed using SigmaPlot 11.0 to determine the statistical significance if any, between different $D_{10}$ values obtained for individual microorganism present in aerobically and anaerobically treated sludge sample.

## 20.4. RESULTS AND DISCUSSION

This study evaluated the inactivation of different bacterial, viral pathogens as well as indicator organisms present in sewage sludge at various eBeam doses. The radiation sensitivity of microorganisms is expressed in terms of its decimal reduction dose or $D_{10}$ value, which refers to the amount of dose (expressed in kGy) required to inactivate 90% of the starting population (Espinosa et al., 2012). Since the reduction of microorganisms as a function of eBeam dose is considered to be linear, linear regression analyses of the inactivation data were performed and the $D_{10}$ value calculated as previously described. The $D_{10}$ values of the target organisms (Table 20.1) as a function of the background sludge matrix (i.e., aerobically digested sludge or anaerobically digested sludge) was obtained.

TABLE 20.1. MEAN D10 VALUES OF DIFFERENT TARGET ORGANISMS IN AEROBICALLY AND ANAEROBICALLY DIGESTED SEWAGE SLUDGE SAMPLE WHEN EXPOSED TO 10 MEV EBEAM IRRADIATION

| Target Organisms | Mean D10 value (kGy) | |
|---|---|---|
| | Aerobically digested | Anaerobically digested |
| Spiked Salmonella Typhimurium | $0.28 \pm 0.01^{A}$ | $0.23 \pm 0.01^{B}$ |
| Indigenous Escherichia coli | $0.31 \pm 0.01^{A}$ | $0.25 \pm 0.01^{B}$ |
| Indigenous Aerobic spores | $3.75 \pm 0.24^{A}$ | $4.04 \pm 0.33^{A}$ |
| Indigenous Anaerobic spores | $4.96 \pm 0.34^{A}$ | $3.12 \pm 0.08^{B}$ |
| Spiked Somatic coliphage | $4.02 \pm 0.38^{A1}$ | $4.07 \pm 0.31^{A1}$ |
| Spiked Male specific coliphage | $2.25 \pm 0.19^{A2}$ | 2.45±0.16 A 2 |
| Spiked Poliovirus | Not determined | 2.07±0.69 |
| Spiked Rotavirus | Not determined | 1.53±0.03 |

Means within the same row having similar letters are not significantly different ($p>0.05$)
Means within the same column with similar numbers are not significantly different ($p>0.05$)

Previous studies have shown that $D_{10}$ value does not remain constant for a particular target organism, but is a function of initial microbial population, innate characteristics of the target organism and the properties of the matrix on which the organisms are present and are irradiated (Espinosa et al., 2012; Gehringer et al., 2003). The results obtained from the current study indicate that the sensitivity to eBeam irradiation differs between different groups of organisms and is also influenced by the matrix (aerobic digester sample or anaerobic digester sample) in which the organisms are present (Table 20.1). Significant difference were observed in case of $D_{10}$ values of *S*. Typhimurium, *E. coli* and anaerobic spores ($p= 0.011$, $0.007$ and $p<0.001$

respectively) present in aerobic and anaerobic sludge. Previous studies using gamma radiation have shown that higher dose of ionizing radiation is required to disinfect sludge borne bacteria compared to those present in water. Coliforms in water have a $D_{10}$ value of 0.11 kGy (Levaillant and Gallien, 1979), whereas the same organisms in sludge require 0.74 kGy to achieve 1 log reduction (Touhill et al., 1969). The organisms present in sludge are somehow protected by the organic matter, which quench the radiolytic species formed during eBeam irradiation. Increasing water content in the matrix is another important factor which increases the indirect damage to nucleic acids by the formation of reactive oxygen species from water molecules.

## 20.5. CONCLUSIONS

This study shows that 10 MeV eBeam irradiation technology is an effective technology that can achieve significant reductions of microbial pathogens that are present in municipal sewage sludges or biosolids. Bacterial pathogens are the most susceptible organism followed by viruses and aerobic and anaerobic spore formers.

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# 21. RADIATION TECHNOLOGY APPLICATIONS USING ELECTRON BEAM ACCELERATOR IN VIETNAM

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**Abstract**

In Vietnam, radiation technology using electron beam accelerator has been developing with three industrial-scale facilities so far. One of them is a 10 MeV, 15 kW UELR-10-15S2 accelerator belonging to VINAGAMMA. While two others that are X-ray converted 5 MeV, 150 kW SB-5/150 LINAC operated in Ho Chi Minh city, Vietnam. Main applications of these accelerators are food irradiation and sterilization of medical products. In addition, the EB facility at VINAGAMMA is using for carrying out some studies and applied developments on radiation modifications of polymers, especially, biodegradable and natural polymers (environmental-friendly and green products) such as a nutrient carrier from carboxymethyl starch (CMS) nanogel, radiation grafted jute fiber for the treatment of waste water containing dying and immune stimulation agent from radiation degraded β-glucan. Carboxymethyl starch (CMS) nanogel was prepared by electron beam radiation intramolecular crosslinking at diluted concentrations of CMS solution and at 15.8 kGy absorbed dose on a 15 kW, 10 MeV electron beam accelerator in VINAGAMMA. Experimental results in viscosity, weight averaged molecular weight, SEM taken coil size and size distribution of radiation cross-linked CMS solution could be anticipated that CMS nanogel has been formed. Both characteristic structure containing hydroxyl groups and nanometer size of CMS nanogel make it easy to adsorb some active substances such as bio actives, nutrition, pesticides, and so on. Leaf-spraying fertilizer that is studied and experimented is a green product and combined CMS nanogel with potassium humate, MnSO4 and ZnSO4. The preliminary formulation of the fertilizer is built up from the typical ingredients and the minimal contents. The fertilizer is used for field test on rice, peanut, Chinese cabbage and dragon fruit. The harvesting yield of these plants is increased at least 8% compared to blank samples.

## 21.1. INTRODUCTION

CMS is a polysaccharide family derivative. In fact, CMS is a starch etherified in NaOH and $ClCH_2COOH$ solution under a certain reaction condition. CMS is used popularly in oil drilling industry, pharmaceutics, cosmetics, nutrients, pesticides and foodstuff [21.1, 21.2]. The CMS nanogel is an another new form of a polymer (dendrimer; linear, branched, comb, star and cycle chain), which is a tightly coiled one through a radiation intra-molecular cross-linking process performed from a diluted CMS solution and impacted by a highly pulse-intensive electron beam radiation. The characteristic properties in order to determine a CMS nanogel formed are a reduction of coil size, of intrinsic viscosity but an unchanged weight averaged molecular weight [21.3, 21.4]. Some diluted polymeric solution such as poly(ethylene oxide), poly(vinyl pyrrolidone), poly(vinyl alcohol), and poly(acrylic acid), which when irradiated by pulses of fast, high intensive electrons from an accelerator are reported to form polymeric coils with nanometer sizes due to intra-molecular cross-linking [21.5,–21.6]. Cross-linking of CMS is easier than that of starch. CMS at a high concentration can be cross-linked either by chemical method (using initiator) or by irradiation one (physical initiation in paste-like form) [21.7]. The CMS nanogel prepared in the study is chosen at 0.7% CMS concentration, 15.8 kGy absorbed dose, and an obtained coil size of 31 nm [21.7]. The role of CMS nanogel in leaf-spraying fertilizer (foliar feeding) is played as a nanometer-scaled carrier of nutrient ingredients such as potassium humate, $Mn^{2+}$, and $Zn^{2+}$ for decrease of leaf surface intension aiming at promoting nutrient absorbance of easier plant leaves. The leaf-spraying fertilizer has some advantages over the common fertilizers, which include [21.8]: Nutrients delivered to plant through leaves faster than that to root; nutrient-utilizing efficiency of leaf-spraying fertilizer is higher that of the others; applied expenses of the fertilizer is lower than that of the others; polluted effect of the fertilizer on environment and soil is not significant.

In this paper, the typical characteristics of the CMS nanogel such as intrinsic viscosity, coil size and weight averaged molecular weight are investigated. From the experimental results, CMS nanogel is combined with some nutrients, for instant, potassium humate, $MnSO_4$ and $ZnSO_4$ used as leaf-spraying fertilizer for field test on rice, dragon fruit, peanut and Chinese cabbage.

## 21.2. EXPERIMENTS

### 21.2.1. Chemicals

Na-carboxymethyl starch ($M_w$=10 kDa, DS=0.85), Emsland-Stärke, Germany. Distilled water, Vietnam. Potassium humate, $MnSO_4$, $ZnSO_4$, China.

### 21.2.2. Equipment

Ubbelohde viscometer, AVS-470, Germany; Gel permeation chromatography 110, detector R1, Agilent, USA; Scanning electron microscope; FE-SEM 4800, Hitachi, Japan; Laser light scattering analyzer, Horibala-920, Japan; UELR-10-15S2 Electron beam accelerator, 15 kW, 10 MeV (VINAGAMMA, Ho Chi Minh city, Vietnam).

### 21.2.3. Preparation of samples and irradiation

Antioxidants in CMS was removed by immersing it in methanol for overnight, filtered and dried in vacuum oven at 60°C for 18 hours before use. CMS was dissolved in distilled water while stirred at 40°C for overnight. The 1% CMS aqueous solution was filtered through a 0.8 µm Sartorios filter and diluted into CMS solutions at concentrations of 0.3; 0.5; 0.7% respectively. All prepared solutions were divided into 25 ml glass vases with the caps, which were saturated by nitrogen inert gas for 15 minutes, tightened and then irradiated by electron beams in VINAGAMMA, at following absorbed doses of 0, 6, 16, 20 and 26 kGy.

### 21.2.4. Analysis of characteristic properties

Weight averaged molecular weight ($M_w$) of the sample was measured on the GPC 110 at 30 $^0$C, 250 and 500 Ultrahydrogel column (Waters), flow rate of solvent of 1 ml/min, Pullulan ($M_w$=780-380.000 Da) used as a standard agent. Viscosity of the solution was measured on a AVS-470 Ubbelohde viscometer at 25$^0$C with water solvent. Nanogel samples were taken on FE-SEM 4800. Particle (coil) size distribution was measured on Horibala-920.

### 21.2.5. Field test

Usage of leaf-spraying fertilizer: 25 ml of the fertilizer solution is taken into 18 liters pressured container that an amount of tapping water of approximately 16 liters is added into. Each crop is sprayed for three times; and every spraying time is about 16 liters of the diluted fertilizer solution. So, the amount of the fertilizer solution used for 3 spraying times is 75 ml for an area of 1,000 m$^2$.

The nutrient components were analyzed in foliar feeding (GEF).

TABLE 21.1. ANALYTICAL RESULTS OF FOLIAR FEEDING

| Measured unit | Component | Content | Analytical method |
|---|---|---|---|
| % | N-CMS | 0.6-0.7 | TCVN 4594-1988 |
| % | $K_2O$ (Potassium) | 1-2 | AOAC 957.02 |
| % | Nitrogen (N) | 2-3 | TCVN 5815-2001 |
| % | Humate | 8-12 | TCN 365-99 |
| ppm | Zn (Zinc) | 350-400 | AOAC 965.09 |
| ppm | Mn (Magnesium) | 300-400 | AOAC 965.09 |
| ppm | Sulphur (S) | 350-450 | AOAC 980.02 |

### *21.2.5.1. Rice tree*

Soil and place: Alluvium soil, in Thanh Duc ward, Ben Luc district, Long An province; test time duration: March–December 2011; rice variety: VND 95-20, Sowing density: 110kg/ha.

The test formulations: CT1: Substrate + water; CT2: Substrate + GEF

Substrate: (110 kg N + 70kg $P_2O_5$ + 55kg $K_2O$)/ha.

Chemical fertilizers applied: Basal fertilizing: 100% $P_2O_5$.

Additional fertilizing: The first time (after sowing for 10 days): 1/3 N + 1/4 $K_2O$; the second time (after sowing for 20-22 days): 1/3 N + 1/4 $K_2O$; the third time (after sowing for 40-45 days): 1/3 N + 1/2 $K_2O$). Observed standards: blooming no./$m^2$, firm paddy grain no., and yield.

### *21.2.5.2. Chinese cabbage*

Soil and place: Rich soil in Nhuan Duc ward, Cu Chi district, HCMC; croptime duration: March-September 2011; variety: Chinese cabbage seeds supplied by Trang Nong Co. Ltd.

Substrate: (150 N + 90 $P_2O_5$ + 65 $K_2O$)/ha.

The test formulations: CT1: Substrate + water; CT2: Substrate + GEF.

Planting density: 15 x 15 cm. Observed standards: tree height; tree weight; and yield.

### *21.2.5.3. Peanut tree*

Soil and place: Rich soil in Nhuan Duc ward, Cu Chi district, HCMC; croptime duration: March–December 2011; variety: A local one; planting density: 10 x 15 cm;

The test formulations: CT1: Substrate + Water; CT2: Substrate + GEF.

Substrate: (40kg N + 80kg $P_2O_5$ + 80kg $K_2O$)/ha.

The chemical fertilizers applied: Basal fertilizing: 100% muck + 100% super phosphate

Additional fertilizing: Time 1 (after sowing for 20-25 days): ½ N + ½ KCl; Time 2 (after seeding for 40-45 days): ½ N + ½ KCl.

### *21.2.5.4. Dragon fruit tree*

Soil and place: Alluvium soil in Thanh Duc ward, Ben Luc district, Long An province; time duration: March – December 2011; variety: Red meat dragon fruit at 4 years old; planting density: 1,000 trees/ha.

The test formulations: CT1: Substrate + water; CT2: Substrate + GEF.

Substrate: (170kg N + 90kg $P_2O_5$ + 120kg $K_2O$)/ha.

The chemical fertilizers applied: Time 1 (after finishing the prior harvested crop): 50% N+70% $P_2O_5$+30% $K_2O$; Time 2 (before having flower buds for 25-30 days): 30% $P_2O_5$ + 30% $K_2O$; Time 3 (as fallen pollen with a ratio higher than 80%): 50 N% + 40% $K_2O$.

Observed standards: Fruit no./tree, average weight/ fruit, Brix index, and yield.

## 21.3. RESULTS AND DISCUSSION

### 21.3.1. The influence of absorbed doses on the intrinsic viscosity ($V_s$) and weight averaged molecular weight ($M_w$) of CMS nanogel formed

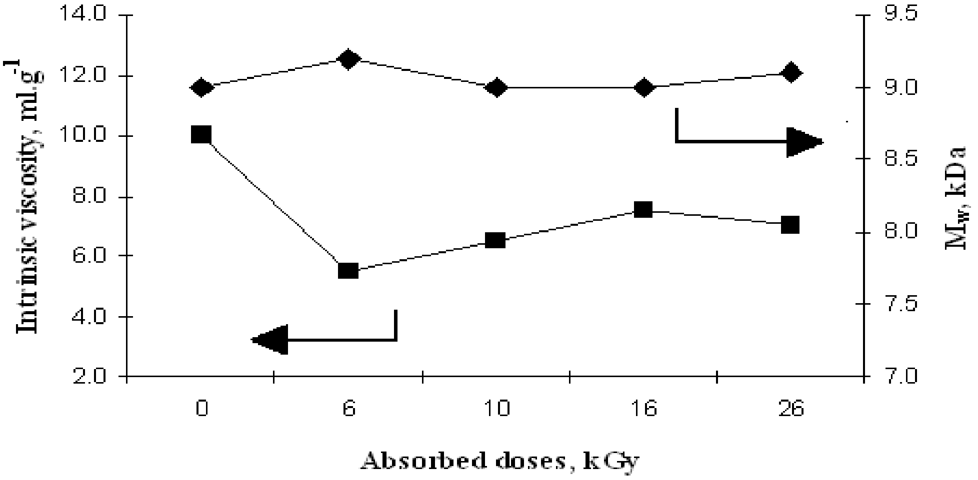

*FIG 21.1. The influence of absorbed doses on $M_w$ and $V_s$ of CMS at 0.7%.*

Figure 21.1. shows the influence of various EB absorbed doses on $M_w$ and $V_s$ of CMS solution at 0.7% concentration. In the range of absorbed doses from 0–6 kGy, the $V_s$ reduces and $M_w$ increases slightly with increasing absorbed dose. It is revealed that radiation degraded process of CMS solution is happening. From 6–16 kGy, the $V_s$ has an increased tendancy while $M_w$ decreased with increasing absorbed dose. In fact, this range of absorbed dose makes the CMS solution crosslinked intramolecularly to induce the CMS nanogel. When the absorbed doses are over 16 kGy, the predominant degradation of CMS solution again occures due to going the viscosity down, but the $M_w$ unchanges any more.

### 3.1.The effect of absorbed doses on coil size and coil size distribution of CMS nanogel

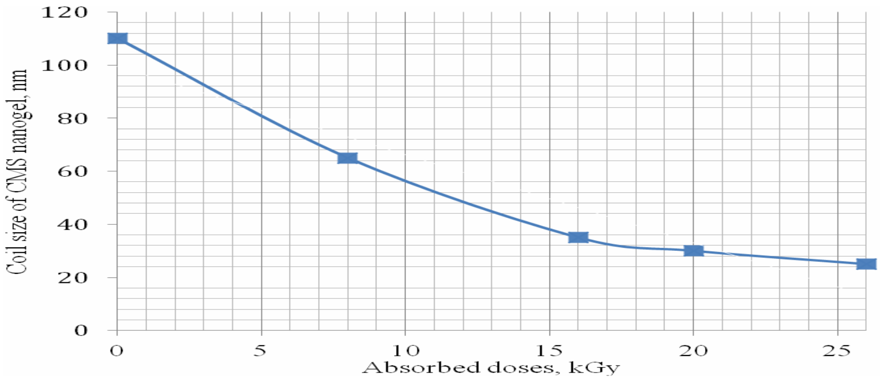

*FIG. 21.2. The effect of absorbed doses on change of coil size of CMS at 0.7%.*

Figure 21.2. shows the effect of absorbed doses on change of coil size of CMS at a 0.7% concentration. The coil size of CMS is going down quickly from 0–16 kGy; and then the coil size reduces slowly. It can be explained that in the range of 8–16 kGy, the coil size is miniatured because of dominant intrachain crosslinking.

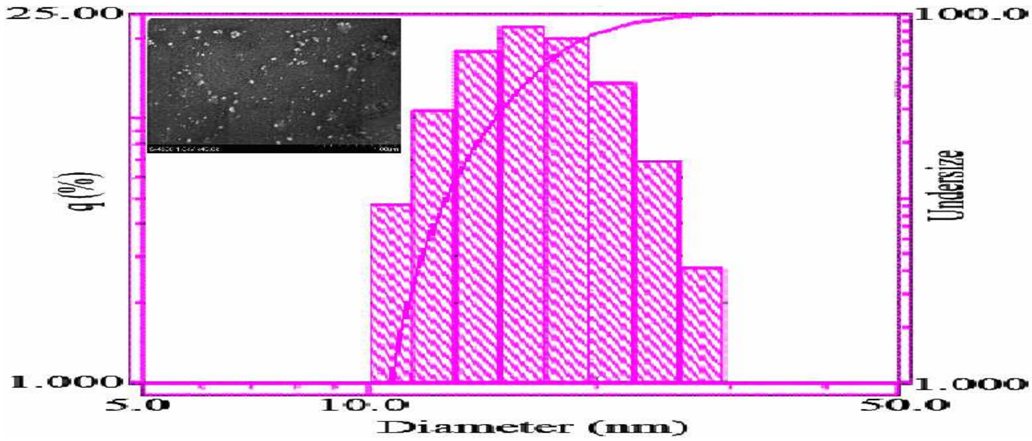

*FIG. 21.3. The coil size and size distribution of CMS nanogel at 0.7% and 15.8 kGy.*

Figure 21.3. shows coil size in the SEM image in the inserted photo in the left top side of the figure and the size distribution of CMS nanogel prepared at the 0.7% concentration and the 15.8 kGy absorbed dose. The averaged coil size measured by laser light scattering technique is about 31 nm. The size distribution of CMS nanogel under the same condition is shown in Fig.21.3. is relatively narrow.

### 21.3.2. The results of field tests

TABLE 21.2 THE EFFECT OF GEF ON RICE

| Formulations | Firm grain no./bloom | P1000 grain, g | Yield, T/ha | Increased yield | |
|---|---|---|---|---|---|
| | | | | T/ha | % |
| *Crop 1 (March- July, 2011)* | | | | | |
| Substrate | 74.13b | 21.18 | 5.01b | - | - |
| Sub.+GEF | 81.61a | 21.78 | 5.53a | 0.52 | 10.3 |
| CV, % | 8.80 | 9.89 | 7.2 | | |
| LSD $_{0.05}$ | 6.63 | ns | 0.48 | | |
| *Crop 2 (August – December, 2012)* | | | | | |
| Substrate | 69.14b | 21.21 | 4.85b | - | - |
| Sub.+GEF | 75.64a | 21.22 | 5.36a | 0.51 | 10.5 |
| CV, % | 10.90 | 10.28 | 7.1 | | |
| LSD $_{0.05}$ | 6.27 | ns | 0.46 | | |

Table 21.2. shows that the rice yield once used additional GEF is higher than 10.40 % compared to that without using the fertilizer because of increasing bloom no./m$^2$ and firm grain no./bloom in both of crops. There is a meaning difference in statistics of the formulations used the added GEF if compared with reference.

TABLE 21.3. THE EFFECT OF GEF ON CHINESE CABBAGE

| Formulations | Tree wt., g | Yield, T/ha | Increased yield | |
|---|---|---|---|---|
| | | | T/ha | % |
| *Crop 1(March- May, 2011)* | | | | |
| Substrate | 40.52b | 24.32b | - | - |
| Sub. + GEF | 44.62a | 26.67a | 2.35 | 9.66 |
| CV (%) | 7.2 | 7.3 | | |
| LSD $_{0.05}$ | 3.12 | 2.34 | | |
| *Crop 2 (July – September, 2011)* | | | | |
| Substrate | 41.12b | 23.45b | - | - |
| Sub. + GEF | 45.15a | 25.81a | 2.36 | 10.06 |
| CV (%) | 7.10 | 7.1 | | |
| LSD $_{0.05}$ | 3.87 | 2.19 | | |

Table 21.3. shows that the yield of Chinese cabbage is up to 9.66–10.06 % when used GEF compared to that of reference including an increase of tree height and weight in 2 crops. There is a meaning difference in statistics of the formulations used the added GEF if compared with reference.

TABLE 21.4. THE EFFECT OF GEF ON THE YIELD OF PEANUT

| Formulations | P100. dried nut, g | Kernel ratio/nut, % | Yield, T/ha | Increased yield | |
|---|---|---|---|---|---|
| | | | | T/ha | % |
| *Crop 1 (March - July, 2011)* | | | | | |
| Substrate | 109.14 | 70.51b | 3.23b | - | - |
| Sub.+ GEF | 109.76 | 77.78a | 3.54a | 0.31 | 9.60 |
| CV, % | 11.23 | 6.7 | 9.89 | | |
| LSD $_{0.05}$ | ns | 6.12 | 0.28 | | |
| *Crop 2 (August – December, 2011)* | | | | | |
| Substrate | 105.51 | 68.76b | 3.12b | - | - |
| Sub.+ GEF | 108.76 | 75.16a | 3.41a | 0.29 | 9.29 |
| CV, % | 9.65 | 10.53 | 8.4 | | |
| LSD $_{0.05}$ | ns | 5.57 | 0.25 | | |

Table 21.4 shows that the yield of peanut tree is up to 9.29 – 9.60% using the GEF compared to that without using fertilizer (reference) because of an increase of nuts/tree and nuts/bush. There is a meaning difference in statistics of the formulations used the added leaf-spraying fertilizer if compared with reference.

TABLE 21.5 THE EFFECT OF GEF ON DRAGON FRUIT

| Formulations | Brix index, % | Wt./ fruit, g | Yield, T/ha | Increased yield | |
|---|---|---|---|---|---|
| | | | | T/ha | % |
| Substrate | 14.45 | 445.1 | 21.11 | - | - |
| Sub.+ GEF | 14.57 | 461.1 | 22.45 | 1.34 | 6.34 |
| CV (%) | | 9.68 | 10.18 | | |
| LSD $_{0.05}$ | | ns | 1.26 | | |

Table 21.5. shows that the yield of dragon tree is up to 6.34 – 8.34% using the GEF compared to that without using fertilizer (reference) because of an increase of fruit/tree. There is a meaning difference in statistics of the formulations used the added leaf-spraying fertilizer if compared with reference.

*Photo 21.11. GEF product produced on pilot –scale*

## 21.4. REMARKS

– A preparation of the CMS nanogel with 31 nm coil size from CMS solution at 0.7% can be cross-linked at 15.8 kGy by electron beam irradiation.

– From the field tests, CMS nanogel can be promoted the growth of some plants such as rice tree, peanut tree, Chinese cabbage vegetable and dragon tree through an increase of their yield.

## 21.5. CONCLUSION

– The VINAGAMMA Center is a leading R&D institution of Vietnam in the field of Radiation Technology.

– The accelerators in Vietnam are utilized economically. Products and services originated from them have been commercialized and significantly contributed to the development of the national economics.

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