Report of the 2ⁿᵈ RCM on

Radiation Treatment of Wastewater for Reuse with Particular Focus on Wastewaters Containing Organic Pollutants

Jeongup, Rep. of Korea, 29 October to 2 November 2012

Working Material

FOREWORD

Chronic shortages of water in arid and semi-arid regions of the world and environmental policy regulations have stimulated the search for appropriate technologies capable of treating wastewater for reuse or safe discharge. Industrial effluents often carry chemical contaminants such as organics, petrochemicals, pesticides, dyes and heavy metal ions. The standard biological treatment processes commonly used for wastewater treatment are not capable of treating some of these complex organic chemicals that are found in varying quantities in the wastewaters. Another emerging problem is the increasing presence of pharmaceuticals and endocrine disruptor compounds in municipal wastewater entering into the receiving stream, for which new treatment techniques and procedures are needed to remove excreted drugs before releasing the effluent into public waterways or reuse. Radiation-initiated degradation of organics helps to transform various pollutants into less harmful substances or reduced to the levels below the permissible concentrations. Studies in several Member States (MS) have demonstrated the usefulness and efficiency of radiation technology for treatment of different organic pollutants. The lack of comparative data in pilot scale studies using radiation technique (alone or in combination with other methods) has been a major issue in further utilization of this method for wastewater treatment. There is a need to study further the radiation effects, evaluate reliability and cost of treating specific group of organic pollutants in cooperation with other stakeholders who are involved in using other technologies.

The Co-ordinated Research Project (CRP) on "Radiation treatment of wastewater for reuse with particular focus on wastewaters containing organic pollutants" has been launched with the objective to study the effectiveness, reliability and economics of radiation processing technology to treat wastewater contaminated with low and high concentration of organic compounds using validated analytical methods and develop guidelines for selection of areas where the radiation treatment has high potential for rendering treated wastewater suitable for industrial and irrigation purposes.

The first Research Coordination Meeting (RCM) of the CRP was held at the Agency's Headquarters in Vienna, during 2-6 May, 2011. The meeting summarized the current status of investigations in this field and discussed the ways to meet the CRP goals. All participants were encouraged to make use of the available material of the CRP participant and work plan, networking and sub-groups activities were defined to enhance cooperation among the participants.

The second RCM, held in Republic of Korea from 29 October 29 to 2 November, 2012 reported on the progress achieved since the first meeting, critically evaluated the results obtained by different groups and formulated the work programme and networking activities for the next period.

The IAEA wishes to thank all the participants in the CRP for their valuable contributions. The IAEA officer responsible for this publication is Mr Sunil Sabharwal of the Division of Physical and Chemical Sciences.

CONTENTS

1. EXECUTIVE SUMMARY

1.1. Background

Chronic shortages of water in arid and semi-arid regions of the world and environmental policy regulations have stimulated the use of appropriate technologies in treating wastewater for reuse, for example, in urban irrigation, industrial uses (cooling, boilers, and laundry), gardens and parks, cleaning purposes, etc. Additionally, water re-use is becoming increasingly important in large industrial centres, where water scarcity represents high operational costs for impounding and adduction. Industrial effluents often carry chemical contaminants such as organics, petrochemicals, pesticides, dyes and heavy metal ions. The standard biological treatment processes commonly used for wastewater treatment are not capable of treating many of the complex organic chemicals that are found in varying quantities in the wastewaters (e.g. persistent organic pollutants, POPs). Another important problem arising is the increasing presence of pharmaceuticals and endocrine disruptors compounds in municipal wastewater entering into the receiving stream, for which new treatment techniques and procedures are needed to remove excreted drugs before releasing the effluent into public waterways or reuse. Table 1 list the major pollutants presents in waste waters and sludges. Radiation-initiated degradation of organics helps to transform various pollutants into less harmful substances or reduced to the levels below the permissible concentrations. Studies in several Member States (MS) have demonstrated the usefulness and efficiency of radiation technology for treatment of different organic pollutants.

The lack of comparative data in pilot scale studies using radiation technique (alone or in combination with other methods) is a major issue in further utilization of this method for wastewater treatment. There is a need to study further the radiation effects, reliability and cost on specific group of organic pollutants in cooperation with other stakeholders who are involved in using other technologies. Therefore, focus of this CRP will be on (i) to study the effects, reliability and costs of room temperature radiation processing technology and determine the optimized radiation dose and procedures, in combination with other processes, to treat wastewater contaminated with low and high concentration of organic compounds; (ii) to validate analytical methods to characterize and evaluate effects of by-products in treated wastewaters; (iii) to obtain data on radiation method to treat wastewater with different concentration of organic pollutants and compare it with data from conventional and novel technologies; (iv) to develop guidelines for selection of areas where the radiation treatment has high potential for rendering treated wastewater suitable for industrial and irrigation purposes. The Members States participating in the CRP are well equipped to carry out such studies in close collaboration with each other and the major facilities available are listed in Table 2.

1.2. CRP overall objective

To enhance Member States capacity in applying radiation technology in combination with other techniques for improving environmental safety aspects through effective treatment of wastewater contaminated with organic pollutants and support reuse of treated wastewater for urban irrigation and industrial purposes. This is in line with the objective of the project 2.5.2.5 to enhance Member States capacity in applying radiation technology for managing agricultural and industrial waste and effluents and decontamination of biological agents.

1.2.1. Specific Research Objectives:

— Compare radiation technology with conventional and novel technologies such as Reverse Osmosis, Ultra- and Nano- Membrane Filtration, Activated Carbon Adsorption, and Advanced Oxidation Process (AOP) as Ozonation, UV, Sonolysis, Fenton process, in regard to costs and effects for different application cases and local situations.
— Assess the analytical methods to characterize and evaluate the effects on micro-pollutant reduction as well as impacts of radiation by-products in treated wastewaters (aquatic eco-toxicity studies)
— Study the effects, reliability and costs of room temperature radiation processing technology for specific groups of contaminants and specific application areas where the radiation technology is promising according to the assessment of existing knowledge.
— Determination of optimized radiation dose and procedures for different application cases, in combination with other pre- and post-treatment processes for contaminated wastewaters
— Develop guidelines for selection of areas where the radiation treatment has high potential for rendering treated wastewater suitable for industrial and irrigation purposes including boundary conditions for successful application.

1.2.2. Expected Research Outputs

The CRP is envisaged to yield the following outputs:

— Procedures and technical requirements, including optimal radiation doses, for radiation treatment of wastewater contaminated with microbiological pollutants and organic compounds; scope for treatment of different pollutants in wastewaters.
— Improved analytical and biological methods to characterize and evaluate the effect of radiation and the effects of by-products in radiation-treated wastewaters.
— A comprehensive feasibility study comparing radiation technology and the conventional technologies to treat wastewater for reuse purpose.
— Guidelines for selection of areas where the radiation treatment has high potential for rendering treated wastewater suitable for industrial and irrigation purposes, in order to facilitate the utilization of this technology in interested Member States.

The CRP is expected to enhance the capability of Member States in the use of radiation processing technology to treat wastewater contaminated with organic pollutants and support reuse of treated wastewater for urban irrigation and industrial purposes.

1.3. Current status and future work plan of R&D, work plan and collaborations

1.3.1.1. Algeria

Summary

In recent decades, the environment is continuously polluted by industrial effluents which often carry extremely toxic chemical contaminants that remain intact for long periods in the environment. The industrial wastes can cause irreversible ecological disasters and lead to cause an imbalance of marine and terrestrial ecosystems. The control of organic pollutant in water is an important measure in environmental protection.

Various research groups around the world have developed physical-chemical techniques to eliminate or degrade pollutants. Degradation by gamma radiation has been recognized as a promising method for the treatment of wastewater contaminated with organic pollutants. It converts non-biodegradable substances in other more easily degradable.

Previous works performed were dealing with the degradation of pesticides by gamma radiation. It was shown that dichlorvos in aqueous solution was completely degraded at the dose of 10kGy and the chlorpyrifos-ethyl, which was completely degraded at the absorbed dose of 50kGy.Other results showed that the degradation of PAH by gamma radiation leaded to a disappearance of acenaphthalene at the dose of 10kGy, for naphthalene, the dose of 30kGy degraded 99.96% of the molecule. The industrial effluent wastewater sample was analyzed by GC-MS before and after gamma irradiation. The results showed that in global view, gamma radiation decreased significantly the contamination level, with the increase of the absorbed dose. In detailed view, the relative content of the naphthalene, 2,7 dimethyl in the effluent sample decreased with the increase of the absorbed dose. At the dose of 6 kGy the molecule was completely degraded. The COD of effluent sample presented a reduction of 58%, when 10 kGy dose was applied. However, the decomposition products were still present in the medium. Several research groups have studied the possibility of using adsorption technology which gave excellent results for the removal of these toxic species present in treated water.

Work plan

— To continue to study the effect of radiation on the degradation of persistent organic pollutants, such as PAHs, present in industrial wastewaters, using ionizing radiation.
— To study the degradation of pesticides found in stormwater, using radiation, to prevent contamination of the sea. The compounds will be determined using GC/MS and HPLC, on samples before and after treatment.

1.3.1.2. Brazil

Summary

In the framework of the CRP IPEN has worked on the irradiation and toxicity assessment for the improvement of dyes standard solutions and real complex effluents (textile) in order to achieve recommended quality for reuse of treated effluents during the process as well as for a suitable environmental discharge. Three different types of effluents were submitted to irradiation including standard solution of two reactive dyes (Remazol Black B - RPB and Remazol Orange 3R – R3AR). It was also identified that different chemical forms of these reactive dyes can contribute to a higher toxic charge during effluents discharges. In general the toxicity control was carried out on crustaceans and luminescent bacteria but a lot of experiments were performed with the aquatic snail *Biomphalariaglabrata*, this last biological assay was developed at "Instituto Butantan (USP, SP)". Irradiations and measurements with UV spectrophotometer resulted always on less colored effluents and most often on less toxic liquid residues, after irradiation. Percentage of reductions for toxicity and color depended on the effluent source and the radiation doses applied varied from 1 to 10 kGy. The discoloration of remazol black B and orange 3R solutions were effective for 1kGy and 2.5 kGy which is a relatively low dose and may contribute to a suitable cost for irradiation technology. Since the possibility of different formula of dyes be present at environment exist, the toxicity was measured for all of them and it was noted that vinylsulphone form was the worst in terms of effects for *V. fischeri* (Black B 133%) and *D. similis* (Orange 3R). Regarding biological

effects of these remazol dyes after irradiation, this same dye solution resulted at 60% removal only for *V. fischeri* (not for daphnids) and when treated with 5 kGy and 10 kGy. Irradiation of real textile BVT effluents resulted in good color removal but the acute toxicity reduction varied widely 97% (0.5kGy), 54% (2.5kGy) and 19% (1.0kGy), BTV1 – BTV3. The chemical effluent required higher radiation doses to reduce toxicity (20kGy up to 40kGy).

Work plan

— To conclude studies for effluents from the Vicunha plant to include the possibility of water reuse;
— To irradiate fluoxetine in water and in wastewater to understand the degradation and potential toxicity of reaction by-products;
— To demonstrate the efficacy of radiation for treatment of surfactants and complex mixtures of organic compounds in wastewater;
— To complete the studies at the Suzano WWTP, with respect to dose and toxicity;
— To organize seminars in Sao Paulo region to present the results of the demonstration project.

1.3.1.3.   China – (Ms. Libing Chu)

Summary

The response of sewage sludge exposed to ^{60}Co gamma irradiation at a dose of 0-25 kGy was investigated. Results showed that gamma irradiation could disintegrate sludge flocs and release proteins, polysaccharides and extracellular enzymes into the bulk solution. The maximum oxygen uptake rate decreased by 58%, and 99% of the culturable bacteria were inactivated at 25 kGy. However, the tested protease, superoxide dismutase and catalase showed slight inactivation during irradiation treatment. Around 7.3% of SOD and 8.4% of catalase was inactivated at a dose of 20 kGy. Interestingly, the extracellular protease activity increased at irradiation doses lower than 15 kGy, and thereafter gradually decreased by around 6.5% at a dose of 25 kGy. The efficiency of sludge solubilization reached around 6.5% with a dose of 25 kGy. The efficiency of sludge solubilization with aeration was increased by around 25% compared to that without aeration at an irradiation dose of 2.5-9 kGy. The soluble protein, polysaccharide and humic-like substance concentrations were higher under aerated conditions. With aeration the overall reaction appears to be oxidative as evidenced by the higher nitrate and nitrite ion concentrations in solution. The results of the study suggest that sludge treatment by gamma irradiation will reduce the amount of solids necessary for disposal.

Work plan

— To study the effects of gamma and electron beam irradiation on the degradation of bio-hazardous contaminants in sewage sludge, e.g. antibiotics sulfadiazine and sulfamethazine will be chosen as the targets.
— To study the combined effect of ionizing irradiation with hydrogen peroxide and metal oxides.

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Summary

This study investigated the effects of irradiation and coagulation on the molecular weight distribution of soluble organic substances in the paper mill effluent. Various parameters of wastewater samples before and after treated were investigated, including chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), dissolved organic carbon (DOC) and absorbance at 254 nm wavelength (UV_{254}) as well. In addition, the effects of irradiation on oxygen uptake and on acute toxicity were also presented. The present results showed that irradiation alone cannot promote the biodegradability and oxygen uptake as originally expected. The whole acute toxicity of samples was reduced after gamma irradiation. On the other side, coagulation can not only effectively eliminate the sectors with high molecular weight (MW>3000 Dalton), but also improve the capacity of ionizing irradiation initiated the transformation of medium molecular weight (1000 Dalton<MW<3000 Dalton) into low molecular weight (MW<1000 Dalton), which is readily degraded by the subsequently activated sludge process. This inferred that the combination of coagulation and ionizing radiation may be a cost-effective way to treat the paper mill effluent.

Work plan

— Comparison of gamma and electron beam irradiation on the performance of real wastewater samples from paper mill plants.
— Toxicity evaluation of the wastewater irradiated by electron beam irradiation under varying conditions
— Up-scaling of the combined coagulation and irradiation process to pilot scale for paper mill wastewater.
— To compare the techno-economic evaluation to conventional treatment process.

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Summary

The high-energy ionizing radiation induced degradation of ketoprofen, chloramphenicol, paracetamol and phenol was studied both by steady state gamma radiolysis and pulse radiolysis. Degradation mechanism was suggested for the reaction of OH radical with the investigated molecules. The change in toxicity of the solutions during degradation was also followed.

The radiation induced degradation of maleic acid, fumaric acid and 20 aromatic molecules was investigated in air saturated aqueous solutions. The decomposition in the hydroxyl radical induced reaction was followed by chemical oxygen demand (COD) and total organic carbon content (TOC) measurements. Up to ~50% decrease of COD the dose dependence was linear. By the ratio of the decrease of COD and the amount of reactive radiolysis intermediates introduced into the solution the oxidation efficiencies were calculated. Efficiencies around $0.5-1$ (O_2 molecule built in products/$^\bullet OH$) found for most of the compounds show that the one-electron-oxidant $^\bullet OH$ induces $2-4$ electron oxidations. The high oxidation rates were explained by $^\bullet OH$ addition to unsaturated bonds and subsequent reactions of the dissolved O_2 with organic radicals. In amino substituted molecules or in Acid Red 1 azo dye, O_2 cannot compete efficiently with the unimolecular transformation of organic radicals and the efficiency is lower $(0.2-0.5)$.

Work plan

—   We plan to study the radiation induced degradation of the following compounds:
—   ibuprofen, salicylic acid, 2-acetoxy benzoic acid, muconic acid, and chlofibric acid.
—   For the first three compounds a mechanism for the radiation induced degradation will be suggested. For muconic acid the mechanism of degradation by ionizing radiation and by VUV will be compared. For chlofibric acid we plan a very detailed investigation of the degradation compounds, identification by HPLC-MS/MS measurements.
—   We also plan to study the degradation of phenol as a model compound by using ionizing radiation and wet oxidation (10 bar oxygen pressure and 100 °C).
—   We expect a synergistic effect due to the combination of the two methods.
—   Furthermore, experiments using gamma irradiation for the treatment of sludge are planned.

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1.3.1.6.   Italy

Summary

The decomposition of a surfactant (SDBS) and of four emerging pollutants (ofloxacin, carbamazepine, benzophenone-3, benzophenenone-4), alone or in a multicomponent system (MIX-4) has been studied in water by a number of Advanced Oxidation Processes. The remediation methods included UV, γ-rays and e-beam, all running in atmospheric conditions. It is shown that any of them can be improved by adding a photocatalyst (TiO_2), or a radical mediator (H_2O_2). Also a study on the maximization of the OH yield, during the radiolysis of an aqueous/H_2O_2 system, indicates a $G(OH)_{max} = 0.52$ µmol/J when $[H_2O_2] = 5\text{-}10$ mM. The processes were monitored during the intermediate- as well as final-steps, by measuring the TOC content and the concentration of pollutants by HPLC, and UV-vis spectroscopy. The effect of added H_2O_2 on TOC measurement methods has been also investigated, reaching the conclusion that whenever H_2O_2 conc. exceeds 2 mM it masks the real organic carbon content.

Work plan

— Continuation of both basic and applied investigations on using real and model water systems treated with ionizing radiation, UV light, and ultrasound. We will study:
— The influence of oxidation enhancers (H_2O_2, TiO_2) monitored with regard to TOC, BOD_5, COD reduction.
— The optimization of analytical methods in the presence of H_2O_2.
— The possible eco-toxicity of reaction by-products.
— The development of a prototype-reactor implemented with hydrogen peroxide or metal oxide oxidation-enhancers (H_2O_2, TiO_2), for effluents with low flow in applications of domestic eco-laundry machines.
— Pollutant systems in consideration:
  • Surfactants and commercial detergents
  • Emerging pollutants: single and complex systems

Publications

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1.3.1.7.   Japan

Summary

Endocrine disrupting chemicals (EDCs) mimic a natural hormone or disrupt endocrine system in livings to give ill effects. Treatment of EDCs has been attempted by the activated sludge system, and a result of this system is found to be insufficient to eliminate them. Treatment of real wastewater having the estrogen activity was studied by γ-ray irradiation in the present CRP. Three samples of the real wastewater having medakaestrogen activity (mEA) were analyzed by the yeast two-hybrid assay to be 3.1 to 11.3 ng dm^{-3}. Every mEA initially increased and then decreased by γ-ray irradiation, indicating that decomposition products also have the estrogen activity. The doses required to decrease in mEA of samples 1 to 3 below 1 ng dm^{-3}, D_{1ng}, which is the lower limit concentration of appearance of endocrine disrupting property were estimated to be 100, 200 and 150 Gy, respectively. Since the D_{1ng} of 17 β-stradiol at 500 ng dm^{-3} in pure water was estimated to be 5 Gy, the elimination of estrogen activity of real wastewater is considered to be interfered by organic impurities. The economic cost of the treatment process of EDCs using electron beam was estimated at 17 yen m^{-3}. The charges of the treatment plants were set in the range of 30 to 140 yen m^{-3}, the electron beam treatment system is considered to have the potentiality of the attachment to the treatment plants.

Work plan

— Decomposition of the pharmaceuticals (e.g. antibiotics) in wastewater is initially treated by the activated sludge system to decompose the biodegradable pharmaceuticals and reduce the TOC.

— Persistent pharmaceuticals, which are not decomposed by the activated sludge system, will be treated by γ-ray, and the decomposition efficiencies will be determined in wastewater.

— Kinetics of reactions of antibiotics with radiation induced hydroxyl radicals and hydrated electrons in water will be investigated by pulse radiolysis.

— To determine the required dose for the decomposition of pharmaceuticals in wastewater using a combination of activated sludge and ionizing radiation to economically achieve treatment objectives.

— To develop the economic viability of combining treatment methods for real wastewater containing organic pollutants such as endocrine disrupting chemical's, halogenated organic compounds and pharmaceuticals.

1.3.1.8.   3.8 Korea – (Mr. Bumsoo Han)

Summary

On-site pilot scale treatment of wastewater from municipal plant will be applied to optimize the operation parameters by a skid mounted Mobile Electron Beam Plant (MEB) mounted in a 40' box metal cargo shipping container. Self-shielded 0.7MeV (20kW) electron accelerator with control and monitoring system together with water/air cooling system are the main constituents of the plant. Also the wastewater treatment facilities (pumps, gauges, reservoirs etc.) are included. This plant can treat up to 500m^3/day with 2kGy at continuous operation mode. This Mobile Electron Beam Plant (MEB) has proved its on-site adaptability as operating for a pilot scale demo plant for flue gas treatment from the power plant in Jeddah, Saudi Arabia.

To confirm the use of EB as an alternative disinfectant to chlorine for the liquid stream, a bench scale experiments were conducted with samples from the Municipal Wastewater Treatment Plant. In these experiments, electron accelerator of 1 MeV, 40kW with the dose rate of 40kGy/s is used with the injection nozzle. The number of indicator microorganisms decreases 10^2 times with 0.2 ~ 0.5kGy and 10^4 times with 1kGy without any changes in other water quality indices.

For technologies entering the market place, it is crucial to have results for the inactivation of both conventional and alternate indicators since alternate indicators are beginning to enter the permitting arena. Although not currently permitted, trace organic compounds (TOrC) removal is gaining momentum as a concern for many municipalities. Our approach investigates the efficacy of e-beam technology to remove TOrCs at doses used for indicators removal, as well as at environmentally relevant TOrC levels.

The mobile plant will be operated continuously to obtain parameters for collecting datawith various conditions to secure consistency and reliability of EB process despite fluctuating external environmental variables like day versus night operation, weather and seasonality. Evaluation of obtained data for optimization of the EB process for municipal treatment and also the evaluation of energy loss and absorbed dose upon the water thickness will be

conducted to optimize the pre-treatment and post-treatment design parameter. In order to develop the design criteria to construct commercial scale re-use plant, evaluation of alternatives to address unforeseen problems resulting from the actual use of proposed treatment processes will also be conducted.

Work plan

— Treatment of effluent from municipal plant for re-use with mobile electron beam plant:
The approach addresses the fate of not just conventional indicator organisms (*E. coli*, *Enterococcus*, coliforms, and total coliforms), but also provides a framework to track and monitor the fate of alternate indicator organisms like the *Bacteroidales*, which are anaerobic and hence decay faster in ambient waters. Unlike traditional indicators, because they are host-associated, a given *Bacteroidales* genetic marker can be used in the differentiation between human and nonhuman pollution and in the identification of specific animal sources – important information for source control and treatment programs. Both *Enterococcus* and *Bacteroidales* are currently being considered by U.S. EPA in their epidemiological studies to update existing ambient water quality criteria using quantitative PCR (qPCR) methodology.

— Disinfection of marine ballast water:
On-site pilot scale treatment of Ballast water from containerships will be applied to optimize the operation parameters by a skid mounted Mobile Electron Beam Plant (MEB) mounted in a 40' box metal cargo shipping container. Self-shielded 0.7MeV (20kW) electron accelerator with control and monitoring system together with water/air cooling system are the main constituents of the plant. Evaluation of obtained data for optimization of the EB process for municipal treatment and also the evaluation of energy loss and absorbed dose upon the water thickness will be conducted to optimize the pre-treatment and post-treatment design parameter.

— Disinfection of (Hydrothermal Fracturing) Fracing water in Shale Gas production:
The current practice of eliminating bacteria from fracturing fluid is the use of hazardous bactericides, mainly gluteraldehyde, that contain hazardous constituents such as polynuclear aromatic hydrocarbons (PAH). Disinfection of frac make-up water is currently done with chemical biocides, but advanced disinfection ("green") technologies are required. On-site operation of Mobile Electron Beam Plant is planned. The mobile plant will be operated continuously to obtain parameters for collecting datawith various conditions to secure consistency and reliability of EB process.

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1.3.1.9.   3.9 Korea – (Mr. Myun Joo Lee)

Summary

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 the water stream. Therefore, it is very important to control the toxic and non-biodegrable chemicals before those are discharged to water stream. Limited technologies, such as AOPs (Advanced Oxidation Processes), for the control of these toxic and non-biodegrable chemicals have been applied into the wastewater treatment plants. However, the control efficiencies of the existent technologies are not high enough.

Recently, a mobile electron beam accelerator (MEB) was constructed in Korea and 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 study for demonstration of new technology is very important for securing both confidence of the technology and public acceptance on radiation.

According to the KAERI's national research plan, basic radiation application works on sterilization, decomposition of antibiotics and endocrine disruptor contained in effluent by using radiation were conducted in KAERI's laboratory for three years. In 2011, The field study on advanced sewage treatment with a MEB was conducted and the results obtained from study played an important role in the acquiring a certification on advanced treatment of sewage effluent by radiation, NET(New Environmental Technology), which is issued by Korea ministry of environment. The field study was carried out over four seasons in order to make a sure the seasonal effect of temperature 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 bacteria and microorganisms were also sterilized under the same irradiation dose. Toxicity arising by antibiotics on algae reduced according to irradiation dose. For the further work, achievements from field demonstration study will be transferred to industry. Research on by-products from irradiated antibiotics and toxicity before and after irradiation of antibiotics will be kept going on in field with MEB. This information will be very useful for the project by radiation treatment of wastewater for reuse, particularly focused on wastewater containing organic pollutants.

Work plan

⸻ Field studies with the MEB will be continued in order to demonstrate the efficacy of radiation technologies in various waters. The first objective will be control of coliforms. The second objective will focus on the reduction of toxicity. The third objective will be a study on transformation of non-biodegradable pollutants to biodegradable compounds, which are found in livestock wastewater, landfill and waste food.

⸻ Through NET (the New Environment Technology) initiative of the Korean ministry of environment, the electron beam treatment for advanced sewage treatment will be continued.

1.3.1.10.   Malaysia

Summary

The research carried out during the period of contract, 2011-11-17 to 2012-11-16, involved treatment of mixed industrial wastewater using activated sludge system and electron beam irradiation.

In the activated sludge system, the effect of Hydraulic retention time (HRT) on the characteristics of the wastewater was carried out in addition to the identification of the microbes. Results show that the removal efficiency of COD, suspended solids and color is directly related to the HRT period. Six types of microbes were identified in this study.

Effects of different absorbed dose and beam current were also studied in the irradiation treatment. It was found that the wastewater can be treated at lower dose (3 kGy). Higher beam current gives better removal efficiency of COD, suspended solids and color. In addition, destruction of plasticizer in the wastewater was also studied. In this case, the wastewater was spiked with DEHP. It was found that DEHP can degrade when expose to radiation. Aeration prior to irradiation can improve the degradation rate.

Work plan

⸻ To determine the optimum combination of biological and radiation treatment processes in mixed industrial wastewaters.

⸻ Continue studies on biological treatment operating condition to minimize hydraulic retention times, by analyzing the treated wastewater with conventional measures (e.g. BOD_5, COD, TOC, TSS, turbidity, pH and toxicity).

⸻ Study the effect of electron beam irradiation process,on treatability at different doses, by characterizing the treated wastewater with conventional measures (e.g. BOD_5,COD,TOC, TSS, color, turbidity, pH and toxicity).

⸻ Select the optimum operating conditions for the combined biological and irradiation treatment system for mixed industrial wastewater.

⸻ To study the effect of radiation treatment of DEHP at lower doses in mixed industrial wastewater.

1.3.1.11. Poland

Summary

Laboratory and feasibility study for wastewater effluents treatment by radiation was proposed to describe chemical contribution and physical-chemical separation of nonorganic pollutants deposited in industrial waste. The formation of sediments from suspensions and chemical reaction involvement initiated by electron beam will be studied. The evaluation of the radiation process of nonorganic pollutants separation, decomposition and removal will be evaluated from technical and economical point of view.

Different hazardous wastes are produced as the results of mankind activity what creates serious impact on environment, especially in industrialized countries. The radiation processing method may offer unique possibility for wastes recycling, when common processes are too expensive or not offering required efficiency. The suitable evaluation procedure should be applied regarding development status, technical feasibility, retrofitability, process reliability, energy consumption, resources requirements and economical aspects of the radiation process.

It has been confirmed that wastewater treatment by radiation regarding chemical processes contribution and physical-chemical separation of highly concentrated nonorganic pollutants deposited in specific industrial can be successfully performed. The sediment after sediment tank should be irradiated to obtain the highest process efficiency. The dose 2.5 kGy was found to be optimal from point of view process economical effectiveness.

Work plan

— A laboratory facility, based on the electron beam process, should be built to confirm possible mechanisms of the sedimentation process of nonorganic pollutants during separation initiated by ionizing radiation.

— Evaluation of the technical and economic viability of this radiation technology process for an industrial facility of this type will be the main output at the final stage of the project.

1.3.1.12. Portugal

Summary

In the framework of the CRP on "Radiation treatment of wastewater for reuse with particular focus on wastewaters containing organic pollutants" Portuguese team is been developed studies on the implementation of ionizing radiation technology as a complementary treatment for industrial effluents and on the potential of ionizing radiation to increase the added value of these wastewaters. Based on these assumptions, preliminary studies of the gamma radiation effects on the antioxidant compounds present in cork cooking water were carried out. Radiation studies were performed by using radiation between 20 and 50 kGy at 0.4 kGy/h and 2.4 kGy/h. The radiation effects on organic matter content were evaluated by Chemical Oxygen Demand (COD). The antioxidant activity was measured by Ferric Reducing Power (FRAP) assay. The total phenolic content was studied by Folin-Ciocalteau method. Results point out that gamma radiation increases both the amount of phenolic compounds and antioxidant capacity of cork cooking water. On the other hand, the radiolytic degradation by ionizing radiation of gallic acid and esculetin as models for recalcitrants were studied, and the

objective of the study was to find out if radiolytic degradation, followed by microbial degradation could increase the treatment efficiency. A natural cork wastewater bacterium was selected from the irradiated wastewater at 9 kGy. The applied methodology was based on the evaluation of growth kinetics of the selected bacteria by turbidimetry and colony forming units, in minimal salt medium with non-irradiated and irradiated phenolic as substrate. The overall obtained results highlights the potential of this technology for increase the add value of cork waters and raised some issues to explain by new methodological setup on biodegradation studies.

Work plan

— On-going studies are focusing on two main fields:
  - Extraction of potential antioxidants by activated carbon (olive seeds),
  - To determine the economic viability of these techniques,
  - To perform toxicity tests, and,
  - To conduct experiments using an electron beam process for comparison to gamma-irradiation.
— To examine options using a new methodological setup for biodegradation of recalcitrant organic compounds,
— Investigate different microbial populations to optimize the biological treatment after ionizing radiation.

Publications

Accepted scientific papers

Madureira, J., Melo, R., Botelho, M.L., Leal, J.P., Fonseca, I.M., Effect of ionizing radiation on antioxidant compounds present in cork wastewater, Water Sci. (2012)

Technol.doi:10.2166/wst.2012.544.

Oral communications

Madureira, J., Melo, R., Botelho, M. L., Leal, J. P., Fonseca, I. M., Effet of ionizing radiation on antioxidant compounds present in cork wastewater, 1st International Congress on Water, Waste and Energy, Salamanca, Spain, 23 – 25 May 2012.

Thesis

Melo, R.: Aplication of Ionizing Radiation to Persistent Organic Pollutants Decomposition, PhD thesis on Technological Chemistry, Supervisor: Leal, J.P., (IST/ITN, CQB/FCUL), Botelho, M.L., (IST/ITN). (Defense in December 2012)

Madureira, J., Estudo do efeito da radiação ionizante na capacidade antioxidante doscompostos presents na água de processo da indústriacorticeira, Master in Chemical Engineering, Faculty of Sciences and Technology – New University of Lisbon.

Supervisor: Melo, R., (IST/ITN).

Silva, T., Avaliação dos antioxidants presents nas águas de processo da indústria corticeira, Master in Food Safety and Technology, Faculty of Sciences and Technology, New University of Lisbon, Supervisor: Melo, R., (IST/ITN).

Junqueira, C., Valorização das águas corticeiras: extracção de antioxidantes, Master in Chemical Engineering, Faculty of Sciences and Technology, New University of Lisbon, Supervisor: Melo, R., (IST/ITN).

1.3.1.13. Romania

Summary

Although Romania is not on a map of the water crisis, water resources of our country are relatively poor and unevenly distributed in time and space. Water bodies assessed in 2011, which meet the environmental objectives (have good ecological status and good ecological potential): only 80 % of all surface water bodies; and only 82 % of groundwater bodies.

In 2011, the volume of water required by businesses is 7.7 billion cubic meters (bcm) of water, down from the previous year and almost three times lower than in 1990. Broken down by categories, total water requirement for 2011 is as follows: 1.22 bcm of water (17 %) for the population; 1.32 bcm of water (17%) for agriculture; and 5.16 bcm of water (67%) for the industry.

From official data (http://www.rowater.ro), the degree of connection to sewerage equivalent population is 57 %; while the degree of connection to wastewater treatment plants is 46 %, which makes enough room for both conventional and non-conventional water treatment technologies.

In accordance with the Accession Treaty to EU, Romania obtained following transition periods for compliance with EC Directive no. 91/271/EEC concerning urban waste water: until 2015, for 263 agglomerations of > 10,000 inhabitants; and until 2018, for 2,346 agglomerations between 2,000 and 10,000 inhabitants. About 170 new or rehabilitated wastewater treatment plants will be connected, producing an increase in the volume of treated wastewater from 35 % to 60 %. It is also anticipated an increase in people connecting to water at the regional system from 52% to 70%.

Organochlorine pesticides and polychlorinated biphenyl's are groups of toxic compounds, most of them being included in the Stockholm convention list of persistent organic pollutants. They are characterized by high chemical stability and may lead to marked changes in the aquatic ecosystem via bioaccumulation and biomagnification. Gamma radiolytic degradation is thought to be a promising treatment for their decomposition to more environmental friendlier compounds.

The experimental part was focused on optimization and extension of applicability of ISO 6468:1996 standardized analytical method for the validation of radiation treatment of waste waters containing certain organochlorine insecticides or poly-chlorinated biphenyls (PCBs). The analytical methods used were gas chromatography coupled with mass spectrometry and micro electron capture detector. The decomposition of organochlorine insecticides or poly-chlorinated biphenyls (PCBs) from spiked sewer waste water samples was achieved with gamma irradiation. An on-going radiolytic study is currently carried out on model wastewater samples spiked with organochlorine insecticides (e.g. hexachlorobenzene) and PCBs (e.g.

PCB 52). To identify most convenient irradiation conditions for wastewater treatment, samples were irradiated at different doses: 1.3, 4.5 and 13 kGy (1.3 kGy/h).

The dependence of organochlorine insecticides and polychlorinated biphenyls concentration of the irradiation dose was monitored with gas chromatography (GC) with simultaneous micro electron capture detection (ECD) and mass spectrometric detection (in single ion monitoring mode). The molecular structure confirmation of target compounds was also performed with the mass spectrometric detector in SCAN mode.

Gamma irradiation experiments on spiked waste water with PCB 52 enabled us to calculate the dose necessary to decrease by 10 times the concentration of PCB 52 by radiolytic decomposition. The GC/MS screening in SCAN mode was unable to evidence the presence of persistent organic pollutants radiolysis products. Other studies in correlation with molecular modelling may be performed in order to determine the order of magnitude for the concentration of possible persistent organic pollutants radiolysis products, whether it is significant or not when compared with the concentration of parent molecules and with the detection limits of the current available instrumentation.

Work plan

— Determination of optimum absorbed dose for the gamma irradiation treatment of synthetic and natural municipal waste water contaminated with EDCs (e.g. DDT or HCH) by GC-ECD and GC-MS and/or pharmaceuticals by HPLC quantitative analysis.
— To use GC-FID screening for identification of microorganisms which survive after the irradiation treatment of municipal wastewater.

Publications

Oral communications

Virgolici, M., Bugheanu, P., Stanculescu, I.R., Medvedovici, A.V., Manea, M.M., Negut, C.D., Cutrubinis, M., Moise, I.V., Ponta, C.C., Decomposition of organochlorine insecticides from wastewater by gamma irradiation, 12th Tihany Symposium on Radiation Chemistry, Zalakaros, Hungary, August 27- September 1, 2011.

1.3.1.14. Turkey

Summary

In this period of the research, aerobic and anaerobic digestion, characterization of alkaloids present and radiolysis products formed after irradiation, irradiation under different conditions of ambient and additives, optimization of radiation dose to achieve desired end characteristics for discharge of waste water were aimed. In this regard, non-irradiated and irradiated wastewaters were subjected to aerobic and anaerobic digestions. Substrate removal efficiencies of non-irradiated and irradiated wastewater with various initial COD values were determined with SBR aerobic digestion treatment method. On the other hand Fenton's advanced oxidation treatment method was also applied for pre-treatment. BMP tests of anaerobic digestion were also completed. LCMS studies were carried out on non-irradiated and irradiated alkaloid standard solutions of morphine, codeine, thebaine, papaverine, and noscapine to determine the degradation mechanisms and byproducts. Dose optimization

studies were completed and found to be a lower dose of 5 kGy rather than 40 kGy for ambient irradiation conditions.

Work plan

— To study the effect of effluent characteristics on the radiation treatment of alkaloid industrial wastewater.
— To characterize the specific organic pollutants present in the alkaloid industrial wastewater and to determine the radiolysis products.
— To optimize the radiation treatment of alkaloid industrial wastewater using both aerobic and anaerobic digestion for the reduction of COD.
— To examine the toxicity of the alkaloid industrial wastewater before and after radiation treatment.

1.3.1.15.   USA (Mr. Suresh Pillai)

Summary

The EChO technology developed at Texas A&M University's National Center for Electron Beam Research is currently in the final stages of a United States utility patent approval. The Office of Technology Commercialization at the university has signed an option agreement with a multinational company, Headworks, Inc., based out of Houston, Texas. The option agreement allows the company to explore the possibility of licensing the technology. In the meantime the investigators are working with a few wastewater utilities around Texas and elsewhere to better understand the mechanisms by which the technology can be adopted in the wastewater industry. The efforts over the past year have focused on disseminating the technology among the financial investment community, the wastewater industry personnel and a selected number if environmental consulting firms.

Work plan

— Prepare specific cost estimates for adoption in medium –large scale sewage treatment plants.
— Evaluate integration of E-Beam technology into higher end treatment technologies such as Cambi®, thermal hydrolysis.

Publications

Murthi, P., Nair, C., Jesudhasan, P.R., Pillai, S.D., Comparing Extraction Buffers to Identify Optimal Method to Extract Somatic Coliphages from Sewage Sludges, Bioresources Technol. (2012). (in press)

Reed, A.L., Pillai, S.D., E-Beam based ionizing radiation technology for municipal biosolid treatment, Solids Processing Design and Management Manual. (ed Smith, J.), Water Environment Federation, Alexandria, VA (2012).

Mueller, M.T., Lee, S., Kloba, A., Hellmer, R., Kumar, N., Eaton, M., Rambo, C., Pillai, S., Large area radiation source for water and wastewater treatment, Proceedings of SPIE - the international society for optical engineering (2011).

Presentations

Pillai, S.D., Reimers, R.S., (Invited speaker) Municipal Biosolids for Bioenergy, 5th International Conference, International Forum on Industrial Bioprocesses, Taipei, Oct. 2012.

Water Environment Federation - Residuals and Biosolids, Conference: *Biotechnology applications utilizing biosolids*, Raleigh, N. Carolina, March 2012.

World Bank, Electron beam business opportunities for Mexico and Latin America, Washington, DC., February 2012.

Concordia University, High energy electron beam irradiation for sludge disinfection, Montreal, Canada, February 2012.

WEFTEC – Pathogen Indicators and the Search for the Perfect Indicator Organism, Los Angeles, CA, Oct. 2011.

Gwangju Institute of Science & Technology, *Identifying Pathogens and Pathogen Surrogates in Sewage using Deep Sequencing*, Gwangju, S. Korea, October 2011.

World Bank, IFC -Global dissemination of E-Beam/X-ray technologies, Mexico City, October 2011.

Student Honors (2010 and 2011)

2011 International Meeting on Radiation Processing (IMRP) Student Scientific Contribution Award for Charlotte Rambo for her oral presentation titled, "Biological Responses to Varying Ionizing Irradiation Dose Rates and Energies: A Literature Review"

2011 International Meeting on Radiation Processing (IMRP) Student Scientific Contribution Award for Charlotte Rambo for her poster presentation titled, "Biological Responses to Varying Ionizing Irradiation Dose Rates and Energies: A Literature Review"

2010 Texas A&M University Student Research Week Awards.

Chandni Nair, for her oral presentation entitled "Microbial Inactivation of Municipal Biosolids Using Electron Beam and Chemical Oxidants.

1.3.1.16.   USA (Mr. William J. Cooper)

Summary

Advanced oxidation/reduction processes (AO/RPs), utilizes free radical reactions to directly degrade chemical contaminants as an alternative to traditional water treatment. This study reports the absolute rate constants for reaction of diclofenac sodium and model compound (2, 6-dichloraniline) with the two major AO/RP radicals; the hydroxyl radical (•OH) and hydrated electron (e^-_{aq}). The bimolecular reaction rate constants ($M^{-1} s^{-1}$) for diclofenac for •OH was (9.29±0.11) x 10^9, and, for e^-_{aq} was (1.53 ± 0.03) x10^9. Preliminary degradation mechanisms are suggested based on product analysis using ^{60}Coγ-irradiation and LC-MS for reaction by-product identification. The toxicity of products was evaluated using the *Vibrio fischeri* luminescent bacteria.

Work plan

— To study the free radical chemistry of pharmaceutical and other emerging chemicals of concern in wastewater reuse.

Publications

Luo, X, Zheng, Z., Greaves, J., Cooper, W.J., Song, W., Trimethoprim: Kinetic and Mechanistic Considerations in Photochemical Environmental Fate and AOP Treatment, *Water Research* **46** (2012) 1327-1336.

Kim, D.K., O'Shea, K.E., Cooper, W.J., Mechanistic considerations for the degradation of methyl tert-butyl ether (MTBE) by sonolysis: Effect of argon vs. oxygen saturated solutions, *UltrasonicsSonochemistry* **19** (2012) 959-968.

Santoke, H., Song, W., Peake, B.M., Cooper, W.J., Photochemical Fate of Antidepressant Pharmaceuticals in Simulated Natural Waters, *J. Hazardous Materials* 217-281 (2012) 382-390.

Wang, L., Xu, H., Cooper, W.J., Song, W., Photochemical Fate of Beta-blockers in NOM Enriched Waters, *Sci. Total Environ*. **426** (2012) 289-295.

Kim, D.K., O'Shea, K.E., Cooper, W.J., Oxidative Degradation of Alternative Gasoline Oxygenates in Aqueous Solution by Ultrasonic Irradiation: Mechanistic Study, *Sci. Total Environ.* **430** (2012) 246–259.

Mezyk, S.P., Mincher, B.J., Cooper, W.J., Cole, S.K., Fox, R.V., Gardinali, P.R., Kinetic model for the radical degradation of trihalonitromethane disinfection byproducts in water, *Rad. Phys. Chem.* **81** (2012) 1646–1652.

Ayatollahi, S., Kalnina, D., Song, W., Cottrell, B., Gonsior, M., Cooper, W.J., Recent advances in structure and reactivity of dissolved organic matter: Radiation chemistry of non-isolated natural organic matter and selected model compounds, *Water Sci. Technol*. **66** (2012) 1941-1949.

Song, W.; Yan, S., Cooper, W.J., Dionysiou, D.D., O'Shea, K.E., Hydroxyl Radical Oxidation of Cylindrospermopsin (Cyanobacterial Toxin) and its Role in the Photochemical Transformation, *Environ. Sci. Technol*. (in press)

1.4. Conclusions

— Many of the participants have contacted the appropriate authorities or end user, and understand the intended use of reclaimed water. As envisaged, a variety of waste waters and sludge from different industries are being investigated with focus on fundamental aspects as well as technology development through active bilateral collaborations among themselves. The details are presented in Tables 3-5.

— Toxicity evaluation of the irradiation products is understood to be an integral and important part of the whole programme. Many of the participants have made efforts to integrate toxicity testing in their projects. As suggested, process monitoring and control parameters, have utilized commercially available assays that are simple and easy to

use.Any modification of the treated samples, in order to comply with the manufacture's specified protocol, should be reported.

— For highly polluted waters, the need to examine the potential of combining different treatment processes or approaches has been realized, and studies have been conducted to assess the potential of radiation technologies to enhance or improve current technologies.

— The CRP members have taken the necessary steps to ensure that dosimetry is accurate and traceable; however, the members also agree that careful attention be paid to reporting the dosimetry data.

— The CRP members agreed that increased communication would benefit the group and suggest that the easiest form of communication is through group emails.

— The CRP members recognize the value added products that could arise after irradiation treatment. They have also decided to investigate the potential revenue generated and use alternative methods of explanation to potential end users of radiation technology. For example, they agreed that using terminology such as resource recovery facilities rather than wastewater treatment plants conveys a positive approach to radiation processing.

— The CRP members recognize the importance of using mobile electron beam systems in marketing and implementing radiation processing at resource recovery facilities. This facility should be used as a platform for demonstrating radiation processing, in particular where it can be taken to the end-users facility.

1.5. Recommendations

— The members strongly recommend to the IAEA that this CRP be officially extended for one additional year. The results to date are extremely encouraging and the participants feel that the additional time will allow them to advance the studies to appropriate levels to demonstrate the technology at larger scale and provide more value added.

— The CRP members recommend demonstration projects at different scales such as mobile E-Beam platform, bench or pilot scale treatment facilities be encouraged.

— The development of various aspects of radiation technology for treatment of waste water can be carried out by the CRP participants. However, the deployment of the technology at an appropriate level will need additional participants from the industrial sector. It is therefore recommended that the next RCM include personnel from the water and wastewater community.

— The participants acknowledged the need of disseminating their scientific results to professional societies in related areas and end user agencies through scientific seminars, discussion meeting, conferences and publications. It is also recognized that end user trade magazines should be utilized for disseminating technical results.

— Vienna or Budapest is recommended as the possible venue for the next meeting of the CRP.

TABLE 1. SUMMARY OF POLLUTANTS IN WATER, WASTEWATER AND SLUDGE

	Wastewater			Solid	
	Industrial Wastewater	Water	Municipal Wastewater	Sludge	Contaminated Soils
Organic Matters (man-made)	Dyes, chemicals, surfactants, Alkaloids, pharmaceuticals	Pesticides, endocrine disrupters, pharmaceuticals	Pesticides, endocrine disrupters, pharmaceuticals	Pesticides, endocrine disrupters	PCBs, heavy oils, pesticides, petrochemicals etc.
Organic Matters (natural)		organics from humic substances		organics from humic substances	organics from humic substances,
Inorganic Matters	Heavy metals, minerals	Heavy metals, T-N, T-P, minerals	Heavy metals, T-N, T-P, minerals	Heavy metals, etc.	Heavy metals
Micro-biological	-	Bacteria, Viruses, Parasites, (Algae)	Bacteria, Viruses, Parasites	Bacteria, Viruses, Parasites	Bacteria, Viruses, Parasites etc.
Goals	decreasing Toxicity, COD, BOD, S/S	human activities, agricultural and industrial uses	discharge to the environment, or re-use for human activities	re-use for agricultural purpose	decreasing toxicity, remediation

TABLE 2. SUMMARY OF RADIATION SOURCES AND ANALYTICAL METHODOLOGIES BEING UTILIZED

	Source of Radiation			Analytical tools				
	Gamma ray	E-Beam	Others	Chemical	Toxicology	Micro-biology	Computer Modeling	Pulse Radiolysis
Algeria	☺			☺				
Brazil	☺	☺		☺	☺			
China	☺	☺		☺	☺	☺		
Egypt	☺	☺		☺				
Hungary	☺	☺	AOP	☺	☺		☺	☺
Italy	☺	☺	AOP	☺	☺		☺	
Japan	☺	☺		☺	☺		☺	
Korea	☺	☺	AOP	☺	☺	☺	☺	
Malaysia	☺	☺		☺				
Poland	☺	☺		☺			☺	☺
Portugal	☺	☺		☺	☺	☺	☺	☺
Romania	☺			☺		☺	☺	
Turkey	☺	☺		☺	☺		☺	
U.S.A. (P)		☺		☺	☺	☺	☺	
U.S.A. (C)	☺		AOP	☺				

TABLE 3. SUMMARY OF WORK PLAN OF STUDIES IN WATER, WASTEWATER AND SLUDGE

| | Wastewater | | | | | | | | | | | | Solid | |
| | High Contaminated Industrial Wastewater | | | | | | | Medium to Low Contaminated | | | | | Sludge | Contaminated Soils |
	Textile Dyeing	Paper mill	Petro-Chemical	Animal Waste	Pharmaceutical	Hospital	Others	Municipal	Under-ground	Ballast Water	EDC	Others		
Algeria			☺											
Brazil	☺							☺						
China		☺						☺						
Egypt	☺				☺									
Hungary	☺				☺			☺						
Italy	☺			☺		☺					☺			
Japan								☺			☺			
Korea	☺			☺				☺	☺	☺	☺			☺
Malaysia												mixed		
Poland							inorganic						☺	
Portugal												☺		
Romania								☺			☺		☺	
Turkey							Alkaloid							
U.S.A. (P)								☺			☺		☺	
U.S.A. (C)								☺					☺	

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TABLE 4. SUMMARY OF WORK PLAN FOR CRP AT A GLANCE

	Activities			
	Fundamental and New analytical	Feasibility studies	Technology Demonstration and/or economic analysis	Technology Deployment
Algeria	☺	☺	☺	
Brazil	☺	☺	☺	
China	☺	☺	☺	
Egypt	☺	☺	☺	
Hungary	☺	☺	☺	
Italy	☺	☺	☺	
Japan	☺	☺	☺	
Korea	☺	☺	☺	☺
Malaysia		☺	☺	
Poland		☺	☺	☺
Portugal	☺	☺	☺	
Romania	☺	☺	☺	
Turkey	☺	☺	☺	☺
U.S.A. (P)		☺	☺	
U.S.A. (C)	☺	☺	☺	

TABLE 5. SUMMARY OF COLLABORATIONS

	Alg	Bra	Ch	Egy	Hun	Ita	Jap	Kor	Mal	Pol	Por	Rom	Tur	USA (P)	USA (C)
Algeria		T		CS	TG	BP		CS		CS		CS			BP
Brazil	T				T, BP, M		BP, T	EA			T				BP
China					T		BP	EA, CS						T	
Egypt	CS					BP					T				BP
Hungary	CS	T, BP, M	TG			EA CS		EA				BP			
Italy	BP CS		BP		CS EA		BP	BP			T, EB	BP, EB			
Japan		BP, T	BP			BP		BP	CS, BP			CS, BP, TG			
Korea	CS		EA, CS				BP, CS		CS, EA				CS	CS	
Malaysia		T	CS				CS, BP	D, TG		CS					
Poland	CS								TG		EB			D*	EB
Portugal		T		T	CS	CS		EB		EB				M	BP
Romania	CS	T			BP		CS, BP, TG	EA, CS, EB			M			EA, M	BP
Turkey								EA, CS		BP				EA	EB, CS
USA (P)		T	T					EB EA		EB		EA, M			EB, EA
USA (C)	BP	BP								EB	BP	EA			

Toxicity Assays= T, Byproduct Analysis= BP, Dosimetry= D, Electron Beam =EB
Microbiological Assays =M, Training=TG, Economic Analysis=EA, Complementary Studies: CS
__ = Established Collaborations
__ = Future Collaborations

INDIVIDUAL REPORTS

APPLICATION OF GAMMA RADIATION FOR REMOVAL OF ORGANIC POLLUTANTS FROM WASTEWATER

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Abstract

The study of this research is focused on the possibility of using gamma radiation in order to decrease the concentration of polycyclic aromatic hydrocarbon (PAH) in effluents. The research was initiated with a concentration of 100ppm of synthetic naphthalene aqueous solution submitted to different absorbed doses. The HPLC analysis has shown that the dose of 30kGy degraded 99.96% of the naphthalene molecule. The identification program of NIST library has identified the by-products formed during the radiation process. Concerning the industrial effluent wastewater sample, we opted for analysis by GC-MS before and after gamma irradiation, to monitor the degradation of PAH and other pollutants from the refinery. The results show that in global view, gamma radiation decreases significantly the contaminated level, with the increase of the absorbed dose. In detailed view, the relative content of the naphthalene, 2,7 dimethyl in the effluent sample decreased with the increase of the absorbed dose. At the dose of 6 kGy the molecule was completely degraded. The COD of effluent sample presented a reduction of 58%, when 10 kGy dose was applied. After irradiation a secondary treatment, based on adsorption using a natural adsorbent, has to be applied in order to remove the by-products of radiation degradation, to get a better quality of effluent and consequently improve the environmental condition.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants (POPs) of major concern in environmental pollution in the world [1]. Polycyclic aromatic hydrocarbons (PAHs) are organic compounds which have received considerable attention due to their toxicity, mutagenicity, and carcinogenicity for human beings and animals [2,3], and have been the subject of much concern in the recent years [4].

The effluents generated by the industries (refineries, chemical factories…) are the main causes for the environmental pollution; most of these contaminants biodegrade very slowly [5].The conventional treatment and available technologies to treat such waste have generally low efficiency, and industries are searching for alternative technologies to degrade chemical compounds to get a better quality of effluent and consequently improve the environmental condition.

Industrial wastewater differs from domestic sewage by the nature of the pollutants they contain and their higher concentrations, such as organic compounds which are a kind of substances that are not only toxic but difficult to be degraded as well[6].

The use of ionizing radiation has great ecological and technological advantages when compared to physical-chemical and biological methods. This clean technology never left residues [7]. It degrades organic compounds, generating substances that are easily biodegraded. For more effective treatment of industrial wastewater, it is necessary to combine the radiation treatment with another conventional treatment such as adsorption.

The presented work was carried out on a synthetic solution and industrial wastewater effluent sample. The aim of this study was to evaluate the effectiveness of gamma radiation to improve and preserve the environment by degrading the PAH contained in wastewater and elimination of by-products formed during the application of ionizing radiation. Thus, we started the study on a synthetic aqueous solution of naphthalene then we studied the real samples of industrial wastewater which were collected from an oil refinery in Algeria. The study of degradation was followed by HPLC and GC-MS. However, the study regarding the adsorption was interrupted, this is due to a technical problem and we could not finalize the synthesis of the absorbent based on grafted natural polysaccharide.

2. Materials and methods

2.1. Materials

Naphthalene analytical grade 99.9% purity was purchased by Aldrich. Acetonitrile and methanol, HPLC-grade and dichloromethane for residue analysis were supplied by MERCK, Darmstadt, Germany. Anhydrous sodium sulfate was supplied by Fluka.

2.1.1. Preparation of samples

- **Synthetic solution**

Stock solution of naphthalene (C_0 =100ppm) was prepared, dissolved in water in a proportion of volume 1/9 methanol/deionized water. Addition of co-solvent such as methanol, is a technique used to increase the solubility of PAH [8].The working standard solution was protected from light and stored at 4^0C in volumetric flask, wrapped in aluminum.

- **Real sample**

The industrial effluent was treated by decantation for removal of the bulk of the oil content, and then discharged into the sea. The effluent sample was collected from the lower part of the treatment station of a refinery in Algiers, Algeria. The sample was collected in amber glass flasks, 1 liter capacity, fitted with closures lined with aluminum foil, protected from exposure to direct sunlight, which can lead to the degradation of PAHs and preserved for storing at 4°C prior to extraction and analysis [9].

2.2. Irradiation procedure

The naphthalene, synthetic aqueous solution ($C_{0=}$ 100ppm) was irradiated at room temperature with C_o-60gamma rays at the doses of 0.5, 1, 5, 15, 20, 25 and 30kGy with the dose rate of 11.85Gy/min. The industrial effluent sample was irradiated at the doses of 1, 2, 4, 6, 8 and 10kGy with the dose rate of 14.25 Gy/min. The Frick dosimetry system was used to determine the dose rate.

2.3. Extraction procedure

The whole glassware was rinsed with acetone before the analysis. A liquid-liquid (L/L) extraction was performed in ambient temperature. A proportion of V/V volume of (naphthalene synthetic solution (C_0) or, a real sample of industrial effluent of refineries) with dichloromethane [10, 11], as a solvent extractor, were made into the Erlenmeyer. The extraction was performed employing a magnetic stirrer during 30 min. After the mixed solution was poured into the separator funnel, the phase separation was observed, the organic

phase was passed through a layer of anhydrous sodium sulfate in view to fix remaining water. The organic extract was concentrated in a rotary evaporator at $38^0C \pm 1^0C$ to 2 ml and finally to dryness under a flow of nitrogen and re-dissolved in a volume of 1ml of dichloromethane, then analyzed by GC-MS.

2.4. Analysis of synthetic solutions by HPLC

Naphthalene content in synthetic solutions prior and after irradiation was followed by liquid chromatography analysis (HPLC) on Perkin Elmer 200 series chromatograph, equipped with a diode array UV/ Vis detector [12]. The detection was realized at 275nm wavelength, using an Eclips XDB-C18 column, 5µm film thickness, temperature of the oven was 25^0C. Chromatographic conditions were as follow: the mobile phase consisting of a mixture of acetonitrile and water in volume proportions of 25:75, at 1ml/min flow rate with injection volume of 50 µl.

2.5. Analysis of irradiated sample by GC-MS

The identification of by-products was carried out on the solution of naphthalene (C_0=100ppm), which was irradiated at 25kGy.

The irradiated effluent samples were analyzed by GC-MS using Agilent Technologies HP 6890N Network GC and Agilent Technologies HP 5973Network Mass selective Detector, equipped with an HP5MS column. The separation of by-products was conducted under the following chromatographic conditions: injector temperature 250^0C, oven temperature program from 100^0C -280^0C at the rate of 4^0C /min and isotherm at 280^0C during 20 min. Helium was used as carrier gas at a flow rate of 1ml/min and the volume injected was 0.8µl(splitless mode). The temperature of the ion source, interface and the quadrupole were set at 230^0C and 280^0C and 150°C respectively. The MS operated in electron impact ionization mode with a potential of 70eV.

3. Results and discussion

3.1. Analysis of naphthalene aqueous solution by HPLC

3.1.1. Concentration of Naphthalene as a function of irradiation dose

The variation of the concentration of naphthalene in aqueous solution as a function of absorbed dose followed by HPLC, is represented on the Fig.1.
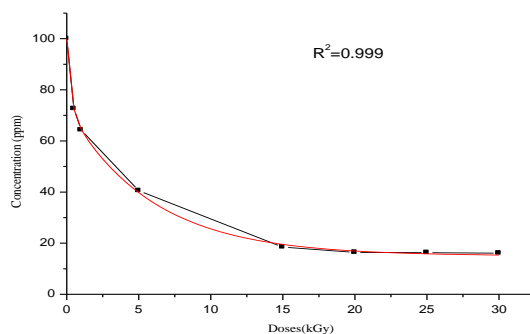
Fig. 1. Irradiation effect on the concentration of naphthalene.

The concentration of naphthalene in aqueous solution passed from 100ppm to 16ppm when irradiated at the dose of 30kGy.This figure shows a drastic decrease of concentration of naphthalene in solution with the increase of radiation dose and denotes that gamma radiation is efficient in degrading the naphthalene [13].
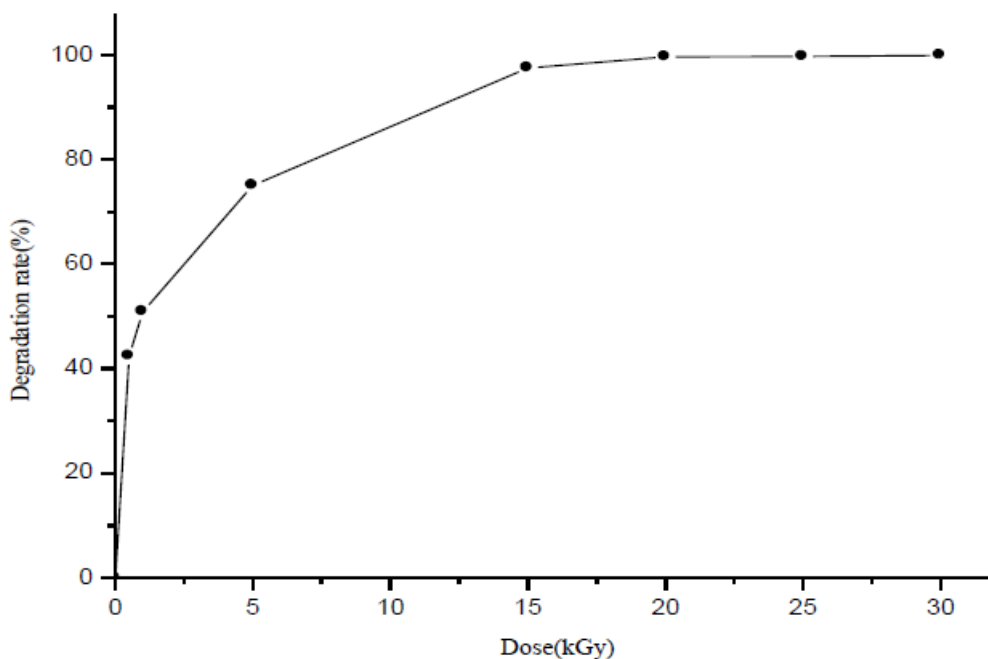

Fig. 2. Degradation rate of naphthalene vs. gamma radiation dose.

Radiation degradation of naphthalene increased as a function of the absorbed dose. At the doses of 0.5 and 5kGy, the degradation rate of naphthalene passed from 43% to 75% respectively and reached 97% at the dose of 15 kGy, but at the doses of 20 to 25kGy, a slow increase of the degradation rate was observed: from 99.67% to 99.72%, then it reached 99.96% at the dose of 30kGy.

To confirm this, the Fig.3 and 4, show the remaining 0.04% of the naphthalene in aqueous solution degraded at the dose of 30kGy, then analyzed by HPLC, compared to non irradiated naphthalene solution, where the peak appears at the retention time of 3.5minutes.
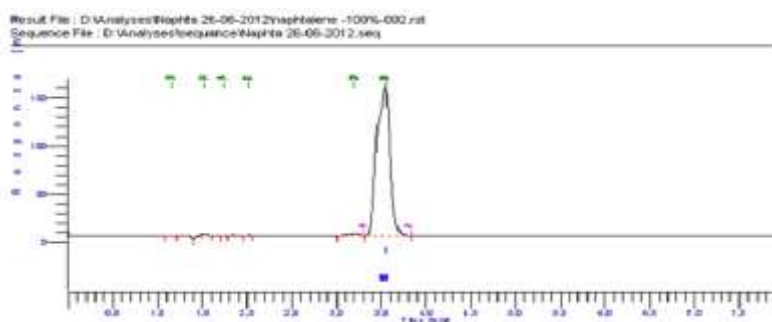
Fig. 3. Analysis of non irradiated control solution of naphthalene, by HPLC.
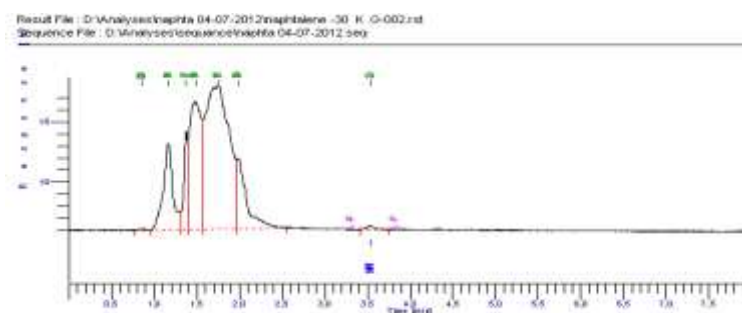
Fig. 4. Analysis of irradiated naphthalene solution at 30kGy, by HPLC.

3.2. Analysis of naphthalene aqueous solution by GC-MS

3.2.1. Analysis of non irradiated solution

On fig. 5, is illustrated the chromatographic profile of non irradiated naphthalene in aqueous solution analyzed by GC-MS. The same figure shows a naphthalene peak which appeared at retention time of 8.22minutes.
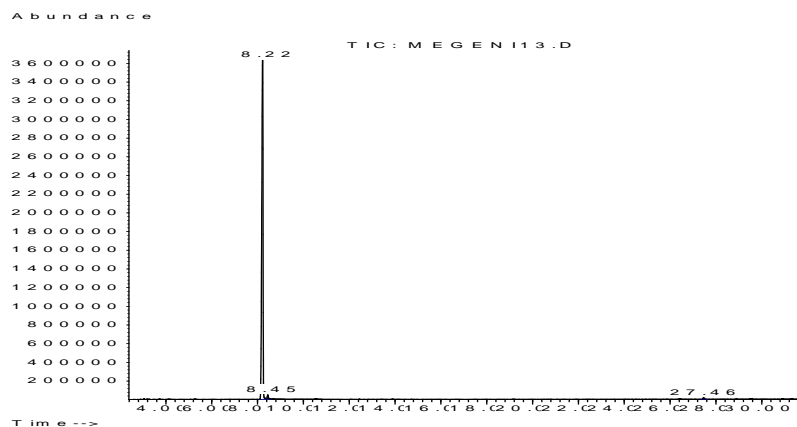
Fig.5. Analysis of non irradiated naphthalene by GC-MS.
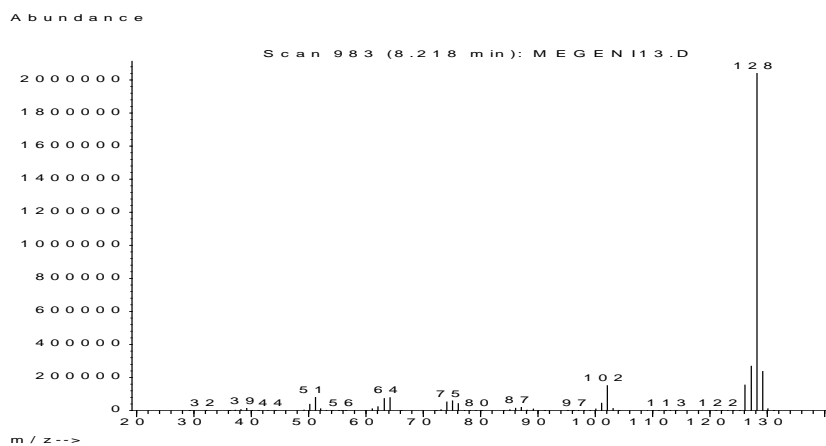
Fig.6. Mass spectra of uniradiated naphthalene solution.

3.2.2 Analysis of irradiated solution at 25kGy
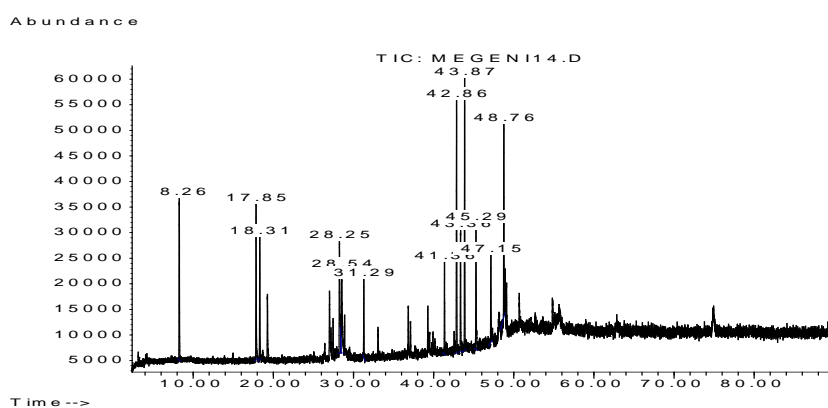
Fig.7. GC-MS analysis of the irradiated solution at 25 kGy.

The initial naphthalene solution was irradiated to the dose of 25kGy. On Fig.7 is shown the existence of the peak of naphthalene at 8.22min retention time, and other peaks attributed to the metabolites resulting from the degradation of the naphthalene molecule. Using the NIST library we identified the by-products formed with a fit value higher than 70% in all cases. The identification process is underway.

3.3. Effect of gamma radiation on the industrial effluent wastewater

In order to follow the effect of radiation on the degradation of PAHs present in industrial effluents discharged into the environment, we opted for analysis by GC-MS before and after gamma irradiation, to monitor the degradation of PAH and other pollutants from the refinery.

3.3.1. Global view

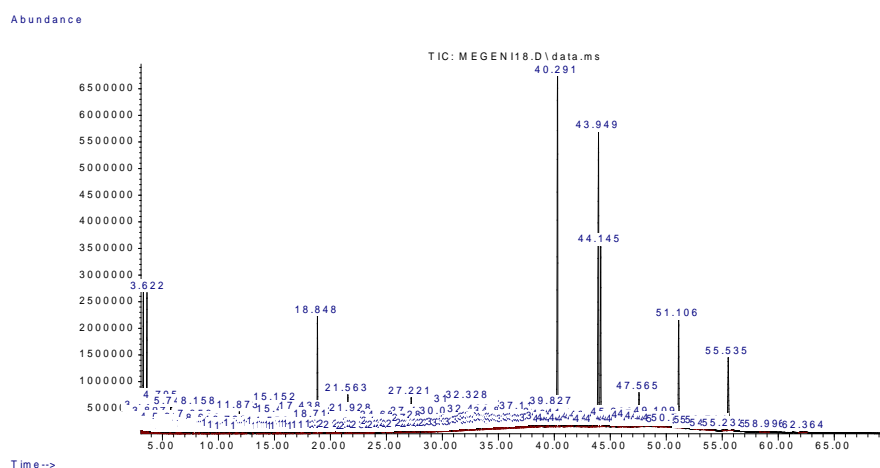In a global way, the fig.8 and 9 show chromatograms of irradiated and non irradiated of industrial effluent samples.

Fig.8. Chromatogram of industrial effluent sample irradiated at 1kGy, analyzed by GC-MS.
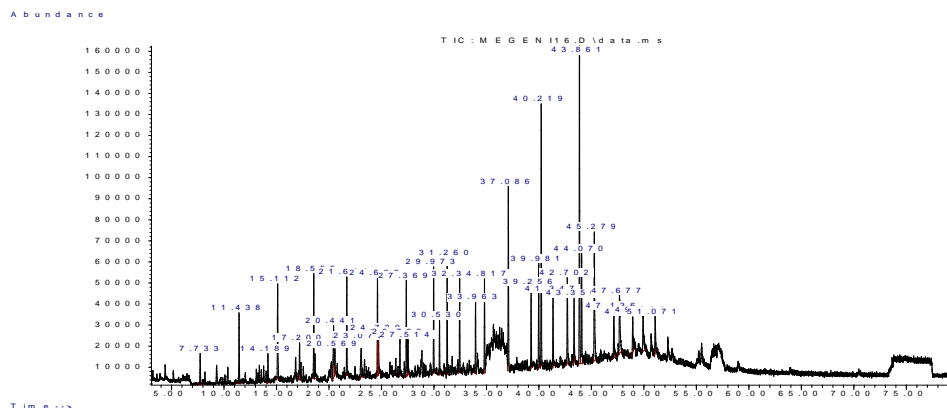
Fig.9. Chromatogram of industrial effluent sample, irradiated at 10 kGy, analyzed by GC-MS.

The above figures show that the contaminated level was significantly reduced with the increase of the absorbed dose. The abundance decreased from 6.5 million at the dose of 1 kGy (fig.8) to reach 160,000 when the effluent was irradiated at 10 kGy (fig.9). This decrease observed in a global way, showed that irradiation is a technique that improves the quality of industrial wastes.

3.3.2. Detailed way

The GC-MS analysis of the industrial effluent sample is shown on the fig.10. When one takes into consideration, a naphthalene, 2,7 dimethyl molecule, the peak height corresponds to the concentration of the molecule dissolved in water PAH [14], this small peak that appeared at retention time of 16.09 min, following the relative percentage depending on the radiation dose.

The same figure denotes that the relative content in the effluent decreases with the increase of the absorbed dose which passes from 0.59 % in the control effluent sample to reach 0.09 % when the sample was irradiated at the dose of 4 kGy. The dose of 6 kGy the naphthalene, 2,7dimethyl was completely degraded.
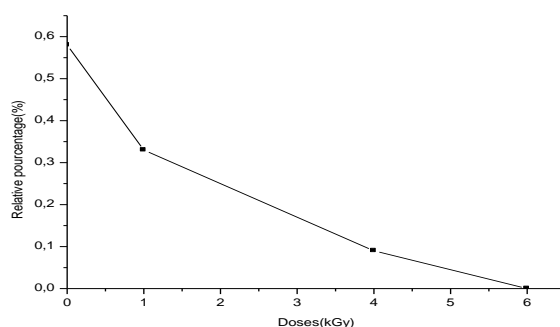
Fig.10. Radiation effect on industrial effluent sample.

3.3. COD vs irradiation dose of sample from the industrial effluent

For more information, we studied the COD of the sample of industrial effluent using DCO meter with "the standard ISO 6060 method". The results are given in the following table 1.

TABLE 1. EFFECT OF GAMMA RADIATION ON THE REDUCTION OF COD OF INDUSTRIAL EFFLUENT

Radiation dose (kGy)	COD(mg/l)	% reduction
0.0	179.1	0
1	170	5
2	160.7	10
4	149.1	17
6	98	45
8	91	49
10	74.5	58

The irradiation of the effluent showed a reduction of COD, chemical oxygen demand. The table 1, shows that the COD decreased from 179mg/l for the control effluent sample to 75 mg/l. The COD of effluent sample presented a reduction about 58%, when 10 kGy dose was applied [15]. The reduction calculated using the formula:

$$\% \, COD = [COD_i - COD_x / COD_i] \times 100$$

Where:

COD_x is the value measured after a given dose and $COD_{initial}$ is the COD value for non-irradiated sample.

The reduction in COD caused by radiation could be due to its direct and/ or indirect effect on the destruction of organic compound [16]. The indirect effect is due to the free radicals produced by water radiolysis such as e_{aq}, $H°$, $OH°$, H_2O_2.

4 .Conclusion

A concentration of 100ppm of naphthalene in aqueous solution was submitted to different absorbed doses of gamma radiation, where, 99.96 % of the synthetic solution was efficiently degraded by gamma radiation at the absorbed dose of 30kGy. The HPLC analysis showed that the concentration of the 4% of the remained naphthalene in the solution was 16ppm.

The naphthalene solution irradiated at the dose of 25 kGy, was analyzed by GC-MS in order to identify the by products formed during the radiation process. The obtained chromatogram show the peak of the remained naphthalene which appears at the retention time of 8.22min and other peaks attributed to the by products resulting from the degradation of the same molecule. The identification program of NIST library has identified the by-products formed with a fit value higher than 70% in all cases. The identification process is underway.

The industrial effluents sample was irradiated at different absorbed doses in order to follow the effect of radiation on the degradation of the persistent organics pollutant (POPs). Thus, we opted for analysis by GC-MS before and after gamma irradiation, to monitor the degradation of PAH and other pollutants from the refinery. The results of analysis shown, the dose of 10kGy has reduced the contaminated level significantly, with the increase of the absorbed dose. As mentioned by[17], that for real effluents lower doses below 50kGy would be reasonable for organic compound reduction.

The same phenomena was observed when we took into consideration, a naphthalene, 2,7 dimethyl molecule and denotes that the relative content in the effluent decreases with the increase of the absorbed dose. The complete degradation was reached at the dose of 6 kGy. This decrease observed in the two cases, shows that irradiation is a technique that improves the quality of industrial wastes. The irradiation process is an alternative for the treatment of industrial wastewater and feasible process, capable of destroying toxic organic compounds for preservation of the environment from toxic substances, whether aquatic or terrestrial.

As a complement, other studies also shown that irradiation of industrial wastewater in presence of air was destroying 58% of the COD at the dose of 10kGy. In this case, the reduction of COD values could be related to the degradation of organic pollutant and its solubilisation. However, more analyses have to be conducted to better understand this behavior.

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RADIATION PROCESSING OF WASTEWATER AND POSSIBILITIES FOR REUSE

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Abstract

In the framework of the CRP IPEN has worked on the irradiation and toxicity assessment for the improvement of dyes standard solutions and real complex effluents (textile) in order to achieve recommended quality for reuse of treated effluents during the process as well as for a suitable environmental discharge. Three different types of effluents were submitted to irradiation including standard solution of two reactive dyes (Remazol Black B - RPB and Remazol Orange 3R – R3AR). It was also identified that different chemical formulas of these reactive dyes can contribute to a higher toxic charge during effluents discharges. In general the toxicity control was carried out on crustaceans and luminescent bacteria but a lot of experiments were performed with the aquatic snail *Biomphalaria glabrata*, this last biological assay was developed at "Instituto Butantan (USP, SP)". Irradiations and measurements with UV spectrophotometer resulted always on less colored effluents and most often on less toxic liquid residues, after irradiation. Percentage of reductions for toxicity and color depended on the effluent source and the radiation doses applied varied from 1 to 10 kGy. The decoloration of remazol black B and orange 3R solutions was effective for 1kGy and 2.5 kGy which is a relatively low dose and may contribute to a suitable cost for irradiation technology. Since the possibility of different formula of dyes be present at environment exist, the toxicity was measured for all of them and it was noted that vinylsulphone form was the worst in terms of effects for *V.fischeri* (Black B 133%) and *D.similis* (Orange 3R). Regarding biological effects of these remazol dyes after irradiation, this same dye solution resulted at 60% removal only for *V.fischeri* (not for daphnids) and when treated with 5 kGy and 10 kGy. Irradiation of real textile BVT effluents resulted in good colour removal but the acute toxicity reduction varied widely 97% (0.5kGy), 54% (2.5kGy) and 19% (1.0kGy), BTV1 – BTV3. The chemical effluent required higher radiation doses to reduce toxicity (20kGy up to 40kGy).

1. Objective of the research

To apply irradiation on effluents for reducing toxicity and achieve suitable conditions for industrial reuse. The Electron Beam Irradiation applied for textile effluents is very related to decolorization of wastewater and reduce biological effects (toxicity and mutagenicity).

2. Introduction

The reuse of water is part of obligation and management for several industrial water use in Brazil. Textile activities are important water user, dischargding hard variation of contaminants on their final effluents due to the variety of chemical which are used during textile manufacture.

In the "Manual de conservação e reuso de água para a industria" the textile reuse of water is possible if color < 5 UH, hardness < 25 $CaCo_3$, Mn $- 0.01 <$ Mn < 0.05; pH: $3.5 - 10.5$ (except for starching process); 100 ppm and 5 ppm for TDS and SS, respectively[1].

In general the color is apparently the worst irregular number for effluent reuse in textile activities and the reactive dyes are widely applied for cotton benefits. Reactive dyes are

termed chemically as colored compounds with a functional group capable of forming a covalent bond with a suitable substrate. In terms of chemical structure, colorants may either be inorganic or organic compounds (both groups natural or synthetic).While pigments consist of small particles that are practically insoluble in those media in which they are applied, dyes are applied to various substrates (textiles, leather, paper, hair etc) from a liquid in which they are completely, or at least partly, soluble.

When classified according to dyeing method (coloristic approach), they can be distinguished between anionic, direct or disperse dyes, depending on whether these substances are used for dyeing protein, cellulose or polyamide fibers. It should be mentioned that certain chemically reactive dyes can be used for different substrates, while others (with the same type of chemical structures) are suitable for a single substrate only[2].

At IPEN Electron Beam irradiation has been studied for reactive dyes and for textile effluents and both authors reported important reduction on general color[3,4]. The sources of real effluents used during the project was presented at Table 1.

TABLE 1 – SOURCE OF EFFLUENTS RELATED TO DYES AND IRRADIATION STUDIES AT IPEN

Item	Origin / Specification	Reference
Site 1	Vicunha – SP (textile)	Higa, 2010
Site 2	Suzano – Dyes manufacture	Higa, 2011
Site 3	Suzano/SABESP	CNPq Report
-	Standard solutions	Pinheiro, 2011

The reactive dyes are very important product in Brazil because they are suitable for cotton dying. National cotton production was 1.015.000 tons in 2010, approximately. According to literature about 10% to 15% of dyes are lost to environment while and after dying processes. The textile effluent may contain dyes at three different chemical arrangements: sulphatoethylsulphone, vinylsulphone and hydroxyethylsulphone. About 60% of all reactive dyes have the azo group (-N=N-) as chromophore combined with different types of reactive groups (e.g. vinylsulfone and chlorotriazine)[3]. The dyes are usually marketed as sulphatoethylsulphone form. During the dyeing of cellulosic fibers, the increase of pH (alkaline) and temperature in the dye bath promotes readily release of sulphato group to form the reactive vinilsulphone which then binds covalently by nucleophilic addition with ionized hydroxyl groups of the cellulose. However, vinylsulphone can react with hydroxyl group in water and promotes hydrolysis generating the hydroxyethylsulphone form. This form is non reactive and cannot bind in cellulose fiber or be used further. Once dyeing is completed, the dye material is washed-off several times to remove unfixed and/or hydrolysed dye. This hot dyeing process usually has little unreacted dye in it. However, in the cold pad process the dye bath, which is done at room temperature, the reaction of the dye with the OH is very slow. The left-over dye bath is not exhausted but rather contains much unreacted dye in various forms of reaction. If neutralized to pH 7 the half-life of the vinyl form can be very long, e.g. 46 years for the vinylsulphone dye C.I. Reactive Blue 19 at 25 ^{0}C. Another source of unreacted dyes in the wastewater is the practice of disposing excess dye formulation in the wastewater. The wastewater generated is characterized by intense color, high BOD and COD values owing to the presence of soluble and insoluble organic residues from both reactive (vinyl) and hydrolysed forms of dye, as well as form bleaching treatments and dyeing auxiliaries.

The structural aspect of the two studied are presented at Figure 1. Both are reactive dyes which were submitted to irradiation and toxicity assays. The other samples were real effluent according to Table 1.

Fig. 1. Black B (133%, Dystar) and Orange 3R(133%, Dystar), structural formula.

The final effluent from SABESP SUZANO (sanitation company - Suzano WWTP) is a product (treated wastewater) not allowed for reuse due to their characteristics with several toxicants out of standard fixed numbers and related residual toxicity. Residual color is one of them.

3. Materials and Methods

The methods for toxicity assays were standardized for a Brazilian Comite, ABNT (Associação Brasileira de NormasTécnicas), based on ISO methods and taking into account Brazilian species and environmental conditions. The assays with *B. glabrata* followed specific methodology, according to the specifications given at Table 2. Irradiations were carried out at batch conditions, fixing the machine energy at 1.4 MeV for all the experiments, at Dynamics EB Accelerator.

TABLE 2. LIVING-ORGANISMS EXPOSED TO REACTIVE DYES AND METHODS

Organism	End-point	Methodology
Daphnia similis	Imobility (48h)	ABNT/ISO
Vibrio fischeri	Luminescence lost (15 min)	ABNT/ISO
Biomphalaria glabrata	Death (48h) and genotoxicity	KAWANO, 1992

3.1.1. Biomphalaria glabrata assays

The *Biomphalaria glabrata* (Mollusca, Gastropoda) adult/pigmented snails were reared under laboratory conditions for several years (at Instituto Butantã). The snails were maintained at 25 ± 2 °C, 18h light photoperiod, in plastic aquarium (50x23x17 cm) with dechlorinated tap water and continuous aeration and they were fed with *ad libitum* lettuce leaves.

The acute toxicity assays were performed with five different concentrations of dyes (three replicates). For each replicates, 10 adult snails with shell diameters of 10-18 cm and 3-6 months of age were exposed to the dyes for 72 h. Room temperature 25 ±2 °C and 18/6 light-dark circle were kept constant. After exposure, snails were washed and observed for 7 days to quantify the number of death organisms. A negative control group was maintained in

dechlorinated tap water under the same experimental conditions and the test was valid if the death rate was less than 10% in this group. Median lethal concentration was obtained from the Trimmed Spearman-Karber method (Hamilton et al, 1977) and the results were expressed in mg L^{-1} [6,7].

Embryos Assays: pieces of plastic were placed on the aquarium water surface to collect the egg masses. The embryos were analyzed and separated according to developmental stages (blastula, gastrula, trocophore and veliger) (Kawano et al, 1992). Egg masses damaged or with high rates of natural mortality and malformation were not used in the experiments.

At least 100 embryos of each stage were exposed to different concentration of the dyes for 72 h at 25 ±2 °C. At the end of exposure, egg masses were washed and observed for mortality for 7 days. The malformed embryos were also counted and considered dead, since it would become non-viable embryos. A negative control group was maintained in dechlorinated tap water under the same experimental conditions. LC50 was calculated using the Trimmed Spearman-Karber method (Hamilton et al, 1977) and the results were expressed in mg L^{-1}.

4. Results and discussion

The efforts carried out for identification of three different chemical forms of the dyes is confirmed by the position of bands and migration into the chromatografhy paper. The *B.glabrata* assay revelead this organism as the less sensitive to the exposed dyes when compared to the others and no genotoxicity was obtained for 1.0 g.l^{-1} for both reactive dyes[3].

Paper chromatography was used to identify the bands and changing formula for the dyes (hydroxy, sulphate or vinyl form), showed as Fig. 2.

Fig. 2. Paper chromatography for remazol black (a) and for remazol orange 3R (b): migrations from left to right indication hidroxi; to sulphate; to vinyl forms.

When *Biomphalaria glabrata* snail was exposed to the reactive dyes only RPB solutions resulted on genotoxic effect but at very high concentrations (2.0 g.L^{-1}), Regarding toxicity it was also noted very low sensitivity of this specie to the reactive dyes and there was no meaning to use irradiation for those given dyes concentration.

4.1.1. Irradiation effects on toxicity for RPB and R3A dye solutions (sulphates)

The toxicity results of both reactive dyes evidenced that the orange R3AR was more toxic than the black B for both organisms and for a good reduction on this biological effect it was

necessary 5 and 10 kGy for *V. fischeri* assay. The same did not happen when *D. similis* were exposed to irradiated samples for RPB dye.
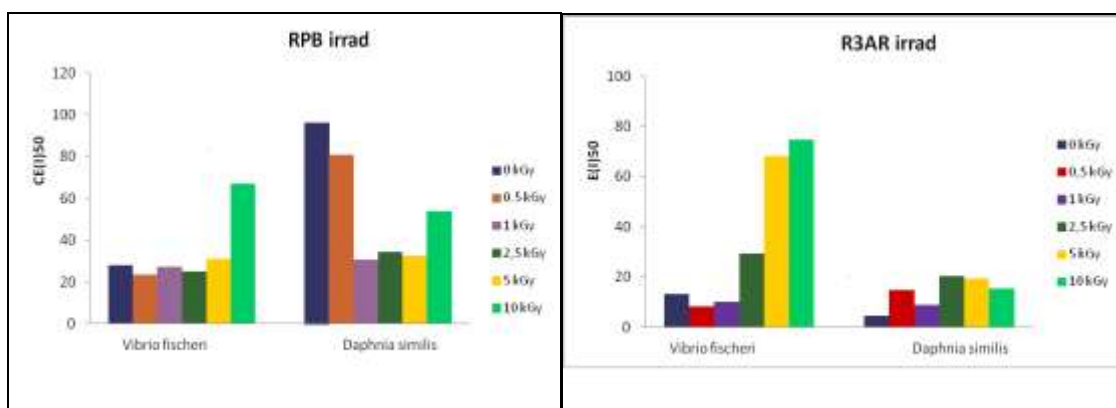

Fig. 3. Comparison of acute toxicity effects for dyes solution before and after EB irradiation (Black B and Orange 3R - 133%, Dystar).

When irradiation was applied to BTV effluents radiation doses lower than 5kGy were enough for general improvement (color and biological effects), on the contrary the ACD samples required from 20 to 40 kGy radiation doses. Nonetheless reasonable variation on the efficacy values can be noted (Table 3).

TABLE 3 – TOXICITY REDUCTION ON INDUSTRIAL SAMPLES INDUCED BY EB IRRADIATION

Dose (kGy)	Toxicity removal (%)	Sample Code
20	0	ACD01
20	97.9	ACD02
40	83.5	ACD03
40	60.0	ACD04
40	83.3	ACD05
0.5	97.42	BTV01
2.5	54.75	BTV02
1.0	19.24	BTV03

For general discussion it was observed that irradiation is an effective technology for color removal on effluents. Due to the great structural diversity of dyes it is necessary to combine techniques for its degradation. Taking into account that 80% of all reactive dyes belong to the class of azo compounds (-N= CH-), these type of chemicals will always be present in effluents from textile. Until 2003, the global colorant market was estimated at USD 12-13 billion and more or less equally distributed among organic dyes, organic pigments, and inorganic pigments: 132 distinct chemical structures were presented by Zollinger and their different synthesis and also 176 examples of carbonyl colorants, main representative by

quinones, antraquinones and indigo dyes, followed by sulfur dyes, fluorescent brighteners. Due to this wide diversity of products it is not always possible to characterize effluents only by chemical analysis and toxicity assays may confirm if a given treatment result in a less toxic effluent allowing us to calculate the toxic charge removal for a given process technology.

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STUDY OF THE EFFECTS OF IONIZING RADIATION ON MICROBIAL ACTIVITIES OF SLUDGE AND DEGRADATION OF BIOHAZARDOUS CONTAMINANTS IN THE SEWAGE SLUDGE MIXTURE

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Abstract

In this report, the response of sewage sludge exposed to ^{60}Co gamma irradiation at a dose of 0-25 kGy was investigated. Results showed that gamma irradiation could disintegrate sludge flocs and release proteins, polysaccharides and extracellular enzymes into the bulk solution. The maximum oxygen uptake rate decreased by 58%, and 99% of the culturable bacteria were inactivated at 25 kGy. However, the tested protease, superoxide dismutase and catalase showed slight inactivation during irradiation treatment. The efficiency of sludge solubilization reached around 6.5% with a dose of 25 kGy. The efficiency of sludge solubilization with aeration was increased by around 25% compared to that without aeration at an irradiation dose of 2.5-9 kGy. The soluble protein, polysaccharide and humic (like) substance concentrations were higher under aerated conditions. With aeration the over all reaction appears to be oxidative as evidenced by the higher nitrate and nitrite ion concentrations in solution.

1. Objective of the research

To elucidate the inactivity mechanism of sewage sludge by ionizing irradiation. To enhance Member States capacity in applying radiation technology in combination with other techniques for enhancing removal of biohazardous substances and to develop suitable irradiation system for treating sewage sludge in practical application.

2. Introduction

The imposition of more stringent legislation governing the disposal and utilization of sewage sludge, coupled with the growth in its generation and the decrease in traditionally accepted disposal routes, has prompted a considerable impetus to develop strategies to reduce sludge production. One alternative that exhibits especial promise is radiation technology. Gamma irradiation is a powerful source for wastewater and sewage sludge treatment [1-5]. This method is advantageous as no additional chemical is required, no residual material is produced and toxic and recalcitrant materials can be degraded by hydroxyl radicals produced by irradiation [6, 7]. However, this promising technology has attracted little interest until recently and has not yet been widely accepted mainly due to the conservative attitude of governments regarding safety concerns resulting from little knowledge on this technology [7].

Radiation process such as electron beam irradiation and gamma irradiation is considered as a promising technology for the treatment of wastewater or sludge. Gamma irradidition has been reported to disinfect wastewater for reuse [8, 9] and as pretreatment of aerobic biological treatment of high strength opium alkaloid wastewater [10]. A gamma-ray irradiation as a pre-treatment process has been used to release soluble carbohydrates from an activated sludge [11].

It is interesting to note that the gamma irradiation process is not similar to ozonation or Fenton oxidation. Following irradiation, the oxidation species ·OH existed with the reduction

species e_{aq}^- and ·H together. Approximately equal amounts of reducing and oxidizing species are formed by water radiolysis. It has been reported that gamma irradiation is very effective in the decomposition of refractory organic compounds such as benzene [4], phenols [1], chlorophenols [12], tetrachloroethane and trichloroethane [3, 13], the herbicide 2,4-D [2, 14] and 2,4,6-trinitrotoluene [15].

In this study, we investigated the effect of gamma irradiation on the microbial activities of sludge to study the biological response of the microbes following gamma irradiation. The changes in physicochemical characteristics of sewage sludge after exposure to gamma irradiation including sludge solubilizaton, the transformation of protein, polysaccharides and inorganic nitrogen were examined. The results of the study suggest that sludge treatment by gamma irradiation will reduce the amount of solids necessary for disposal.

3. Materials and Methods

3.1. Sludge source

The sludge used in this study was obtained from an oxic tank of a Municipal Wastewater Treatment Plant in Beijing, China. The plant adopts an A^2/O (anoxic-anaerobic-oxic) process. The tested sludge was taken from the. Before use, the sludge was allowed to settle. The applied initial total suspended solid (TSS) concentration ranges from 4700 to 14000 mg L^{-1}, with 67-77% of volatile suspended solid (VSS).

3.2. Irradiation

The ^{60}Co-source was designed and built by the Institute of Nuclear and New Energy Technology, Tsinghua University. The radioactivity of the source was around 3.6×10^{14} Bq. The sludge samples were irradiated with a dose rate of 184-201 Gy min^{-1} in sealed glass bottles with a working volume of 100-mL at ambient temperature (around 25 ^{o}C). For the aeration experiments, air was bubbled into the sealed glass bottles during irradiation at a flowrate of 0.25 L min^{-1}. The dose rate was determined by means of Fricke dosimetry using a G-value of G (Fe^{3+}) = 15.6. Irradiation was performed in batch mode with absorbed doses from 5 to 25 kGy.

Oxygen uptake rate (OUR_{max}) was applied to examine the effect of gamma irradiation on the survival of heterotrophic organisms. CFU represents the activity in culturable bacteria. Considering the protein content in activated sludge is reported to be as high as 20-60% (w/w) [16], the protease of the sludge was chosen as the enzymatic indicator. Since hydroxyl radicals are produced during gamma irradiation of the sludge, the antioxidant catalase and superoxide dismutase SOD and catalase activity was used to represent the anti-oxidization activity.

3.3. Analytical methods

The method for the OUR_{max} (mg O_2 g^{-1} TSS min^{-1}) tests has been described elsewhere [17]. Dissolved oxygen was measured by an Orion model 850 dissolved oxygen meter using an Orion Auto-Stir probe. CFU were enumerated using a beef peptone agar plate at 30 ^{o}C for 48 h incubation. The SOD activity was measured using a SOD enzyme activity kit (Jiancheng Technology, China) based on the cytochrome c reduction method [18]. One unit of SOD activity was defined as the amount required to inhibit the rate of cytochrome c reduction by 50%. Protease activity of sludge suspensions and supernatants was assessed using the chromogenic substrate azocasein (0.5%) [19]. One unit of enzyme activity was defined as the amount of enzyme that degraded 1 mg of azocasein in 90 min at 37°C. The catalase activity of

sludge was determined using the procedure described by Dallmier and Martin [20]; one unit of catalase decomposed 1 μmol of H_2O_2 per min at 25 °C and pH 7.

The sludge samples were centrifuged at 5000 rpm for 15 min. The pellets were heated at 105 and 550 °C to measure TSS and VSS, respectively. Sludge solubilization, which was used to evaluate the sludge decomposition, was defined by the following equations ($SCOD_0$ and $TCOD_0$ indicate initial soluble chemical oxygen demand and total COD, respectively):

COD solubilization efficiency = $(SCOD-SCOD_0)/TCOD_0$

The structure of the fresh and irradiated sludge was examined directly by an optical microscope (E600, Nikon, Japan) and a scanning electron microscope (SEM, JSM- 6700F, JEOL, Japan) after moderate centrifugation at 2,000 rpm for 1 min.

The protein content of the supernatant were measured by the modified Lowry method [21] using bovine serum albumin as the standard. Polysaccharides were measured using the phenol sulfuric acid method [22] using glucose as the standard.

Total organic carbon (TOC) was evaluated by a TOC analyzer (TOC-V_{CPH}, SHIMADZU). The COD, TN, ammonium (NH_4-N), and the total phosphorus (TP) contents were determined according to Chinese SEPA Standard Methods [23]. Nitrate (NO_3-N) and nitrite (NO_2-N) were measured using a DX-100 Ion Chromatograph from Dionex, USA equipped with an Ion Pac As14 column (4 mm × 250 mm). The column temperature was kept at 30 °C. The mobile phase consisted of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ with a flowrate of 1.0 mL/min.

4. Results

4.1. Effects of gamma irradiation on activities of sludge

After exposure to gamma irradiation, the microbial activity in the sludge gradually decreased (Fig. 1). Microbial respiration was inhibited by around 23% at a dose of 5 kGy and by 58% at 25 kGy. Culturable bacteria decreased from 1.4×10^6 to 2.7×10^3 with increasing irradiation dose from 0-25 kGy. Nearly 91% of culturable bacteria were inactivated at a dose of 5 kGy and 99% were inactivated at a dose of 25 kGy. The same trend was also been found during sludge ozonation process. From our previous study, with the increase of ozone dosage within 0-0.10 g O_3/g TSS, the culturable bacteria decreased gradually from 4.5×10^6 to 4.3×10^4 CFU, and after the ozone dosage was increased to above 0.10 g O_3/g TSS, the CFU remained stable (around 10^4) [24].

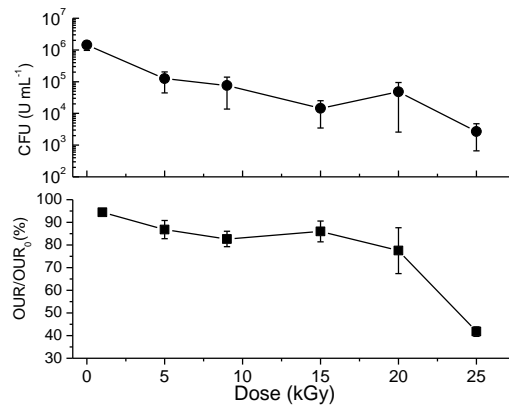*Fig. 1 Changes in CFU and sludge respiration with increasing irradiation dose (n = 3).*

Gama irradiation leads to a slight decrease in protease, SOD and catalase activities (Fig. 2). SOD and catalase activity decreased slowly as the irradiation dose increased. Around 7.3% of SOD and 8.4% of catalase was inactivated at a dose of 20 kGy. Interestingly, the extracellular protease activity increased at irradiation doses lower than 15 kGy, and thereafter gradually decreased by around 6.5% at a dose of 25 kGy. This suggests that irradiation with low dose could release a large amount of extracellular enzymes embedded in the sludge matrix, which might not be measured before irradiation.
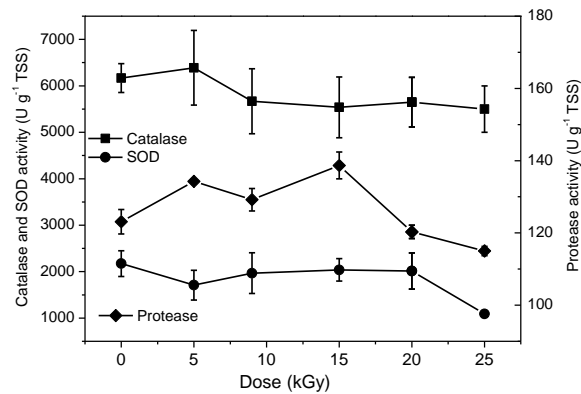
Fig. 2 Changes in enzyme activity with increasing irradiation dose

We have studied the ozonation of sewage sludge obtained from the same plant. From the point of sludge solubilization, gamma irradiation with 25 kGy corresponded to a low ozone dose of around 10 mg O_3 g^{-1} TSS. Around 6% of sludge solubilization efficiency was obtained at these doses. It seems that ozone is more powerful in inactivating sludge. Nearly 37% of protease and 18% of SOD were inactivated at an ozone dose of 10 mg O_3 g^{-1} TSS [25], while only around 7% of protease and SOD was inactivated at 25 kGy of gamma irradiation. Ozone has a strong cell lytic activity, and can kill the microorganisms found in activated sludge and further oxidize the organic substances released from the cells [26, 27]. Gamma irradiation of sludge is similar to ultrasonic treatment. Yu et al. [28] reported that the ultrasonic treatment did not inactivate the extracellular enzymatic activities of protease, α-amylase and α-glucosidase. Instead, the enzymatic activities were markedly increased with ultrasonic pretreatment of 20 min and 3 kW L^{-1} at a frequency of 20 kHz.

4.2. Changes in composition of supernatant following gamma irradiation

The sewage sludge consisted of 41% protein, 25% lipid, 14% carbohydrate, and 20% unknown components on the basis of COD [29]. In this study, soluble organic matter including protein and polysaccharides were analyzed. The gamma-ray irradiation to sewage sludge resulted in a significant increase in protein and polysaccharides in the supernatant (Fig. 3). Obviously, the released protein from sludge floc to supernatant was much more than polysaccharides. Accordingly, the soluble TOC, TN and TP concentrations increased after irradiation (Fig. 3). These results suggested that a large amount of insoluble organics in sludge flocs were transferred into soluble organics. The irradiation treatment destroyed the floc structure, promoting the release of colloidal and soluble organics into the solution. Protein significantly contributed to the increase in TN. The fraction of protein-N to TN increased from an initial value of 4% to around 60% after irradiation.
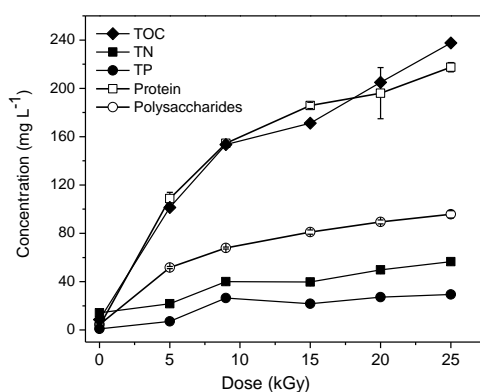
Fig. 3 Changes in protein, polysaccharides, TOC, TN and TP in supernatant following gamma irradiation.

4.3. Effect of gamma irradiation on sludge solubilization

Following irradiation, sludge solubilization occurred slowly. The efficiency of sludge solubilization was only around 1.7% at an irradiation dose of 5 kGy, and thereafter gradually increased to nearly 6.5% at 25 kGy. Little change in the ratio of VSS/TSS was observed at an irradiation dose of 0-25 kGy implying that the primary effect of irradiation was sludge disintegration and solubilization.

A non-significant dependence on initial TSS concentration and sludge solubilization was observed. The degree of sludge solubilization remained almost constant at the applied range of sludge concentrations (4700-14000 mg L^{-1}) with the same irradiation dose.

Microscopic observations showed that some flocs were broken after irradiation. Furthermore, the SEM images showed a distinct difference in the appearance of the cells. The fresh sludge cells were relatively smooth and integrated. After irradiation, the surface of some sludge cells were deformed, and the breakdown of filamentous bacteria was observed.

Figure 4 shows the changes in sludge solubilization with and without aeration following irradiation. As expected, the sludge solubilization efficiency with aeration was increased by around 25% compared to that without aeration. The content of soluble bio-macromolecules of proteins, polysaccharides and humic substances was also higher under aerated conditions (Fig.

5). These demonstrate the enhancement of aeration on sludge disintegration and solubilization after exposure to gamma irradiation.
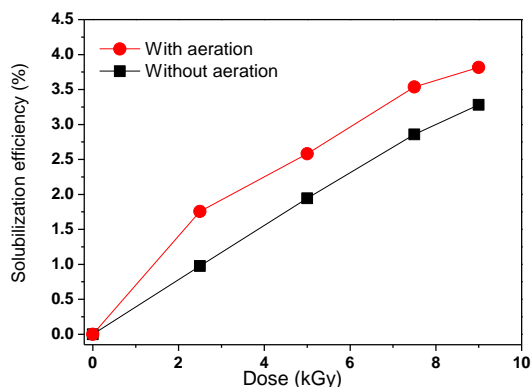

Fig. 4 Comparison of sludge solubilization efficiency following gamma irradiation with and without aeration.
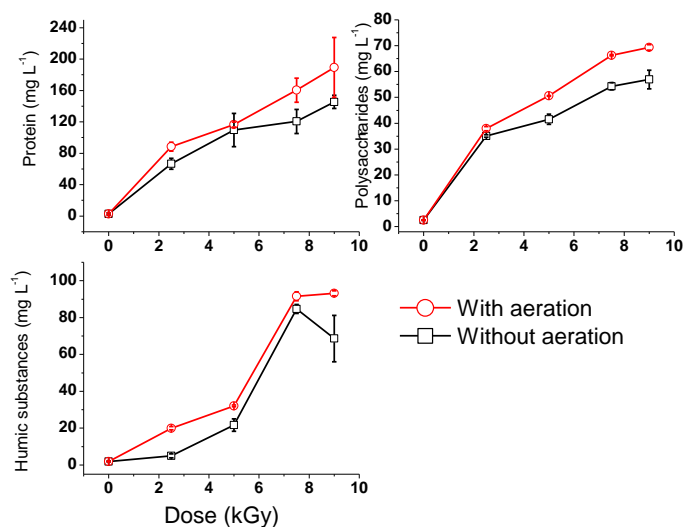

Fig. 5 Changes in soluble protein, polysaccharide and humic substances following gamma irradiation with and without aeration.

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EFFECT OF GAMMA IRRADIATION AND COAGUALTION ON THE MOLEGULAR WEIGHT DISTRIBUTION OF SOLUBLE ORGANIC SUBSTANCES IN PAPER MILL EFFLUENT

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Abstract

In order to look into the insights of the influence of gamma irradiation and coagulation on the molecular weight distribution (MWD) of soluble organic substances in real paper mill effluent, various parameters of wastewater samples before and after treated were investigated, including chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), dissolved organic carbon (DOC) and absorbance at 254 nm wavelength (UV_{254}) as well. In addition, the effects of irradiation on oxygen uptake and on acute toxicity were also presented. The results showed that irradiation alone cannot promote the biodegradability and oxygen uptake as originally expected. The whole acute toxicity of samples was reduced after gamma irradiation. On the other side, coagulation can not only effectively eliminate the sectors with high molecular weight (MW>3000 Dalton, in short HMW), but also improve the capacity of ionizing irradiation initiated the transformation of medium molecular weight (1000 Dalton<MW<3000 Dalton, in short MMW) into low molecular weight (MW<1000 Dalton, in short LWM), which is readily degraded by the subsequently activated sludge process.

1. Objective of the research

The present paper is devoted to investigate the effect of ionizing radiation and coagulation on molecular weight distribution of the soluble organic compounds in paper mill wastewater. Various parameters including chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), dissolved organic carbon (DOC) and absorbance at 254 nm wavelength (UV_{254}) were presented in this study. Furthermore, the oxygen uptake and acute toxicity evaluation were also carried out. It should be noted that, molecular weight distribution (MWD) of soluble organic substances, as an important tool, was introduced and discussed in every detail.

2. Introduction

The pulp and paper industry is considered as the second largest polluter in China. It has been estimated that the pulp and paper industry is responsible for 35% of all wastes dumped into the receiving waters. The effluents from the industry usually cause slime growth, thermal impacts, scum formation, color problems, and loss of aesthetic beauty in the environment[1]. Wuhan Chenming Paper Industry Co., Ltd. was established in 1997, with the major products of newsprint paper made of recycled paper and pulp. Environmental problems were the key issues of this company. In 2000, this company spent 120 million to construct a combustion alkali recovery process (200 tons/d) and a sewage treatment plant (50,000m^3/d). The COD concentration of paper mill effluent decreased successfully from 800 mg/L to 150 mg/L due

to the primary and secondary coagulations in combination with biological treatment. However, a more stringent effluent criteria would be regulated since 2012, in which COD and color indices would be less than 100 mg/L and 40 times, respectively. Therefore, a more advanced treatment process is needed.

Physical, chemical and biological methods have been proposed for the treatment of pulp and paper mill wastewater including coagulation, adsorption, chemical oxidation, membrane filtration and microbial degradation etc.[2]. For example, coagulation and flocculation is commonly employed in the primary or tertiary treatment of paper mill wastewater[3]. Activated sludge process is efficient in the removal of color, BOD, COD, Absorbable Organic halides (AOX) from paper mill effluent[4]. In addition, it is well known that ionizing radiation can be used for the purification of municipal or industrial wastewater (e.g. paper mill effluent)[5, 6, 7, 8]. However, few researches had ever investigated the effect of ionizing radiation and coagulation on molecular weight distribution of the soluble organic compounds in paper mill wastewater.

3. Materials and Methods

3.1 Gamma-ray irradiation facility

Irradiation processing was conducted upon a gamma irradiator, located at Institute of Nuclear and New Energy Technology (INET), Tsinghua University. The ^{60}Co-γ-source holder consists of 16 source rods, with a total activity of about 1.3×10^4Ci. Real wastewater samples were irradiated in Pyrex glass vessels (25 ml) at various doses from 0.5 to 2.5 kGy. Gamma rays dose rate was determined by means of a Fricke dosimeter using G (Fe^{3+}) =15.6. All experiments were carried out at ambient temperature.

3.2 Paper mill effluent

The wastewater samples were collected from a paper mill effluent treatment plant in Wuhan city, Hubei Province, China. Schematic views of the existing activated sludge process for treating paper mill wastewater were shown in Fig.1.
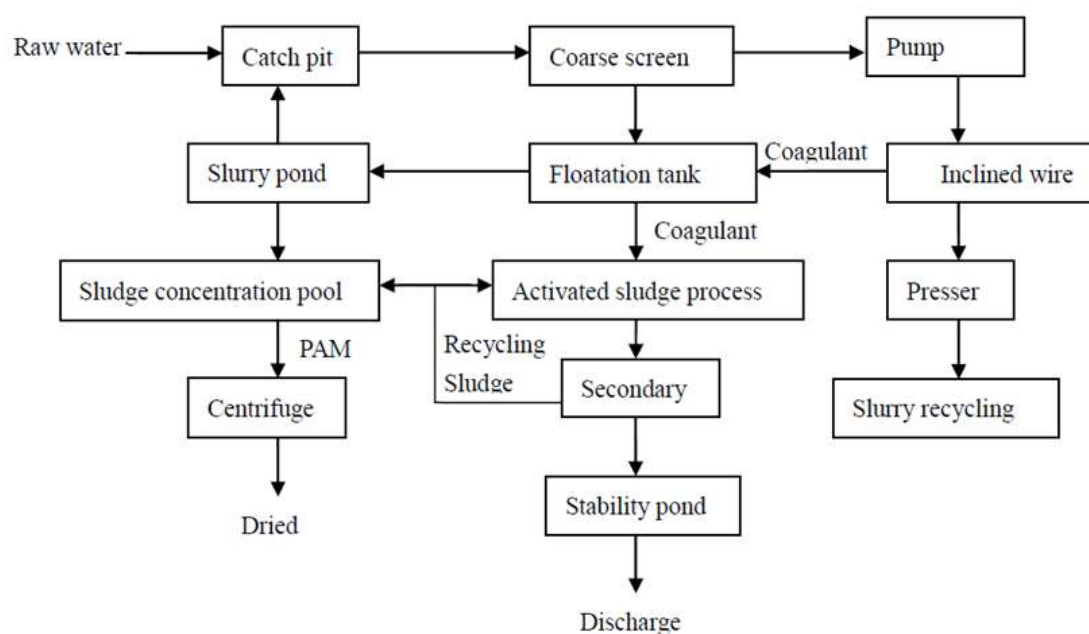

Fig. 1. Existing processing for paper mill WTTP in Wuhan City

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[9]. Dissolved organic carbon (DOC) was measured using a DOC-VCPH analyzer (Shimadzu) according to Ye at al[10]. In addition, optical absorption spectra of the wastewater were recorded by PerkinElmer instrument (Lambda 25).

Molecular weight distribution (MWD) of the soluble organic compounds from wastewater was determined using ultrafiltration (UF) membrane in a stirred cell (Model 8400, Amicon) described by Park et al[11]. Two Polyethersulfone (PES) membranes with nominal molecular weight cut-offs (MWCO) of 1000 Da and 3000 Da were used in a parallel methods as shown in Fig.2. The membranes were rinsed with distilled water before being placed into the cell which was then filled with distilled water and pressurized with nitrogen. Pressures were maintained at the manufacturer's recommended levels.
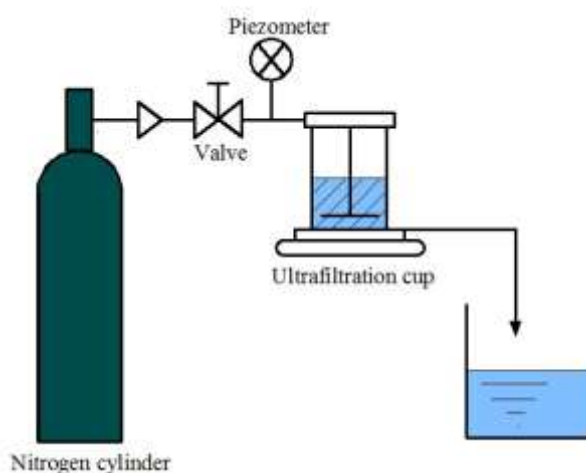
Fig. 2 Installation of molecular weight distribution separation

4. Results and discussion

4.1. Influence of irradiation alone on the characteristics of paper mill wastewater

4.1.1. COD and BOD5 removal

In the present work, ionizing radiation was originally expected to improve the biodegradability of this wastewater by conversion the high molecular weight organic matters into low molecular weight compounds, which are readily degraded in the subsequently biological treatment. The profiles of COD and BOD$_5$ before and after gamma irradiation were shown in Fig. 3 and Fig.4, respectively.

Fractionation of the organic matter in raw wastewater revealed that the organics were composed of two predominant components, one sector is MW<1000 Da and the other is between 1000 Da and 3000 Da. According to the previous reports [12], biological treatment was difficult to assimilate the organic matter with MW >1000 Da from paper mill effluent. Thus, gamma radiation is a crucial factor to transform HMW organic matter to LMW and biodegradable intermediates. However, for the organics with molecular weight (MW>3000 Dalton), COD increased meanwhile BOD$_5$ dropped after irradiation indicated some higher molecular weight and non-biodegradable organic matters may produce. As for the organics

with molecular weight (1000 Dalton<MW<3000 Dalton), BOD increased along with irradiation dose showed the enhancing biodegradability of these fraction organic matters. Finally, for the organics with molecular weight (MW<1000 Dalton), BOD showed a small increase and then reduced. This indicates that the radical species formed by gamma radiation react with organic components without selectivity [13]. The easily biodegradable components can also be converted to non-biodegradable matters, although this effect is opposite to the original idea of enhancing the biodegradability of this wastewater by ionizing radiation. Therefore, if applying the ionizing radiation processing to the mixed wastes composed of biodegradable and refractory organic matter, such as paper mill effluent, it might be more cost-effective to apply ionizing radiation after removing the biodegradable parts using a conventional biological process. This part of investigation will be reported later by the author's laboratory.
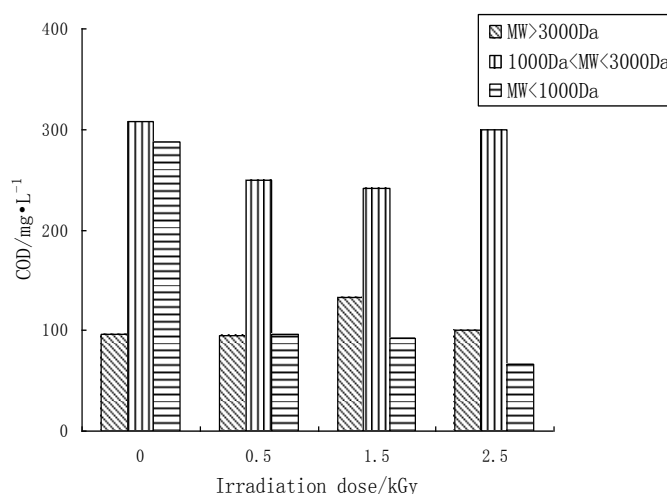
Fig.3 Influence of gamma irradiation on COD of raw wastewater
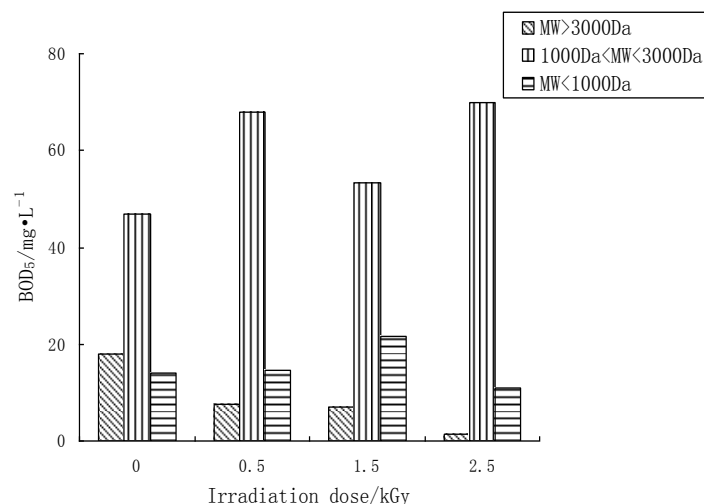
Fig.4 Influence of gamma irradiation on BOD$_5$ of raw wastewater

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4.1.2 Oxygen uptake

In this report, we particularly measured the effect of irradiation on the oxygen uptake for paper mill effluent. The results were displayed in Fig.5. Among the irradiated and un-irradiated samples, the raw water showed the highest oxygen utilization rate. This confirmed that it is a highly biodegradable wastewater. After the exposure to high energy irradiations, however, oxygen uptake decreased step by step with the increasing of absorbed dose.
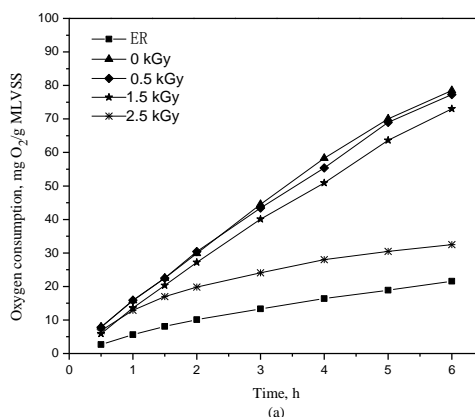

Fig. 5 change of oxygen uptake as a function of absorbed doses

4.1.3 Acute toxicity evaluation

Determination the toxicity has been chosen here because toxicity assays are standardized and reliable. Biodegradability, in contrast, depends heavily on the biomass selected and results obtained are usually difficult for other researchers to reproduce. Numerous bioassay procedures for toxicity evaluation are now available, such as (a) bacteria Vibrio Fischeri with Microtox system-Basic Test Protocol-15 minute exposure and (b) Microcrustacean Daphnia Similis, acute test for 24 and 48 h exposure. In this report, luminescence bacteria (Photobacterium phosphorem T3 spp.) were used with 30 minute exposure to investigate the acute toxicity evaluation for irradiated and un-irradiated samples. Radiation doses were 0, 0.5 kGy, 1.5 kGy and 2.5 kGy, respectively.

From the data in Table 1, it may be seen that relative inhibition of un-irradiated water was 75.1%. This indicated raw samples before irradiation had high original toxicity. With the absorbed dose increased to 2.5 kGy, the relative inhibition was elevated to more than 90 %. In this aspect, ionizing radiation process seems to improve the industrial wastewater toxicity. In fact, this negative radiation effect has already been reported as a consequence of hydrogen peroxide as a radiolysis byproduct[14]. To eliminate the effect of hydrogen peroxide on whole acute toxicity evaluation, a certain amount of MnO_2 （For example, 1mg/mL）was put into the irradiated samples[15]. The toxicity of samples in means of relative inhibition decreased drastically from 75.1% to 39.8% as long as the absorbed dose increased to 2.5 kGy.

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TABLE1 ACUTE TOXICITY EVALUATION OF SAMPLES BEFORE AND AFTER IRRADIATION

Samples	Dose (kGy)	luminescence intensity (mV)	Relative inhibition (%)	luminescence intensity after MnO_2 (mV)	Relative inhibition after MnO_2 (%)
Distilled water (Control sample)	0	1235	0	1298	0
Paper-mill effluent	0	307	75.1	——	——
	0.5	134	89.1	620	52.2
	1.5	262	78.8	777	40.1
	2.5	67	94.6	782	39.8

4.1.4 GC-MS analysis of paper mill effluent

In order to look deep insight of irradiation on the change of dissolved organic substances in wastewater, we conducted GC-MS analysis for irradiated and un-irradiated samples. In Fig.6, about eleven kinds of compounds were detected. Based on the specific professional software, these compounds were most likely to have the structural of aromatic ring (e.g. phenol, 4-methyl-phenol, benzoic acid, etc.) and other long chain hydrocarbons (e.g. dodecane, etc.). After irradiation of 0.5 kGy (Fig. 7), the concentration of long chain hydrocarbons decreased rapidly meanwhile there is little change of aromatic compounds. When the absorbed dose continued to increase to 1.5 and 2.5 kGy, less than five kinds of aromatic compounds were identified in treated samples. On the other side, the peak of long chain hydrocarbons almost disappeared completely.
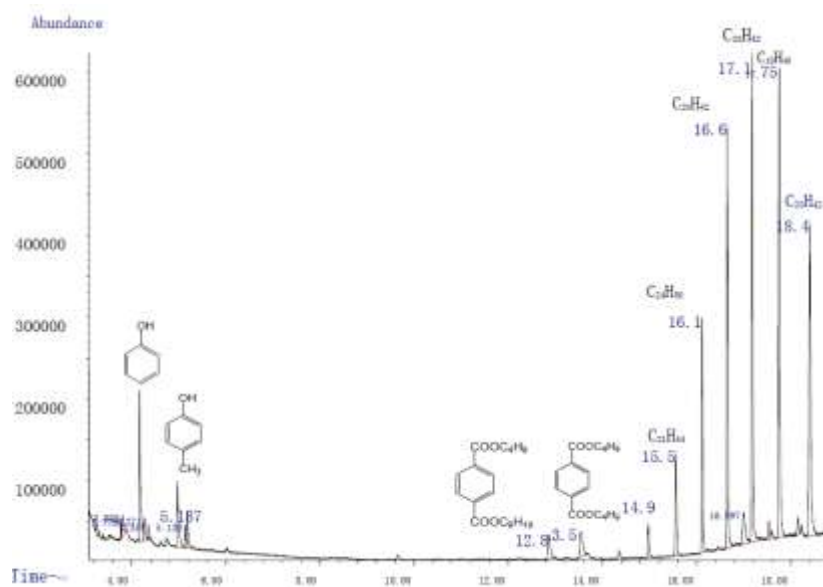

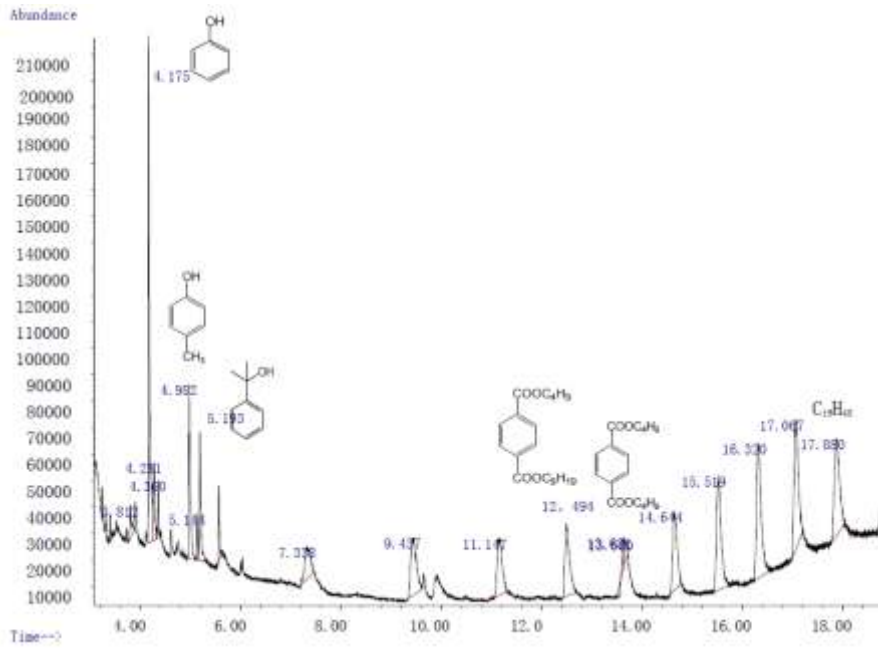*Fig.6. GC-MS analysis of un-irradiated samples*
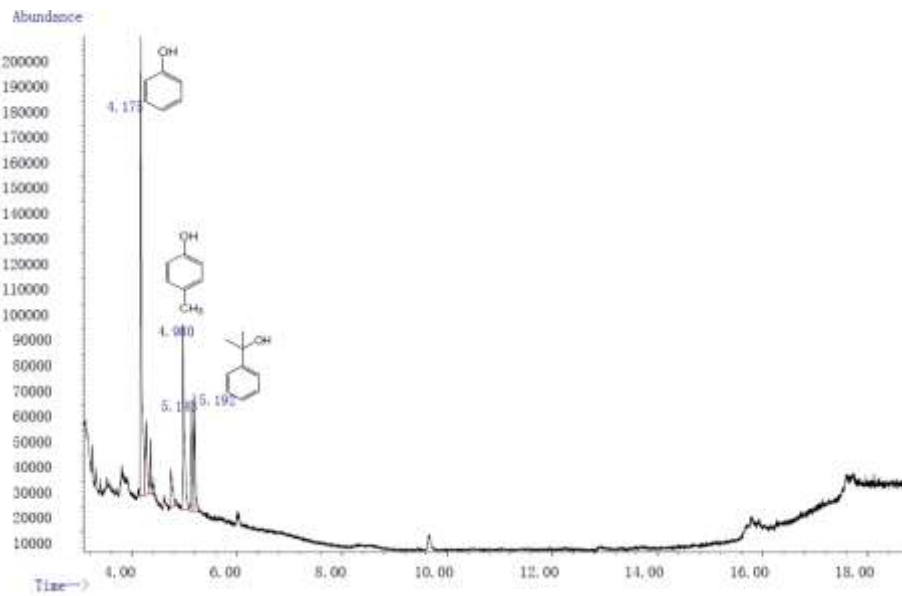
Fig.7. GC-MS analysis of irradiated samples with 0.5kGy
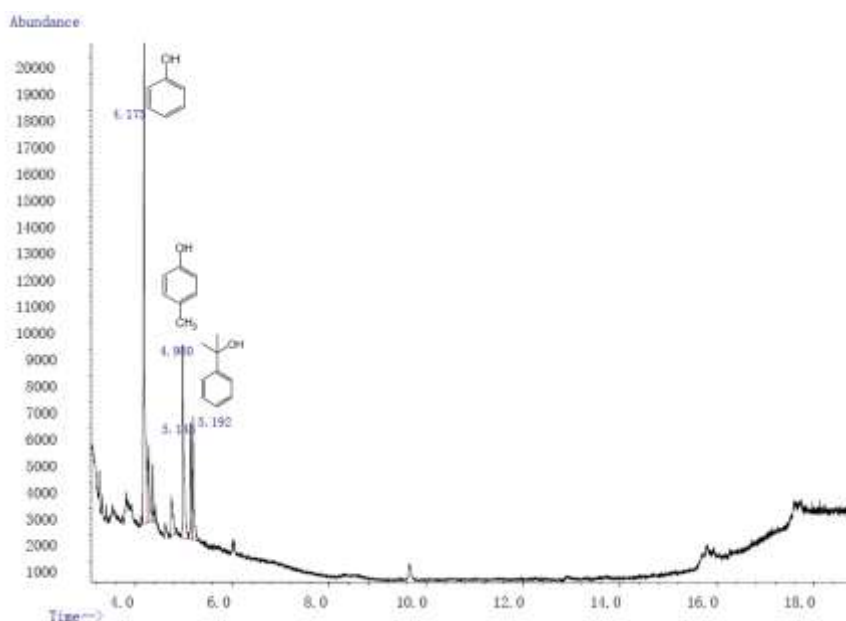

Fig.8 GC-MS analysis of irradiated samples with 1.5kGy

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Fig.9 GC-MS analysis of irradiated samples with 2.5kGy

4.2. Combination of coagulation and irradiation for pretreatment of paper mill wastewater

4.2.1 COD and BOD$_5$ removal

Polyaluminium chloride (PAC) solutions were used as a coagulant for pretreatment of paper mill wastewater. The optimized dose was 300 mg/L to obtain 27.7% of total COD removal. The profiles of COD and BOD$_5$ before and after gamma irradiation are shown in Fig. 10 and Fig.11, respectively.

Fig.3 and Fig.10 show that HMW contributes 14% of whole COD. Coagulation can effectively eliminate this part of organic compounds with the removal rate of 44.7%. After coagulation, COD concentration of HMW first increased and then reduced with the absorbed dose. This is consistent with the observation in Fig.3, which confirmed the accumulation of some higher molecular weight and non-biodegradable organic matter induced by gamma irradiation. For LMW, COD and BOD$_5$ values continue to increase with the applied dose. In authors understanding, this is mainly attributed to the removal of HMW by coagulation, normally this part of organic matters showed poor biodegradability. After coagulation, the deposited energy by ionizing radiation can transform more MMW into LMW. As small molecules are easily biodegradable, so the biodegradability of this wastewater may be improved through irradiation processing. Similar conclusions have been reported in the ozonation treatment of paper mill effluent by Bijian et al[16].
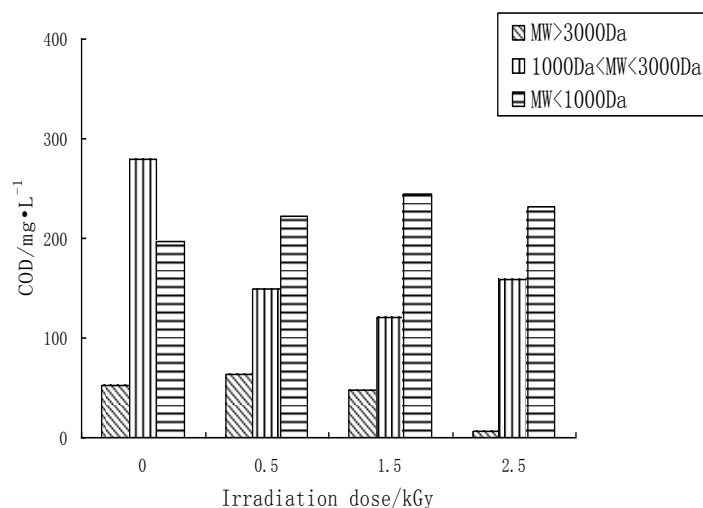
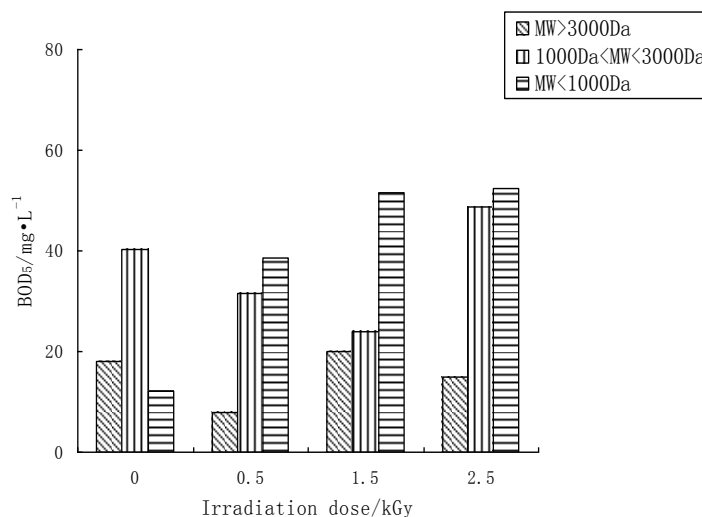*Fig.10. Influence of coagulation and gamma irradiation on COD of raw wastewater*

Fig.11. Influence of coagulation and gamma irradiation on BOD5 of raw wastewater

4.2.2 Absorbance of wastewater and UV_{254}

Effects of different treatment methods on the absorbance of wastewater are shown in Fig.12. It can be found that coagulation can reduce the absorbance of wastewater significantly. In contrast, gamma irradiation alone showed little effects on the absorbance of wastewater. This is possible due to the accumulation of some higher molecular weight and non-biodegradable organic matter (MW>3000 Da) during gamma irradiation. Another reason maybe the present irradiation conducted without continuously air bubbling into paper mill wastewater compared with the previous reports[6]. Therefore, ionizing radiation alone may cause an increase of absorbance. However, after coagulation treatment, absorbance of wastewater reduced to a further low extent at any absorbed doses.

In addition, UV_{254} is the absorbance of wastewater at 254 nm wavelength. It is an indicator that reflects the concentration of organic compounds. Some countries consider it as one of the indicators of organic compounds removal[17]. It was found that the UV_{254} value has a certain degree of correlation with DOC, COD and other indicators of water[18]. This indicator is helpful to investigate some target organic compounds with aromatic ring or those compounds with double bonds or hydroxyl groups, such as lignin, tannin and humic acids in paper mill

effluent, which have strong absorbance at 254 nm wavelength. Table 2 shows that UV_{254} in raw wastewater were composed of two predominant components, high molecular weight (MW>3000 Dalton) and medium molecular weight (1000 Dalton<MW<3000 Dalton). Coagulation can effectively remove the absorbance of these two parts. In contrast, irradiation alone cannot reduce UV_{254} of paper mill effluent. Even more, a small increase of UV_{254} was observed for HMW. This indicated that irradiation cannot completely decompose the target organic compounds (e.g. lignin, tannin and humic acids) at reasonable dose. The intermediates of paper mill effluent irradiation still have the structural of aromatic ring or double bonds or hydroxyl groups[19].
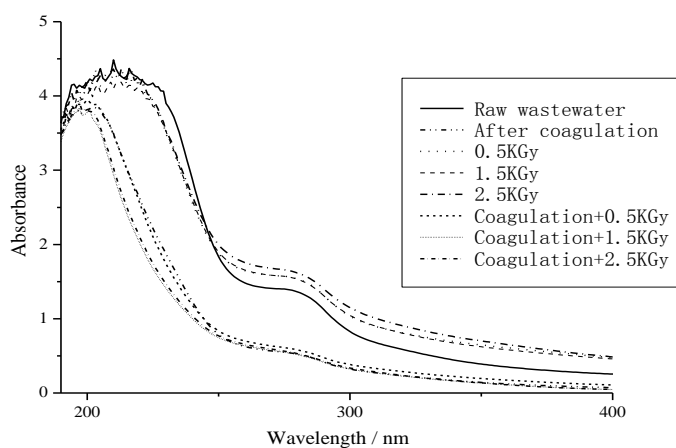

Fig.12. Influence of different treatment methods on the absorbance of wastewater

TABLE 2 UV_{254} OF RAW WATER AND TREATED WASTEWATER BY GAMMA-RAY IRRADIATION

Sample	MW>3000Da	3000Da>MW>1000Da	MW<1000Da
Raw water	0.6085	0.528	0.104
0.5kGy	0.6871	0.5839	0.0568
1.5kGy	0.8280	0.5192	0.1102
2.5kGy	0.9861	0.4374	0.1059
Coagulation	0.2053	0.3192	0.0437
Coagulation +0.5kGy	0.1709	0.3177	0.0837
Coagulation +1.5kGy	0.1549	0.4713	0.0651
Coagulation +2.5kGy	0.2672	0.4518	0.0407

4.2.3 DOC removal

DOC concentration of raw wastewater and treated water is presented in Table 3. It showed that in raw water 12.5 % of total DOC was contributed from HMW, 56.9 % was from MMW, and the other 30.6 % was from LMW. After coagulation, DOC concentration was 5.2% from

HMW, 58.7% from MMW, and 36.1% from LMW, respectively. This indicated that coagulation can effectively remove organic with HMW. On the other side, ionizing radiation alone has little effect on the total DOC removal. For example, a small increase of DOC was observed for HMW. This may due to irradiation can only convert high molecular weight organic matters into low molecular weight compounds, or transform toxic or refractory organic compounds into low toxic or easily degradable organic compounds. When ionizing radiation was in combination with coagulation, however, a sharp decrease of HMW and MMW meanwhile increase of LMW was obtained. So, it is prefer to integrate coagulation and ionizing radiation to largely eliminate HMW and to improve the component of LMW, which is readily degraded by subsequently activated sludge process.

TABLE 3 DOC (MG·L^{-1}) OF RAW WATER AND TREATED WASTEWATER BY COAGULATION AND IRRADIATION

Sample	MW>3000Da	3000Da>MW>1000Da	MW<1000Da
Raw water	21.7	98.7	53.2
0.5kGy	34.1	81.6	31.3
1.5kGy	37.1	64.9	33.8
2.5kGy	23.1	61.9	25.7
Coagulation	8.8	99.2	61.1
Coagulation +0.5kGy	15.2	41.1	89.1
Coagulation +1.5kGy	10.0	59.9	62.0
Coagulation +2.5kGy	11.1	52.4	74.6

5. Conclusions

This paper investigated the effects of irradiation and coagulation on the molecular weight distribution of soluble organic substances in the paper mill effluent. The present results showed irradiation alone cannot promote the biodegradability and oxygen uptake as originally expected. The whole acute toxicity of samples decreased after irradiation. On the other side, coagulation not only effectively eliminate HMW, but also improve the ability of ionizing irradiation initiated the transformation of HMW and MMW into LMW. This inferred that the combination of coagulation and ionizing radiation can be a cost-effective way to treat the paper mill effluent.

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RADIATION TREATMENT OF WASTEWATER CONTAINING PHARMACEUTICAL COMPOUNDS

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Abstract

High-energy ionizing radiation induced degradation of maleic acid, fumaric acid and 20 aromatic molecules was investigated in air saturated aqueous solutions. Hydroxyl radicals were generated water radiolysis. The decomposition was followed by chemical oxygen demand (COD) and total organic carbon content (TOC) measurements. Up to ~50% decrease of COD the dose dependence was linear. By the ratio of the decrease of COD and the amount of reactive radiolysis intermediates introduced into the solution the oxidation efficiencies were calculated. Efficiencies around $0.5-1$ (O_2 molecule built in products/$^\bullet OH$) found for most of the compounds show that the one-electron-oxidant $^\bullet OH$ induces $2-4$ electron oxidations. The high oxidation rates were explained by $^\bullet OH$ addition to unsaturated bonds and subsequent reactions of the dissolved O_2 with organic radicals. In amino substituted molecules or in Acid Red 1 azo dye, O_2 cannot compete efficiently with the unimolecular transformation of organic radicals and the efficiency is lower ($0.2-0.5$).

1. Objective of the research

High-energy ionizing radiation induced degradation of toxic organic compounds in wastewater can be followed by measuring chemical oxygen demand (COD) and total organic carbon content (TOC) as a function of absorbed dose.

The objective of the present work was to study the degradability of various toxic organic compounds of different chemical structure by measuring the change in the COD and TOC values and find a relationship between the chemical structure and the degradability.

2. Introduction

Wastewaters of municipal or industrial origin, containing large number of organic impurities of various chemical structures are usually characterized by two techniques: COD and biological oxygen demand (BOD). In both cases, the total concentration of substances that can be chemically or biologically oxidized to inorganic products is determined [1]. Both COD and BOD are expressed in mg O_2 needed for oxidation in 1 dm^3 solution. In COD measurement the oxidation is carried out usually by dichromate, in BOD microorganisms make the transformation.

Oxygen uptake measurement may also be applied to follow up oxidation. This measurement is carried out in closed system and the dissolved oxygen concentration is determined before and after the treatment. The uptake value usually changes between 0.5 and 1 O_2 molecule/$^\bullet OH$. The lower value is found when half of the O_2 molecule reacting with the organic radical reforms, the higher value when all O_2 is consumed during peroxy radical decay [2]. TOC, the amount of carbon bound in organic compounds (mg dm^{-3}) is also used as a non-specific indicator of water quality.

In laboratory experiments the oxidation of many organic compounds was studied, however, very few works reported on the comparison of degradability of different compounds. Here the radiation induced degradation of 22 molecules is studied investigating the efficiency – structure relationship. The oxidative degradation under radiolysis is attributed to $^{\bullet}$OH reactions (G($^{\bullet}$OH) = 0.28 µmol J^{-1}) the contribution to degradation of the other two reactive intermediates, hydrated electron and H-atom (e_{aq}^- and H$^{\bullet}$, 0.28 and 0.06 µmol J^{-1}) is generally neglected.

3. Materials and Methods

COD was measured according to the ISO Standard 6060:1989 by a Behrotest TRS 200 system. The theoretical COD value for a $C_nH_aO_bN_c$ molecule with m molar concentration is calculated as:

$$COD_{theor} = m(n + a/4 - b/2 - 3c/4)32000 \qquad (1)$$

In TOC measurements Shimadzu TOC-VCSN equipment was used. All irradiations were made in unbuffered solutions with a ^{60}Co γ-irradiator at room temperature, dose rates 6–12 kGy h^{-1}. During irradiation gentle air bubbling was applied to avoid oxygen depletion. The degradation of phenol was also investigated in solutions bubbled with N_2O/O_2 5/1 mixture.

The chemical structures and names of investigated compounds are shown in Scheme 1 and Table 1, respectively.
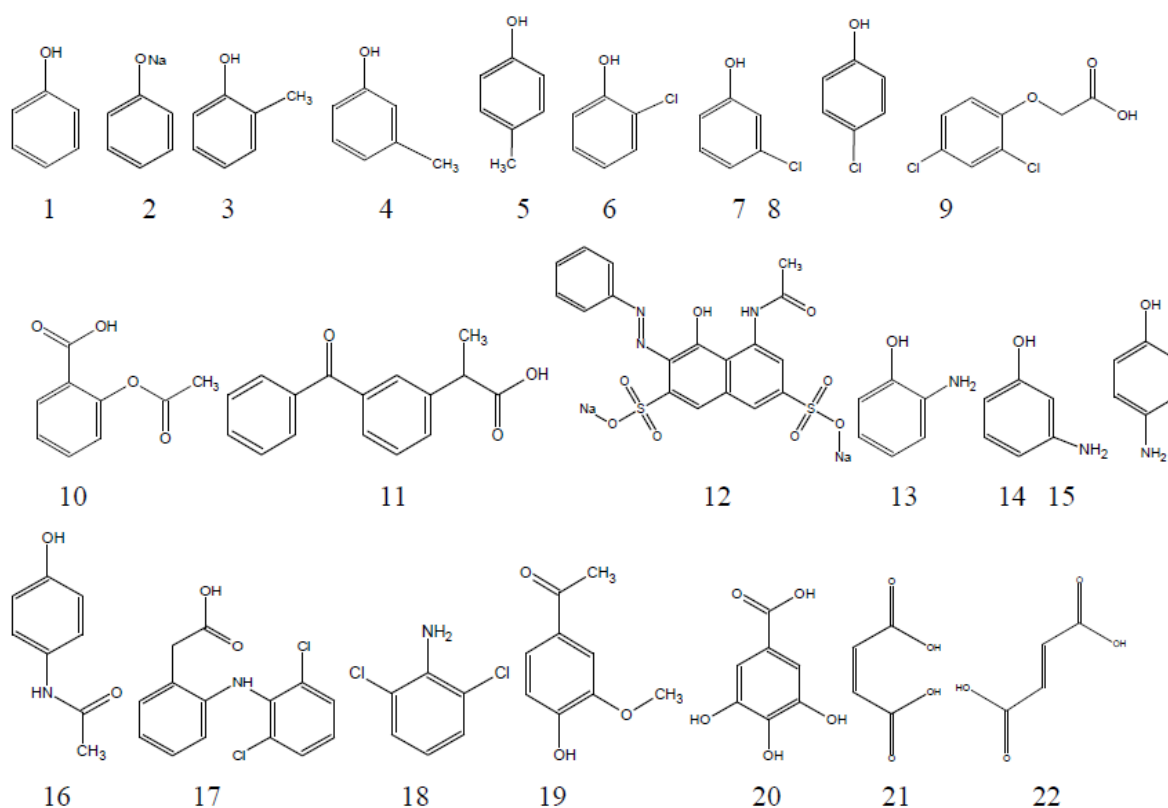
SCHEME 1. Chemical structures of compounds investigated

4. Results

Figure 1 shows the COD-values in 2 mmol dm^{-3} phenol solutions. The value for the non-irradiated solution, 453 mg dm^{-3} (COD$_{meas}$) is close to the theoretical value, 448 mg dm^{-3} (COD$_{theor}$) (Table 1). Two series of irradiations were made and all results fall on the same straight line showing the reliability of the technique. The slope (ΔCOD/dose) is 8.8 mg dm^{-3} kGy^{-1} with 0.6 mg dm^{-3} kGy^{-1} standard deviation (σ). Similar linear dependence was found in our previous works in degradation of sodium phenolate [3], diclofenac [4], 2,4-dichlorophenoxyacetic acid [5] and Acid Red 1 azo dye [6]. Initial linear dependence was also reported in oxygen uptake measurements [7,8]. In experiments with N_2O/O_2 bubbling the slope was higher: 11.3$\pm$0.9 mg dm^{-3} kGy^{-1}.

Fig. 2 shows the degradation of *o*-, *m*- and *p*-cresol at 1.5 mmol dm^{-3} starting concentration. The slopes of linear dependences are practically the same for the three isomers, 8.6$\pm$0.6, 8.5$\pm$0.3 and 7.6$\pm$0.8 mg dm^{-3} kGy^{-1}, respectively, they are close to the value determined for phenol. For *o*-, *m*- and *p*-chlorophenols 2 mmol dm^{-3} concentrations seemed to be good choices (Fig. 3), the slopes are 8.0$\pm$0.8, 7.1$\pm$0.6 and 9.4$\pm$0.4 mg dm^{-3} kGy^{-1}, respectively.
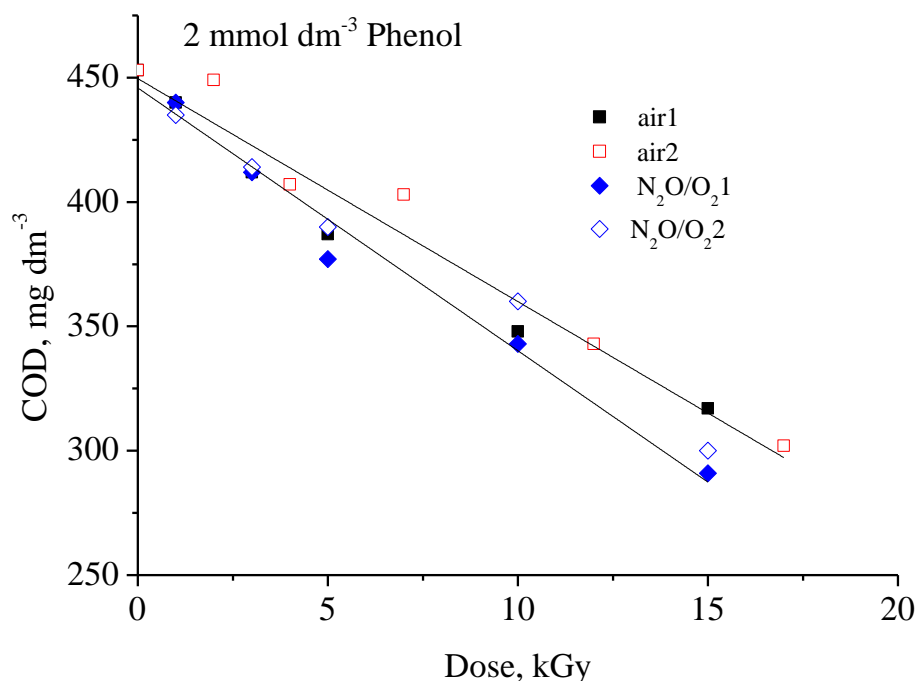

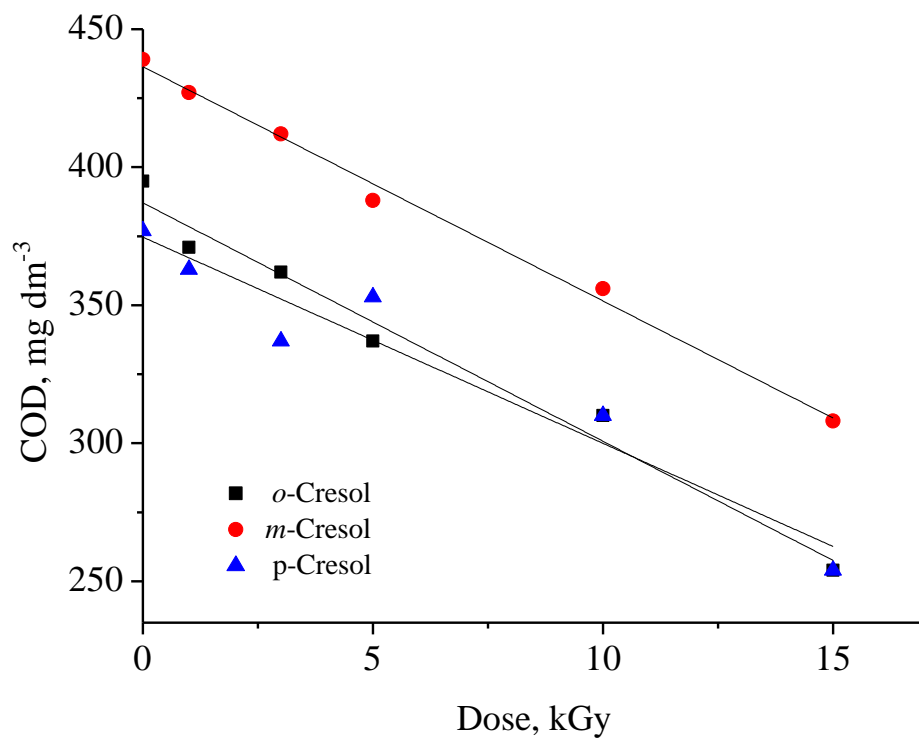*Fig. 1. COD measured in 2 mmol dm^{-3} aerated or N_2O/O_2 bubbled phenol solutions.*

Fig. 2. COD measured in 1.5 mmol dm^{-3} aerated cresol solutions.

TABLE 1. CHEMICAL OXYGEN DEMAND VALUES AND OXIDATION EFFICIENCIES (E).

No	Compound	Concentration, mmol dm^{-3}	COD$_{meas}$/COD$_{theor}$, mg dm^{-3}	Slope, mg dm^{-3} kGy^{-1}	E
1	Phenol	2	453/448	8.8±0.6	0.98
		2		11.3±0.9[a]	0.63
					0.63[b]
2	Na phenolate (pH 10.5)[c]	5	1120/1120	18	2.0
3	*o*-Cresol	1.5	395/408	8.6±0.6	0.96
4	*m*-Cresol	1.5	439/408	8.5±0.3	0.95
5	*p*-Cresol	1.5	377/408	7.6±0.8	0.85
6	*o*-Chlorophenol	2	418/432	8.0±0.8	0.89
7	*m*-Chlorophenol	2	442/432	7.1±0.6	0.79
8	*p*-Chlorophenol	2	410/432	9.4±0.4	1.05
9	2,4-Dichlorophenoxy-acetic acid (2,4-D)	2	441/496	8.0±0.5	0.9
					1.2[d]
10	2-Acetoxybenzoic acid (aspirin)	1.5	401/432	8.1±0.5	0.9
11	Ketoprofen	0.4	222/230	9.0±1.0	1.0
12	Acid Red 1 [e]	1.5	840/850	5.5±0.8	0.61
13	*o*-Aminophenol	1	216/208	4.7±0.7	0.52
14	*m*-Aminophenol	1	213/208	3.5±1.0	0.39
15	*p*-Aminophenol	1	216/208	5.0±0.9	0.55
		1.5	288/312	4.6±0.8	0.51
16	*N*-(4-hydroxyphenyl)acetamide(paracetamol)	1	253/272	3.7±1.2	0.40
17	Diclofenac	0.5	230/236	9.0±0.3	1.0
18	2,6-Dichloraniline	0.5	89/91	5.5±1.0	0.61
19	Acetovanillone	0.5	153/160	6.9±0.4	0.77
20	Gallic acid	2	340/384	8.5±0.8	0.95
	Formate				0.55[f;g]
	Isopropanol				0.55[f]
	t-Butanol				0.80[f]
	Diethyl ether				0.84[f]
21	Maleic acid	4	374/384	7.4±0.7	0.82
22	Fumaric acid	4	411/384	9.0±0.7	1.0

[a] Measured in 5:1 N_2O/O_2 atmosphere; [b] Oxygen uptake measurement, 25% O_2 in bubbling gas [9]; [c] In oxygen saturated solution [3]; [d] Oxygen uptake measurement [8]; [e] COD taken from Földváry andWojnárovits, [6]; [f] The efficiency-values were estimated from oxygen uptake measurement [7]; [g] Oxygen uptake measurement [10].
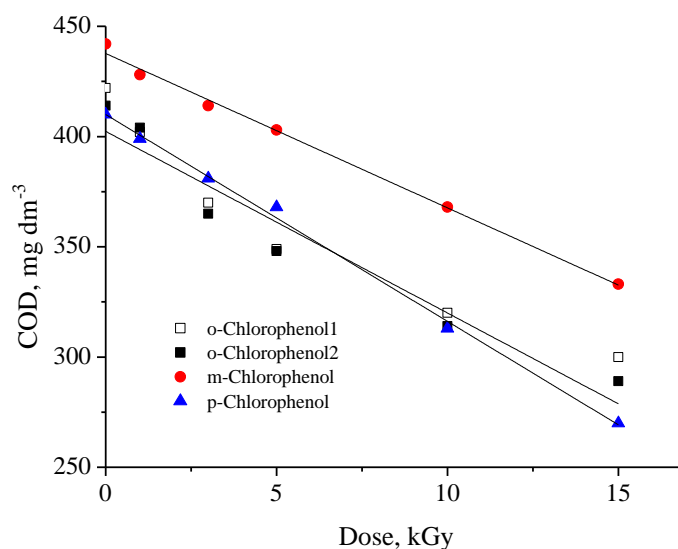
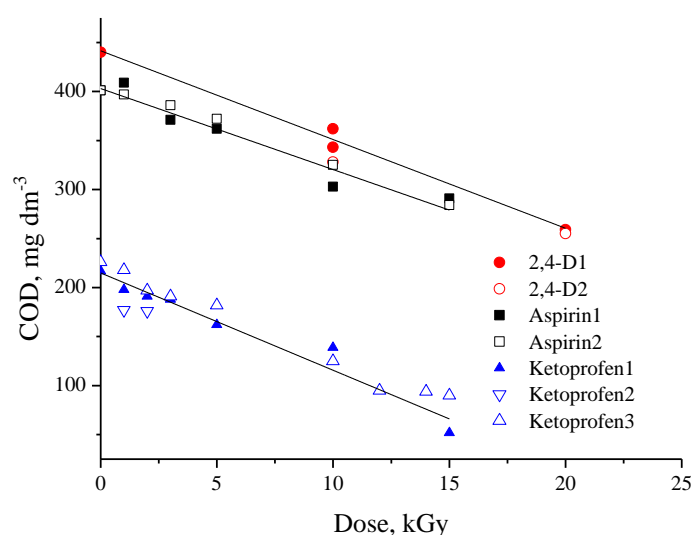*Fig. 3. COD measured in 2 mmol dm^{-3} aerated chlorophenol solutions.*

Fig. 4. COD measured in aerated 2,4-D (2 mmol dm^{-3}), aspirin (1.5 mmol dm^{-3}) and ketoprofen (0.4 mmol dm^{-3}) solutions.

2-acetoxybenzoic acid (aspirin) and ketoprofen were investigated with 2, 1.5 and 0.4 mmol dm^{-3} concentration and the ΔCOD/dose values are 8.0$\pm$0.5, 8.1$\pm$1.0 and 9.0$\pm$1.0 mg dm^{-3} kGy^{-1}, respectively (Fig. 4). The *o-*, *m-*, *p-*aminophenol and *N*-(4-hydroxyphenyl)acetamide solutions had 1 mmol dm^{-3} concentrations, the slopes are 4.7$\pm$0.7, 3.5$\pm$1.0, 5.0$\pm$0.9, 3.7$\pm$1.2 mg dm^{-3} kGy^{-1}, respectively (Fig. 5A). The ΔCOD/dose of *p-*aminophenol solution with 1.5 mmol dm^{-3} concentration was 4.6$\pm$0.8 mg dm^{-3} kGy^{-1}. Diclofenac was investigated at 0.5 mmol dm^{-3} concentration, ΔCOD/dose was 9.0$\pm$0.3 mg dm^{-3} kGy^{-1}. The concentration of the poorly soluble 2,6-dichloroaniline was 0.5 mmol dm^{-3} (5.5$\pm$1.0 mg dm^{-3} kGy^{-1}), the same concentration was selected for acetovanillone (6.9$\pm$0.4 mg dm^{-3} kGy^{-1}) (Fig. 6). Gallic acid has good solubility; its oxidation was investigated at 2 mmol dm^{-3} (8.5$\pm$0.8 mg dm^{-3} kGy^{-1}).
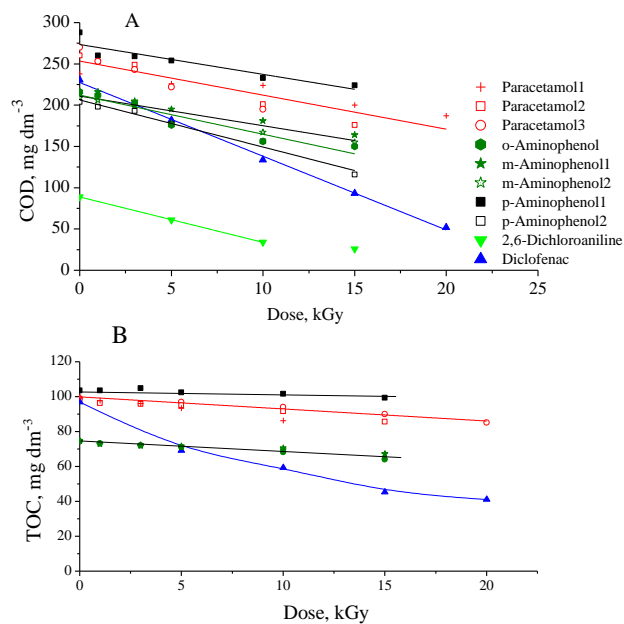
FIG. 5. *COD measured in aerated paracetamol (1 mmol dm^{-3}), diclofenac (0.5 mmol dm^{-3}), o- (1 mmol dm^{-3}), m- (1 mmol dm^{-3}), p-aminophenol (1 and 1.5 mmol dm^{-3}) and 2,6-dichloroaniline (0.5 mmol dm^{-3}) solutions (A), and TOC for paracetamol, diclofenac and aminophenol solutions (B).*
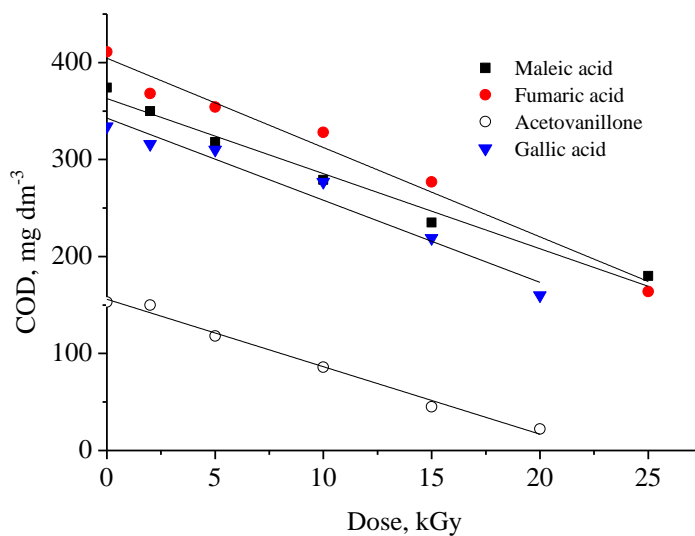

Fig. 6. *COD measured in aerated maleic acid (4 mmol dm^{-3}), fumaric acid (4 mmol dm^{-3}), acetovanillone (0.5 mmol dm^{-3}) and gallic acid (2 mmol dm^{-3}) solutions.*

The experiments with maleic and fumaric acids (ΔCOD/dose-values, 7.4 ± 0.7 and 9.0 ± 0.7 mg dm^{-3} kGy^{-1}, respectively) were carried out in 4 mmol dm^{-3} solutions. In non-buffered solution both acids were mainly in monoionic form.

5. Discussion

Most of the ΔCOD/dose-values are in the 7–9 mg dm^{-3} kGy^{-1} range (Table 1). With 1 kGy dose 0.28 mmol $^\bullet$OH, 0.28 mmol e$_{aq}^-$ and 0.06 mmol H$^\bullet$ are introduced into 1 dm^3 solution. The oxidation efficiency (E) is characterized here by the ratio of the number of O$_2$ molecules built in the products and the number of water radicals (R$^\bullet$) introduced into solution with ρ density (kg dm^{-3}):

$$E = \frac{\Delta COD / dose}{3.2 \times 10^7 G(R^\bullet)\rho} \tag{2}$$

The efficiencies based on oxygen uptake measurements (published in literature) are also shown in Table 1 calculated as the ratios of G(Oxygen consumption) and hydroxyl radical yields, $G(^\bullet$OH).

E's in column 6 of Table 1 are calculated assuming that only $^\bullet$OH contributes to degradation. (If all water radiolysis intermediates contribute equally to oxygen building in, the efficiencies are 55% lower). Most of efficiencies are close to 1, for phenol 0.98 was obtained. E around 1 shows that the one-electron-oxidant $^\bullet$OH induces four electron oxidations. In Scheme 2 the example of phenol is used to rationalize the high efficiency. Sato et al. [11] classified the phenol degradation products in three categories: 1. hydroxylation products (dihydroxybenzenes), 2. dimers like o,o'-biphenol, and 3. ring degradation products like dihydroxymukondialdehyde, mukonic acid derivatives, maleic acid, glyoxal.
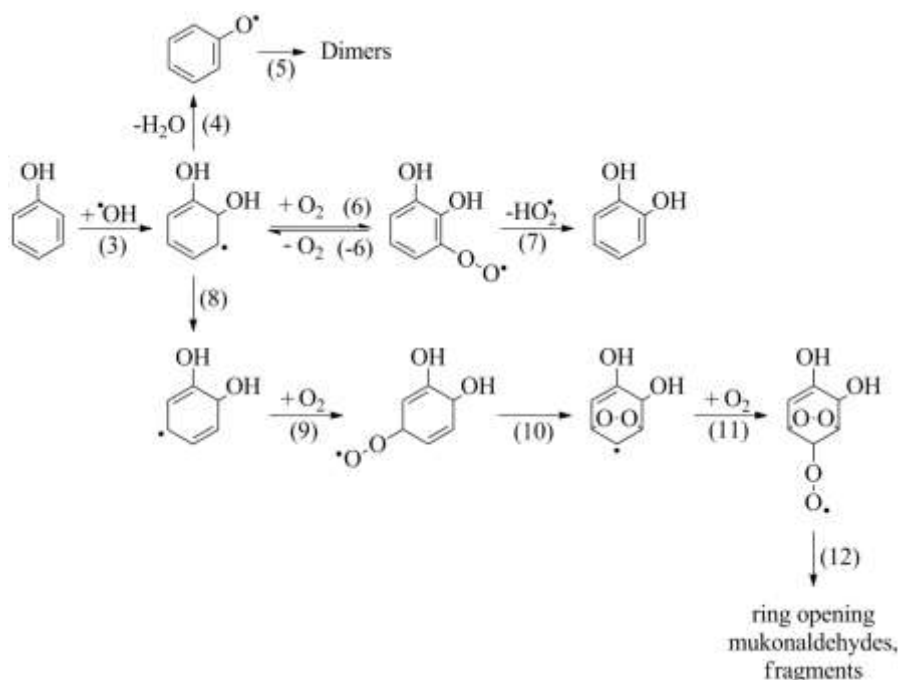
SCHEME 2. $^\bullet$OH induced degradation of phenol

$^\bullet$OH preferably adds to phenol in *ortho-* (Scheme 2, Reaction (3)) and *para*-positions [9]. The hydroxycyclohexadienyl radicals produced may undergo water elimination yielding phenoxy radical (4). Phenoxy radicals decay in dimerization (5). Due to these reactions one $^\bullet$OH decreases O_2 needed for oxidation by 1/4 O_2 molecule (one-electron-oxidation). This reaction does not cause change in dissolved oxygen concentration.

The hydroxycyclohexadienyl radical reacts with O_2 in (6) forming peroxy radical in reversible process [12]. The O_2 addition is fast, the adduct is relatively stable when there is an electron donating substituent on the ring; the opposite is true for electron withdrawing substituent. With phenol the reversible reaction is shifted towards the peroxy radical. When the O_2-adduct in (7) eliminates an $HO_2^\bullet$ two-electron-oxidized phenol (catechol) is obtained; with this product $^\bullet$OH reduces the oxygen demand by ½ O_2 molecule. *Meta-* and *para*-additions yield resorcinol and hydroquinone.

The hydroxycyclohexadienyl radical in (8) may undergo a rearrangement to semiquinone radical. This intermediate is capable of taking-up two O_2, after reacting with O_2 in (9) the peroxide isomerizes (10) to endoperoxide, the carbon centered radical in (11) reacts with a second O_2. Degradation of this intermediate leads to mukonic acid and aldehyde derivatives and smaller organic fragments [11,13]. If the latter reaction route is dominating *E* can be 1 or higher. Based on the efficiencies close to 1 determined for many compounds, we assume that reactions (8) to (12) play important role in degradation.

The efficiencies for cresol isomers are similar; they are close to the value obtained for phenol. Surprisingly the efficiencies for chlorophenols are similar to the values obtained for cresols and phenol: the electron withdrawing Cl-atom on the ring decreases the electron density and is expected to shift the equilibrium of O_2 + hydroxycyclohexadienyl reaction towards dissociation. For chlorobenzene a rate coefficient of 2.6×10^8 mol^{-1} dm^3 s^{-1} was found for the O_2 + hydroxycyclohexadienyl reaction, 5.5×10^4 s^{-1} for the reversed process, the first value is lower and the second one is higher than obtained for benzene (3.1×10^8 mol^{-1} dm^3 s^{-1} and 1.2×10^4 s^{-1} [12]).

E of 2,4-dichlorophenoxyacetic acid is also high, although there are two chlorine atoms on the ring. In our studies efficiency of 0.9 is obtained, the oxygen consumption measurements of Zona and Solar [8] suggest 1.2. The presence of electron withdrawing substituents (-COOH and -OCOCH$_3$) in 2-acetoxybenzoic acid does not reduce the oxidation efficiency either. Ketoprofen was shown to be easily oxidized in $^\bullet$OH reactions [14], *E* = 1.0. *E* is lower (0.61) for Acid Red 1 than for the other aromatics. Here $^\bullet$OH may also attack the azo group [6]. The hydrazyl radical thus formed does not react with O_2.
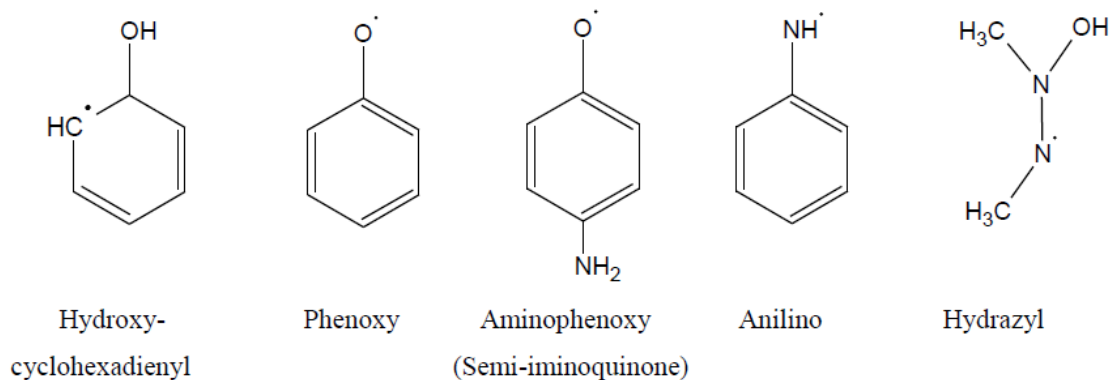
Scheme 3. Some radical types mentioned in the text.

The efficiencies for phenols with amino- or acetamide-group (*o*-, *m*-, *p*-aminophenol, *N*-(4-hydroxyphenyl)acetamide) are low (0.4–0.5). The $^{\bullet}OH$ induced transformations of aminophenols, especially that of *p*-aminophenol, were investigated in pulse radiolysis experiments and fast formation of aminophenoxy (semi-iminoquinone) or anilino radicals (Scheme 3) was observed [15,16]. The O_2 + hydroxycyclohexadienyl reaction probably cannot compete effectively with hydroxycyclohexadienyl transformation to phenoxy or anilino radicals: formation of these radicals decreases the oxidation rate. The same reasoning may also be applied to explain the low *E* of paracetamol. In pulse radiolysis experiments the hydroxycyclohexadienyl radicals were shown to transform quickly to aminophenoxy radicals. These radicals do not react with dissolved O_2 [17]. In end-product experiments the efficiency of $^{\bullet}OH$ in destroying paracetamol molecules was estimated 0.2–0.3 [18], the efficiency in COD is 0.4. In agreement with this reasoning TOC measured in paracetamol and aminophenol solutions show hardly any decrease with the dose (Fig. 5B). The efficiency in 2,6-dichloroaniline oxidation is also low, 0.61. In pulse radiolysis experiments preferred formation of anilino radical was observed [19]. For diclofenac, which has an -NH- group between two rings, *E* is high, 1.0. The main degradation starts with $^{\bullet}OH$ addition to the ring without Cl-atom [4]. The subsequent reactions may be similar to the ones discussed for phenol. In diclofenac solutions the TOC decreased considerably with the dose (Fig. 5B).

E for acetovanillone (0.77) is close to the values obtained for phenol, cresols and chlorophenols, although it is somewhat lower than the average for these easily degradable compounds (0.93). End-product experiments also reflect lower efficiency [20]. In pulse radiolysis at neutral pHs the intermediate hydroxycyclohexadienyl radical was detected on the 10 μs timescales in deoxygenated solutions [21]. In solutions containing dissolved oxygen reaction with O_2 and degradation from this intermediate is probable. The degradation of gallic acid proved to be highly efficient both in COD (0.95) and final product experiments [22].

The efficiencies found here for maleic and fumaric acid (0.82 and 1.0) are close to the values calculated for *t*-butanol and diethylether (0.80 and 0.84, respectively) based on oxygen consumption measurements [7]. These measurements for formate and isopropanol [7,10] yield smaller *E* (0.55 for both). The high oxidation rates for maleic and fumaric acids reflect incorporation of the two oxygen atoms of the peroxy radicals into products without release of O_2 as suggested by Isildar et al. [7].

6. Conclusion

The hydroxyl radical initiated oxidation of phenols, maleic and fumaric acids proceeds with high efficiency; the one-electron oxidant $^\bullet$OH when dissolved oxygen is present induces two-four electron oxidations. When amino, acetamide or hydrazo groups are attached to the ring of phenol the rate is lower, one $^\bullet$OH induces one−two electron oxidations. The low rate is probably due to intermediate radicals (phenoxy, anilino, semi-iminoquinone, hydrazyl) with low reactivity with oxygen. The experiments also revealed that in aerated solutions the reductive water radiolysis intermediates, e_{aq}^- and H$^\bullet$ also contribute to oxidative degradation.

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COMPARISON BETWEEN IONIZING AND NON-IONIZING RADIATION TECHNOLOGIES FOR WASTEWATER REMEDIATION

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Abstract

A study on the decomposition of a surfactant (SDBS) and of four emerging pollutants (ofloxacin, carbamazepine, benzophenone-3, benzophenenone-4) in a multicomponent system is presented. These pollutants are decomposed in water by a few types of Advanced Oxidation Processes. The remediation methods included UV and γ-rays, all running in atmospheric conditions. It is shown that UV degradation methods can be improved by adding a photocatalyst (TiO_2), or a radical mediator (H_2O_2). The processes were monitored step by step, by determining the concentration of pollutants by UV, HPLC and a specific surfactant selective kit, and measuring the total organic carbon content.

1. Objective of the research

Many efforts to remediate wastewater are nowadays dedicated to the development of Advanced Oxidation Processes (AOPs), having the objective to destroy more and more efficiently the organic pollutants rather than separate them through filtration. Methods are requested therefore to join effectiveness and speed. However, as cost increases with treatment speed, it is necessary to tailor remediation processes to the quality, amount and fate of water to reuse. Our objective is then to explore and optimize some AOPs like EB, γ-rays, photocatalytic oxidation, UV photolysis, ultrasound cavitation and possibly any hybridization among them to offer a response to different remediation needs.

2. Introduction

The ubiquitous nature of ˙OH associated with its high reactivity and oxidative power has consequences of various type on the aquatic system and atmosphere. Therefore its production for basic knowledge, industrial needs and environmental preservation is matter of a wide range of investigations by governmental groups and private companies. Given that ˙OH attack to organic molecules and the subsequent cascade of radical reactions demonstrated already to achieve the destruction of a plenty of pollutants, nowadays these efforts focus on methods which join the effectiveness of remediation with higher speed and cheaper treatments. However, as cost increases with treatment speed, it seems wise to develop other methods, flexible enough to suit specific application scales and reuse purposes. By far the most efficient ˙OH producing method is performed by hitting water with an electron beam. However, as EB treatment becomes economically appealing when the effluent volumes exceed 1000 m³/day[1], we planned to explore and compare the remediation performances of a few Advanced Oxidation Processes like EB itself, γ-rays, photocatalytic oxidation, UV photolysis and ultrasound cavitation.

Working in the frame of a project supported by the Ministry of Development aiming to promote domestic eco-laundry machines, we developed a prototype reactor to rehabilitate washing water for reuse. As, in the case above, anionic surfactants represent a considerable part of the dissolved organic waste, we show here some results on the decomposition of a dual

system sulfonates (MIX-2), i.e sodium dodecylbenzensulfonate (SDBS), and benzophenone-4 (BP4), by means of TiO_2 photocatalysis.

Also our attention was attracted by the increasing use of new chemical compounds for agriculture, zootechnics and personal care products (pesticides, drugs, UV filters, cosmetics and so on) which show a relatively poor bio-degradability. Recent reports, in fact, pointed out the presence of ofloxacin (OFX) and carbamazepine (CBZ) in several rivers in Italy2,3 [2,3] and of benzophenone-3 (BP3) and the already mentioned (BP4) in sewage, surface and drinking water in Spain4 [4]. Therefore we decided to carry out an investigation on the mineralization of a multicomponent aqueous system, mixing all the four together (MIX-4), by UV methods and ionizing radiation. At the same time we tuned the TOC analysis in the presence of H2O2, as hydrogen peroxide went up to interfere with TOC measurements.

3. Materials and methods

Instrumentation and sample preparation

UV irradiation was performed by a Rayonet irradiator, equipped with 16 UV lamps (8W, 253.7 nm, Hg low pressure, Sylvania).A quartz reactor flask was placed in the center of the irradiation chamber. The flask was equipped with a condenser. γ-irradiation was done in a Nordion 220 gamma-cell. A dose rate of 4.5 Gy/min was measured with the Fricke dosimeter in the reaction cells. For radiolysis in the presence of H_2O_2 10 mM a G(OH) = 0.52 μmol J^{-1} was taken[5]. Air bubbling was provided during all treatments throughout irradiation. To reach a complete dissolution of compounds in MIX-2 and MIX-4, mother solutions were kept under magnetic stirring for 16 h in the dark at 25°C. The progress of degradation was checked as reported in the text; analyses were performed immediately or on samples stored in the fridge, if analyzed afterward (max. 48 h). As for TiO_2, Evonik VP aeroperls P25/20 ϕ=20 mm were used. An Agilent 1260 HPLC instrument equipped with a diode array detector was used to follow the disappearance of the selected compounds. 0.5 mL samples were used as sources for the automated injection of 40 μL of each chromatographic run performed on a reverse phase C-8 poroshell (Agilent) 120, 2.1 × 50 mm 2.7 μm, with a linear gradient from 0.1% trifluoroacetic acid in water to 100% acetonitrile in 5 min, then isocratic up to 10 min; flow rate of 0.5 mL/min. The total organic carbon (TOC) and the anionic surfactants (AS) concentrations were measured by means of the Hach-Lange kits: LCK-385 for TOC and LCK332 for AS. Their performances were validated against standard solutions: the TOC kit showed an experimental error of ± 15% in the 3-30 mg/L range. Its Limit-of-Detection (LOD) is 3 mg/L. A linear overestimation of about 50% of the AS kit was found and considered.

4. Results and discussion

MIX-2

SDBS (20 mg/L) and BP4 (5 mg/L) were mixed and dissolved in water under continuous stirring for 16 hours. After adding TiO_2 pearls, the solution was air saturated by bubbling the gas for 5' before and throughout the treatment. Irradiation by UV light (254 nm) was carried out for 4 hours. The temperature of samples reached a maximum of 56°C. The pH remained almost neutral (7.3-7.5). The destruction of pollutants has been monitored in the intermediate and final samples by comparing the UV-vis absorption bands (Figure 1), and by measuring the relative areas of HPLC chromatograms.

The progressive spectral bleaching shown in figure 1 clearly evidences the full destructuration of BP4, but nothing can say on SDBS fate. The absorption of SDBS is, in fact, too low to be distinguished from the stronger absorbance of BP4. Fortunately, the destructuration of SDBS can be revealed by the progressive extinction of its fluorescence after HPLC separation.

Therefore, by matching UV-vis spectroscopy and HPLC information, it can be observed that BP4 is consumed after 240 minutes. More efficient is the destruction of SDBS, as a 93.5% of it disappeared just after 30 minutes. Interesting, the destruction of the surfactant properties does not match the disappearance of SDBS. In fact, inspecting the concentrations after 30 min in Figure 2, one can notice that 1.3 mg/L (6.5%) of SDBS is left, but the samples contain 7.0 mg/L of AS. It may mean that the intermediates formed during the degradation of SDBS still maintain a surfactant character. To this purpose, any interference of BP4 on AS content evaluation was ruled out by checking the method against BP4 solutions at various concentrations.

The extent of mineralization was controlled by measuring the TOC of the same samples above. The TOC dropped down regularly with time from 13.9 mg/L to a value below the limit of detection (LOD), 3 mg/L (Figure 3).
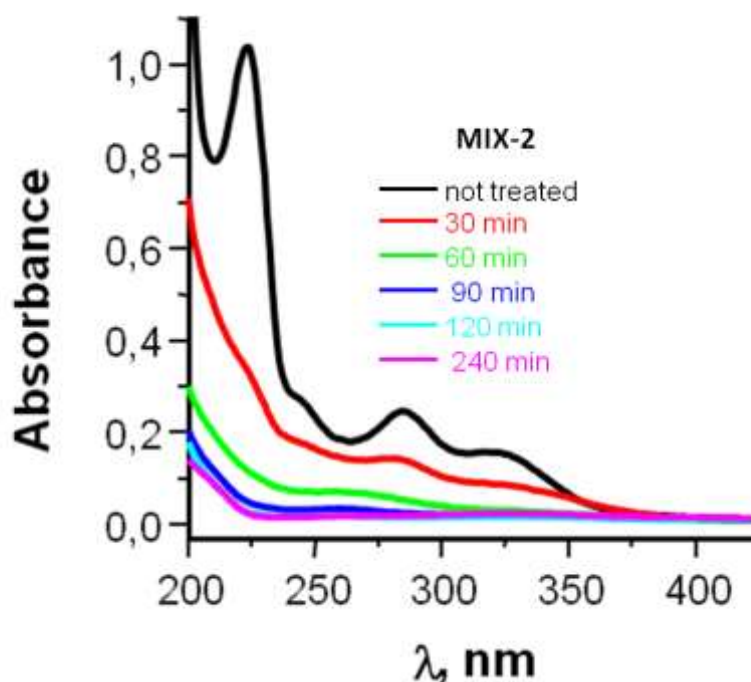

Fig. 5. UV-vis spectra of an aqueous solution of SDBS & BP4 (MIX-2) under heterogeneous photocatalysis induced by UV light and TiO₂.
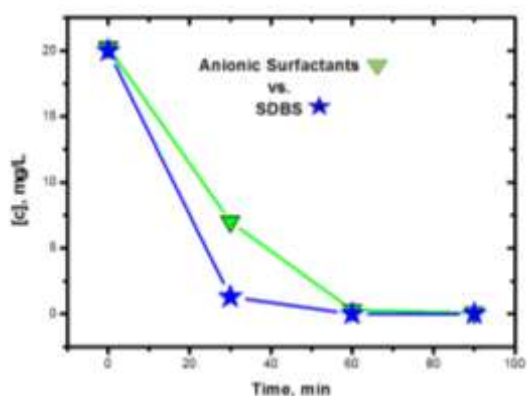
Fig. 2. Initial and intermediate concentrations of Anionic Surfactants AS (LCK332 kit) and SDBS (HPLC) in MIX-2 treated by UV light and TiO$_2$
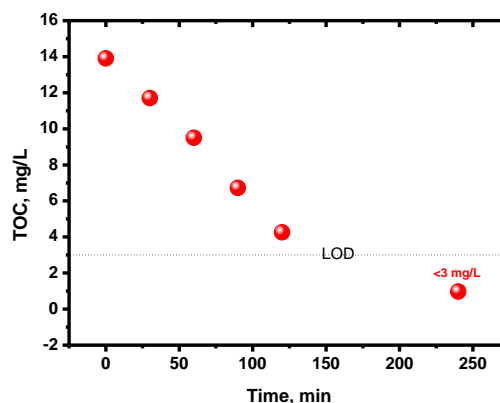
Fig. 3. Decrease of TOC during the photocatalysis of MIX-2. LOD is the limit of detection = 3 mg/L

MIX-4

Regarding the degradation of a complex system containing OFX (0.013 mM), CBZ (0.021 mM), BP3 (0.023 mM), and BP4 (0.016 mM) in water solution, the following methods were used: (A) UV irradiation alone, (B) UV in the presence of TiO$_2$ particles, (C) and (D) UV with addition of H$_2$O$_2$, (E) γ-rays in the presence of H$_2$O$_2$. All degradations were carried out under constant air bubbling.

UV irradiation

Method (A) is obviously the simplest but it cannot be considered a proper AOP, being mostly a photochemical process. It is however of interest because it can be related to the natural degradation under solar radiation. Methods (C) and (D) are well known AOPs[6,7] being hydrogen peroxide easily photolyzed to hydroxyl radicals. They differ only with respect to H$_2$O$_2$ concentration: [H$_2$O$_2$] was 0.6 mM in (C) and 10 mM in (D). Method (B) is the same heterogeneous process used for MIX-2, usually depending on complex parameters[8,9,10].

As OFX, BP4, CBZ and BP3 are consumed in a competition kinetics for ˙OH, two wavelengths, 285 and 294 nm (294 nm specifically for OFX) have been carefully selected to distinguish the four HPLC analytes each other. Their concentrations were quantified calculating the ratio of each peak area with that of the initial sample.

A severe disappearance of the analytes before reaching a substantial reduction of TOC has been observed. For an immediate appreciation of the trend of the mineralization process, the TOC values in mg/L units are reported in Figure 4 in percentage units, beside the remaining pollutants. The temperature of solutions increases of about 40°C for all methods excluding different thermal effects on the processes. On the other hand, the pH decreases at values between 4 and 5, indicating the formation of organic acids and CO$_2$.

These observations are coherent with the general view that advanced oxidations proceed through a complex process consisting primarily in the fragmentation of pollutants

(destructuration), followed by the transformation into CO_2 and carbonates (mineralization) in a second phase. It has yet to be verified whether non-homogeneous processes obey the same behaviour. A detailed comparison between photocatalyzed (heterogeneous), on one side, and UV and γ (homogeneous), on the other, might help to solve the problem.

In (D) the concentration of H_2O_2 was increased to 10 mM: the purpose was to study the effect of H_2O_2 on the photodecomposition rates and compare the efficiencies between UV- and γ-treatments. Fundamentally, with H_2O_2 10 mM the photomineralization rate can be estimated as having a t½ < 5 min, while with H_2O_2 0.6 mM the rate is almost 4 times slower (t½ ca. 20 min). The following section allows the comparison between UV/ H_2O_2 and γ /H_2O_2.

γ-irradiation

Mix-4, containing H_2O_2 10 mM, was also exposed to γ-rays under continuous air bubbling. Figure 5 shows the concentration changes for each component during the treatment as obtained by HPLC measurements. Their overall decomposition follows similar dose profiles, as ·OH reactions occur almost with the same rate constants (ca. 10^9 $M^{-1}s^{-1}$) with any of them. BP3 may be decomposed through more complex pathways than the others. After irradiation the solution became slightly acidic, similarly to UV degradation: i.e. pH changed from 8 to 4.

TOC measurements could be accurate only in the absence of H_2O_2. Actually, it turned out that H_2O_2 interferes on TOC measurements at concentration > 1 mM. At 10 mM for example the initial TOC was underestimated of 50%, while in the absence of H_2O_2, the underestimation was < 8%. It meant that TOC data during the initial and core stages of degradation are meaningless. However mineralization is indeed produced at a very large extent, as it can be ascertained when H_2O_2 concentration is reduced below 1 mM. This occurs after the application of ca. 20 kGy: at this stage, in fact, the TOC value drops down at 3 mg/L (LOD) from an original 12.6 mg/L (Figure 5, inset).
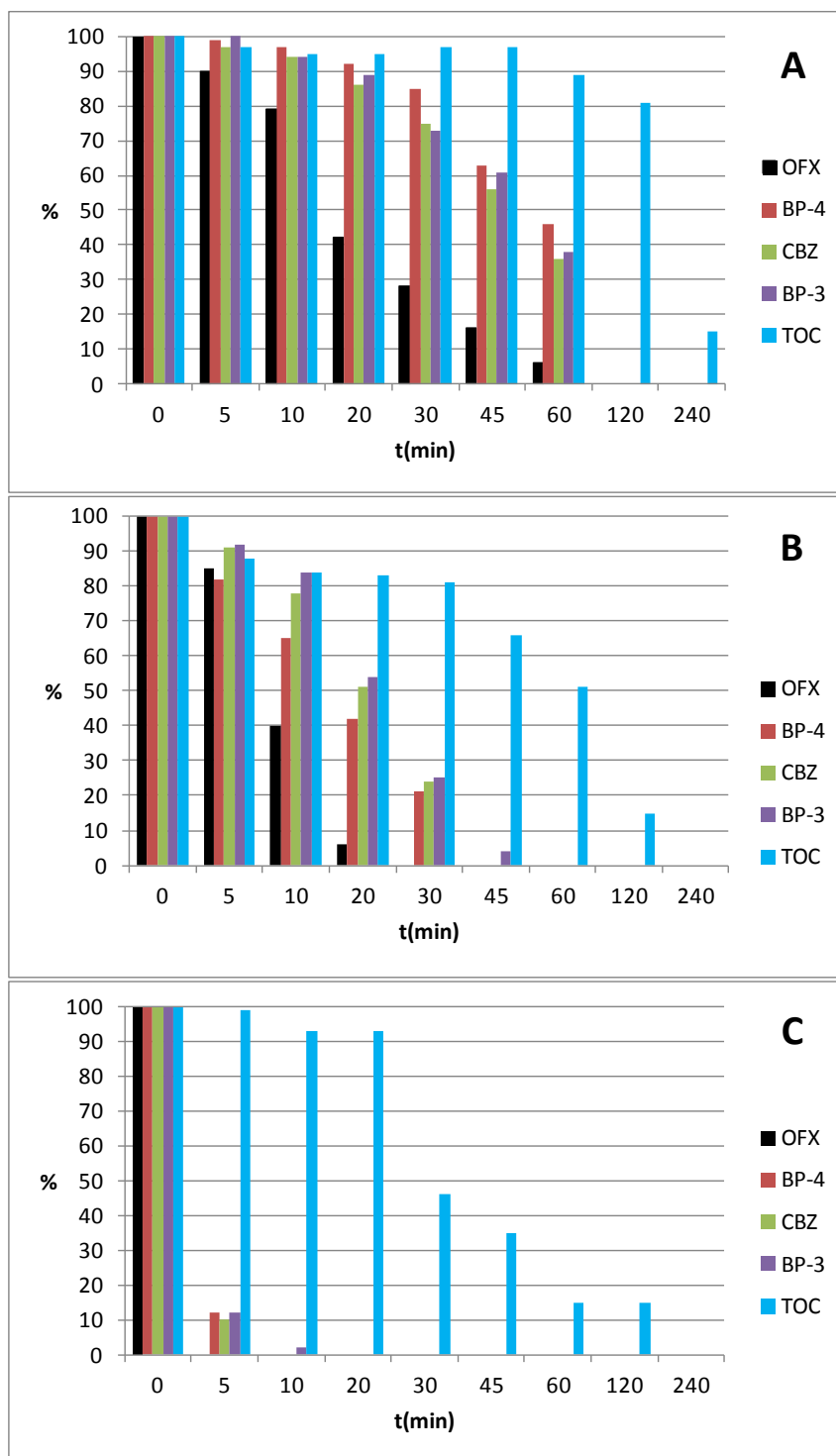
Fig. 4. Relative concentrations of pollutants and relative TOC values for methods (A),(B), and (C), quantified by HPLC at 285 and 294 nm. TOC readings under the limit of detection (3 mg/L) were conventionally plotted at 15% height, corresponding to the uncertainly of the method.
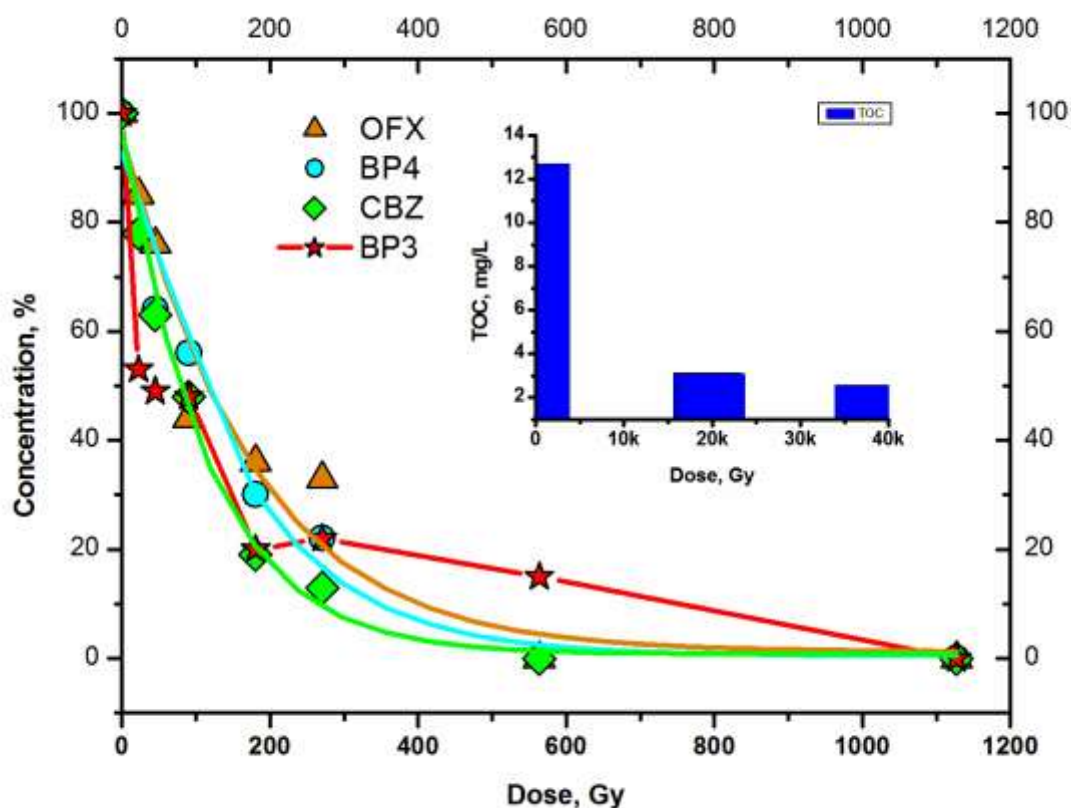
Fig. 5. Relative concentrations of OFX, BP4, CBZ, and BP3 measured by HPLC during γ-irradiation of MIX-4 the presence of 10 mM H_2O_2. In the inset: TOC decreases below 3 mg/L after a dose of 20 kGy.

Conceiving a comparison between γ and UV methods, only specific considerations can be made, valid for our experimental conditions. The TOC limit of detection, constituted by 3 mg/L, is reached after 30 min by UV method (D), while γ-treatment requires almost 3 days (4400 min) of irradiation at a dose rate of 4.5 Gy/min. Generally speaking, this data evidences that the mineralization rate is related to the ˙OH production rate from H_2O_2 in the systems.

5. Provisional conclusions

MIX-2 and MIX-4 treated by UV/TiO₂, UV/H₂O₂, and γ/H₂O₂ under aerated conditions showed an efficient conversion of the organic carbon to inorganic one. In the UV treatments, the progress of mineralization has been evidenced since the very early times of irradiation, although some AOPs with a low ˙OH production rate (i.e. photocatalysis) show a longer induction period. The induction period represents the destructuration of the molecules, as proved by HPLC and spectrophotometric analyses.

Aqueous photolysis, alone, activates different and slower mechanistic routes than hydroxylation does. Photolysis is, however, capable to decompose all the chemicals of MIX-4 and to lead to mineralization as well.

The most efficient degradation of the chemicals was achieved in the presence of hydrogen peroxide. A 10 mM H_2O_2 has to be used to achieve the best efficiency of γ-treatment, while

the optimal value for UV/H_2O_2, under our experimental set up can be lower than that; the definition of this value is under course. HPLC analyses do not reveal significant formations of by-products absorbing in the 190-400 nm range.

In the absence of H_2O_2 (methods A and B), OFX was the fastest molecule to disappear, possibly due to its photolability. Instead, in the presence of H_2O_2, the compounds degrade almost in the same time domain (methods C, D, and E). This may be attributed to the fact that their rate constants with $\cdot$OH are very similar, although BP3 seems to decompose through a more complex kinetics.

In the whole any AOP succeeds in reducing the TOC below 3 mg/L, i.e. the detection limit of the method (see experimental section). Therefore, the starting TOC value (ca. 12-13 mg/L), can be followed since its abatement reaches the 75-76%. It appears however likely that mineralization proceeds to completion.

As photocatalysis with TiO_2 promptly destroys most surfactants, the method is proposed as a valuable choice for the remediation and reuse of water wasted during domestic washing cycles. Despite its complexity, TiO_2 photocatalysis is appealing due to the facts that TiO_2 is a natural, cheap, and non toxic compound. Its efficiency strongly depends on the adsorption of the target pollutants at the metal oxide surface/water interface and on the efficiency of the UV-activation of the complex. For these reasons, work is in progress to build up a prototype reactor using TiO_2 supported on glass, plastic or alloys.

Acknowledgements

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TREATMENT OF WASTEWATER CONTAINING ORGANIC POLLUTANTS BY IONIZING RADIATION

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Abstract

We have investigated the treatment of endocrine disrupting chemicals (EDCs) and halogented organic compounds (HOCs) in wastewater by ionizing radiation in the CRP. Three samples of the actual wastewater having estrogen activity were analyzed by the yeast two-hybrid assay, enzyme linked immunosorbent assay (ELISA) and total organic carbon (TOC) analysis. Treatment of the wastewater is required to decrease the estrogen activity to less than 1 ng / L; the lower limit concentration of appearance of endocrine disrupting property. Medaka estrogen activity (mEA) initially increased and then decreased by γ-ray irradiation, indicating that decomposition products in the real wastewaters also have the estrogen activity. The doses required to decrease in mEA of samples 1 to 3 below 1 ng / L, D_{1ng}, were estimated to be 100, 200 and 150 Gy (J kg^{-1}), respectively. Since the D_{1ng} of 17 β-stradiol (E2) at 500 ng/L (1.8 nmol/L) in pure water was estimated to be 5 Gy as mentioned in the previous CRP, the elimination of estrogen activity of real wastewater is considered to be interfered by organic impurities. The economic cost of the treatment process of EDCs using electron beam was estimated at 17 yen m^{-3}.

1. Objective of the research

The technology for the decomposition of trace amounts of organic pollutants such as endocrine disrupting chemicals (EDCs) was developed. Biological activities of real wastewater were decreased by using ionizing radiation, and required dose for treatment is calculated with simulation code. Further, study the economic viability for treatment of wastewater containing EDCs using electron beam treatment system to confirm the potential of the attachment to the treatment plants.

2. Introduction

Many kind of water pollutants have been world-widely spread in the environmental water, which were persistent, high toxic and low biodegradability. Some of such chemicals mimic a natural hormone or disrupt endocrine system in livings to give ill effects, are so-called endocrine disrupting chemicals (EDCs) [1]. The endocrine disrupting properties of the EDCs were investigated by the cell proliferation bioassay in the 1990s [2-3]. Monitoring and screening tests of EDCs have been carried out from the latter half of the 1990s in Japan [4]. 17 β-estradiol (E2: 1,3,5(10)-estratriene-3,17 β-diol) is a natural chemical having the highest estrogen activity in water-environment and draws much attention as one of EDCs [3, 5-7]. *p*-Nonylphenols (NPs), 2,2-bis-(4-hydroxyphenyl)-propane and *tert*-octylphenol were definitely recognized as EDCs [4]. Treatment of these pollutants already released into water-environment has been attempted by the activated sludge system, and a result of this system is found to be insufficient to eliminate them. Advanced oxidation technologies (AOTs) such as ozolysis, ozone-UV system, ozone-hydrogen peroxide system, and photocatalytic processes have been actively studied to achieve complete elimination of persistent organic compounds [8-18]. However, the commercial plants were not applied these methods since the reactions of

oxidation species with these pollutants have not been clearly understood for real-scale treatment. Ionizing radiation method, one of the AOTs, succeeded to decompose effectively persistent organic pollutants such as dioxin, PCBs, EDCs, and so on [10, 19]. Moreover, the ionizing radiation method was already tried on a practical use stage of water treatment, and the pilot plant using electron beam combined with biodegradation process is operated at the papermill factory and the dye industrial complex [20-21]. The electron beam irradiation promotes the decrease in the amount of total organic carbon (TOC), biological oxygen demand and chemical oxygen demand (COD) of wastewater and results in realization of an efficient process.

Now, our research is in the stage to examine whether the ionizing radiation is applicable or not to the treatment of some organic pollutants in wastewater as the AOTs. In the previous CRP, hydroxyl radicals generated in water by ^{60}Co γ-rays are useful for the decomposition of trace amounts of EDCs [19, 22]. The E2 concentration initially at 1.8 nmol / L in water decreases lower than the detection level of LC-MS (< 0.1 nmol / L) at a dose of 10 Gy but "the estrogen activity" of the E2 solution is not eliminated up to 50 Gy, in other words the decomposition products from E2 has also "the estrogen activity". "The estrogen activity" of chemicals is the cross reactivity of chemicals with the estrogen receptor, and E2 is used as a standard sample of the bioassay because of its 100-% cross reactivity. NPs, which exhibit one of the highest estrogen activity among artificial chemicals, have about 0.1% of the cross reactivity with the estrogen receptor. NPs are also decomposed by radiation-induced hydroxyl radicals to produce two OH-adducts ascribed to *p*-nonylcatechol and 1-(*p*-hydroxyphenyl)-1-nonanol. We showed that irradiation products also have higher estrogen activity than NPs by use of the yeast two-hybrid assay. Estrogen activities of the NPs solution with an initial concentration of 20 μmol / L were also eliminated at 5000 Gy. In the present CRP report, treatments of real wastewater containing EDCs were studied in combination of the activated sludge and the ionizing radiation (FIG.1).
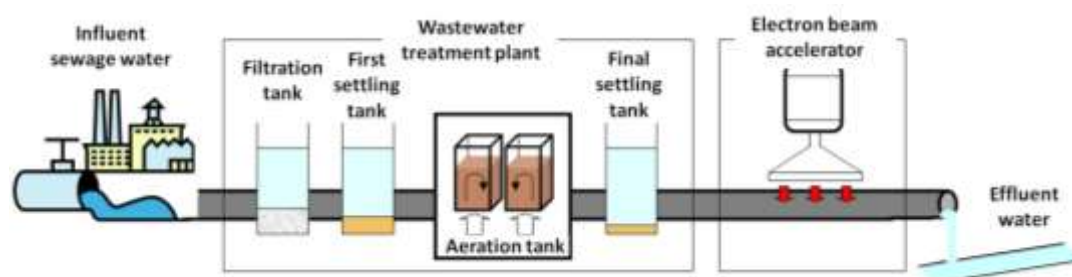

Fig. 1. Wastewater treatment in combination of activated sludge and ionizing radiation.

3. Materials and Methods

Real wastewater samples were obtained from the three different secondary effluents of water treatment plants with the activate sludge system. Each sample at 0.1/ L was used after filtration with a paper (Whatman) to remove dusts. A model wastewater, which has no estrogen activity, of pH value at 7.45 and the amount of TOC at 20.3 mg / L, was collected at an effluent of a water treatment facility. The γ-ray irradiations were carried out using ^{60}Co γ-ray sources at JAEA, Takasaki, to the doses in the range of 133 to 1000 Gy (Gy = J kg^{-1}) at dose rates ranging from 5 to 2,000 Gy h^{-1}. A HPLC (Agilent, 1100 series) with a reverse phase column (Shodex, RS pak DE-613) was used for analyses of E2 or NPs solutions as standards at 313 K before and after γ-ray irradiations. Mixture of pure water and methanol (for HPLC Analysis, Wako) were used as an eluent. Mass spectrometer (JEOL, LC-mate)

connected with the HPLC was used to determine the concentration of E2 before and after γ-ray irradiation. Amount of the total organic carbon (TOC) was measured by a TOC analyzer (Shimadzu, TOC-Vwp). pH value of the wastewater was determined using pH / DO meter (HORIBA, D-25).

The biological activity was evaluated by the yeast two hybrid assay and enzyme-linked immunoserbent assay (ELISA). The real wastewaters after γ-ray irradiation prepared at the pH value of about 3.5 by adding hydrochloric acid were extracted with solid phase column (Waters, Sep-Pak plus PS-2). The samples were eluted with acetone (for RP, PCB Anal., Kanto Chemical Co., Inc.). The eluents were evaporated to dryness with a gentle stream of nitrogen, and reconstituted by addition of dm^3 of borate buffer solution mixed boric acid (GR, Wako) with sodium hydroxide (GR, Kanto Chemical Co., Inc.) of the pH value of 9.0. The solutions were extracted 2 times with 3×10^{-3} dm^3 of ethylacetate (for RP, PCB Anal., Kanto Chemical Co., Inc.). The extracted solutions were purged with nitrogen gas, and were added to 6×10^{-6} dm^3 of dimethylsulfoxide (for Biochem., Wako) and 1.44×10^{-4} dm^3 of MSD medium. The estrogen activities of the solutions were measured by the yeast two-hybrid assay with human estrogen receptor (hERα) or medaka estrogen receptor (mERα). Detailed procedure of the assay was described elsewhere [23].

4. Results and discussion

4.1. Treatment of real wastewater containing EDCs by γ-ray irradiation

Evaluation of estrogen activity is significant for the treatment of the EDCs in wastewater because primary products of the EDCs by irradiation show estrogen activity [19, 22]. Three samples of the real wastewater before irradiation were analyzed by the yeast two-hybrid assay, ELISA, TOC and pH analyses as shown in Table 1. hEA and mEA are the estrogen activity evaluated using human estrogen receptor (hERα) and medaka estrogen receptor (mERα), respectively. Subtraction of estrogen activities (hEA) using hERα from estrogen activities (mEA) using mERα gives existence of the artificial EDCs in wastewater. ELISA with E2 antibody which selectively reacts with E2 was used to confirm the value of hEA. The hEA and the E2 equivalent concentration of sample 1 were 0.5 and 0.8 ng / L, which are lower than the mEA of 8.3 ng / L. Little estrogenic compound, therefore, is included in sample 1. The hEA of sample 2 was measured at 0.4 ng / L but the E2 equivalent concentration was higher (2.8 ng / L), considering that the hERα would be affected by antagonists to suppress the cross reaction. The mEA of 3.1 ng / L was higher than the hEA, and the estrogen activity of sample 2 comes from the artificial chemicals. Sample 3 has 5.1 ng / L of the hEA and 3.3 ng / L of the E2 equivalent concentration before irradiation, and the difference between hEA and E2 equivalent concentration derives from estrogen activities of estrogenic compounds except E2. The mEA which is considered to be the sum of estrogen activity of the estrogenic compounds and the artificial EDCs, was 11.3 ng / L. Estrogen activity of sample 3 partly comes from the estrogenic compounds.

TABLE 1. ESTROGEN ACTIVITY, 17 β-ESTRADIOL EQUIVALENT CONCENTRATION AND THE AMOUNT OF TOTAL ORGANIC CARBON IN WASTEWATERS

	Estrogen activity / ng dm^{-3}		E2 equivalent conc. / ng dm^{-3}	TOC / mg dm^{-3}
	hEA	mEA		
1	0.5	8.3	0.8	7.25
2	0.4	3.1	2.8	8.66
3	5.1	11.3	3.3	25.4

Treatment of the wastewater is required to decrease the estrogen activity to less than 1 ng / L, which is a lower limit concentration of appearance of endocrine disrupting property. Estrogen activities of the real wastewaters as a function of the dose of γ-ray irradiation are shown in FIG. 2. The doses for decrease in mEA of sample 1 to 3 below 1 ng / L, D_{1ng}, were estimated at 100, 200 and 150 Gy, respectively. The D_{1ng} of sample 2 were estimated by an extrapolation of the decomposition curves of mEA. Since the D_{1ng} of E2 at 1.8 nmol / L in pure water is estimated at 5 Gy in a previous work [19], elimination of estrogen activity of real wastewater is considered to be interfered by organic impurities. Every mEA initially increased and then decreased by the irradiation, indicating that decomposition products in the real wastewaters also have the estrogen activity.

The decomposition curves of a trace amount of E2 and NPs in pure water by γ-ray irradiation under air saturated conditions are in agreement with that under deoxygenated condition [19, 22]. Since concentration of the EDCs is very low, a trace amount of dissolved oxygen would enhance the oxidation of EDCs. The decomposition efficiency of EDCs by γ-ray irradiation is constant in the range of pH 2 to 8 [19], being enough to cover the standard pH values of the rivers in Japan (6.0 to 8.5). Effects of the pH and oxygen, therefore, would be negligible even with coexisting organics in this study.
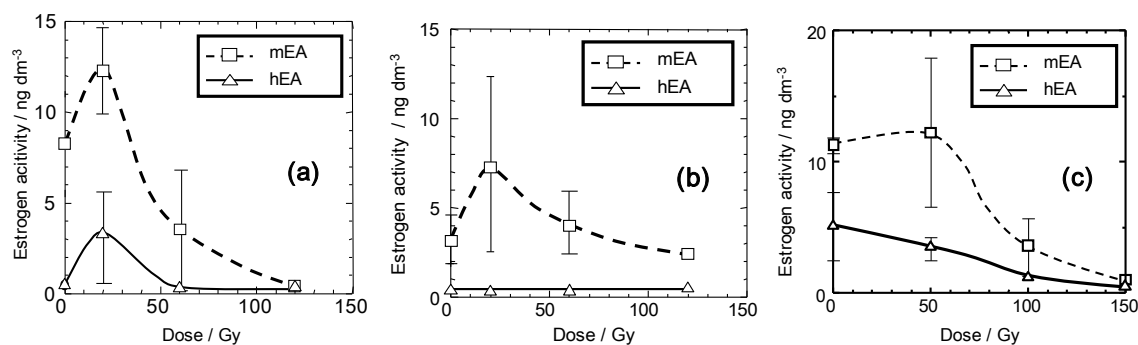

Fig. 2. Estrogen activities estimated using medaka estrogen receptor (mEA:□) and human estrogen receptor (hEA:△) for real wastewaters by γ-ray irradiation. (a):Sample 1 (b):Sample 2 (c): Sample 3.

4.2 Simulation of decrease in estrogen activity of real wastewater

The EDCs react with hydroxyl radicals within a short time span [19, 22]:

$$EDCs + OH \xrightarrow{k_1} Product\ 1a,\ Product\ 1b \tag{1}$$

Product 1a has estrogen activity and aromaticity, but Product 1b does not have and is counted in organic compounds.

$$Product\ 1a + OH \xrightarrow{k_2} Product\ 2\ (Secondary\ product) \tag{2}$$
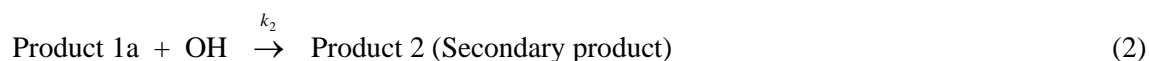
Product 2 is assumed to have no estrogen activity. Decomposition efficiency of EDCs by hydroxyl radicals would be inhibited by the organic compounds in wastewater. Organic compounds (OC) having no estrogen activity in wastewater also react with hydroxyl radicals:

$$OC + OH \xrightarrow{k_3} Unknown\ products \tag{3}$$

These reactions competitively occur and the rate of elimination of [EDCs] is given as follow,

$$-\frac{d[\text{EDCs}]}{dD} = \frac{G_{\text{OH}}}{100 \cdot 1.6 \times 10^{-19} \cdot N_a} \frac{k_1[\text{EDCs}]}{k_1[\text{EDCs}] + k_2[\text{Product1a}] + k_3[\text{OC}]} \qquad (4)$$

where D, G_{OH}, N_a are absorbed dose of the wastewater, G-value of hydroxyl radical and Avogadro's number, respectively. The k_1, k_2 and k_3 are considered to be about $10^7 \sim 10^{10}$ mol^{-1} dm^3 s^{-1}, and the concentration of OC is about 10^7 times higher than that of EDCs and Product 1a. Equation (4) is lead into:

$$-\frac{d[\text{EDCs}]}{dD} = \frac{G_{\text{OH}}}{100 \cdot 1.6 \times 10^{-19} \cdot N_a} \frac{k_1[\text{EDCs}]}{k_3[\text{OC}]} \qquad (5)$$

$$[\text{EDCs}] = [\text{EDCs}]_0 \exp\left(-\frac{A}{[\text{OC}]}D\right) \quad \because A = \frac{G_{\text{OH}}}{100 \cdot 1.6 \times 10^{-19} \cdot N_a} \frac{k_1}{k_3} \qquad (6)$$

Decrease in estrogen activities of the real wastewaters was simulated with equation (1) to (6). The estrogen activity of the real wastewater, EA, is defined:

$$EA = CR_1[\text{EDC}_1] + CR_2[\text{EDC}_2] + \cdots + CR_n[\text{EDC}_n] \qquad (7)$$

CR is the cross reactivity of the EDCs with the estrogen receptors. If the primary products have estrogen activity while the secondary ones do not have, the estrogen activity after irradiation will be presented as follows:

$$EA = CR_1[\text{EDC}_1] + CR_2[\text{Product 1a}] \qquad (8)$$

Formation of Product 1a is assumed to be equal with that of Product 1b. Formation and decomposition of Product 1a is represented by equation (5) as follows:

$$\frac{d[\text{Product 1a}]}{dD} = \frac{A}{[\text{OC}]}[\text{EDCs}_1] - \frac{A}{[\text{OC}]}\frac{k_2}{k_1}[\text{Product 1a}] \qquad (9)$$

Dose dependences of hEA and mEA of the real wastewater are calculated with equations (6), (8) and (9) by FACSIMILE for Windows (version 2.0104, AEA Technology plc) as shown in FIG. 3. The k_1 is set at 1.6×10^{10} mol^{-1} dm^3 s^{-1}, which is the rate constant of E2 or NPs with hydroxyl radicals evaluated by the competition reaction method with phenol in a previous work [19]. This value is the diffusion controlled limit of aromatic compounds with hydroxyl radicals [24-25]. We consider that Product 1a has the same rate constant, because Savel'eva et al., suggest the rate constant of aromatic compounds with hydroxyl radicals increases with OH-addition[26]. The CR_1 and CR_2 for mEA are determined to be 1.0×10^{-4} and 2.0×10^{-4} being constituent with the fact that the irradiation products from NPs would have higher estrogen activity than the NPs [22]. The CR_1 and CR_2 for hEA is set at 1 and 0.1 since estrogen activity of the irradiation products would be less than that of E2, which shows one of the highest estrogen activity in the chemicals. The values of A are used at 1.0×10^{-4} g / L Gy^{-1} and 2.5×10^{-4} g / L Gy^{-1} obtained by the decomposition of NPs and E2 in the model wastewater.

Simulation results of D_{1ng} for sample 1 to 3 were calculated to be 200, 120, and 200 Gy, which were aproximately agreement with experimental results. Sample 1 and 2 have low concentration of TOC and simulation curves of mEA for these samples have shoulder. While the mEA of sample 3 which have high TOC concentration decrease exponentially. Each hEA of samples describes the exponential function and the irradiation products from EDCs in

wastewarter contribute little increment in hEA. The amounts of TOC are significant for treatment of EDCs in wastewater by advanced oxidation technologies.
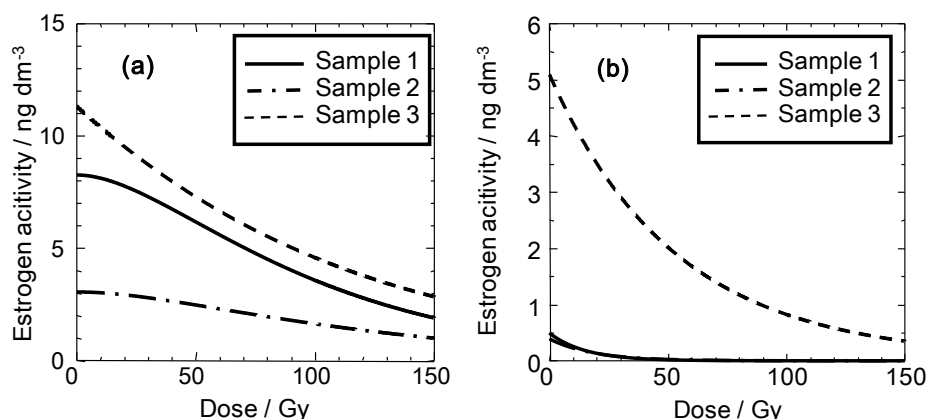

FIG. 3. Simulation of decrease in estrogen activity using medaka estrogen receptor (a) and human estrogen receptor (b).

4.3. Cost estimation for treatment of wastewater containing EDCs

Application of radiation to the treatment of EDCs in secondary effluent from sewage treatment plant is discussed on the basis of the results of the decomposition of EDCs in wastewater by γ-ray irradiation. The irradiation system is assumed to be the electron beam accelerator which is easy to establish and be integrated the existing wastewater treatment facilities. Electron beam is used to decrease chemical oxygen demand (COD) in the secondary effluent from the sewage treatment plant [27]. Electron beam accelerator (5 MeV, total beam power 300 kW) has been applied for the commercial plant of wastewater from a papermill [21]. Economical cost for decomposition of EDCs in wastewater by electron beam is evaluated on the basis of these pilot plant experiments. Consistency of dose evaluation by γ-ray and electron beam has been confirmed by Kojima et al [28], and the replacement of γ-ray to electron beam is suitable for the pilot plant experiment. Elimination of the estrogen activity of wastewater by electron beam is sufficiently accomplished at a dose of about 200 Gy. The treatment plant of electron beam for the recirculation of 10,000 m^3 day^{-1} requires electron beam accelerator at a total power of 280 kW (5 MeV, 56 mA) [27]. The irradiation is carried out under continuous flow condition, and the wastewater is supplied with the jet nozzle as a thin layer. The initial investment is set at about 600 million yen (15 yen m^{-3}), which is the sum of the cost of the electron beam accelerator having the endurance life of 15 years and the personnel costs. The consumption of the electric power for an operation of the electron beam accelerator is estimated to be 2 yen m^{-3}, and the total running cost for the plant is estimated to be 17 yen m^{-3} in Japan. For example, the charges of the treatment plants in Gunma, Japan were set in the range of 30 to 140 yen m^{-3}, the electron beam treatment system is considered to have the potentiality of the attachment to the treatment plants.

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TREATMENT OF WASTEWATER FOR REUSE WITH MOBILE ELECTRON BEAM PLANT

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Abstract

The use of alternative disinfectants to chlorine for the wastewater treatment has received increasing attention in recent years to treat either liquid or solids streams within wastewater treatment plants for pathogens and trace organics (TOrCs). Although several technologies have come to the forefront as an alternative to chlorine (e.g., ultraviolet [UV] and hydrogen peroxide), the majority of these technologies are chemically based, with the exception of UV. An attractive physical disinfection approach is by electron beam (EB) irradiation. EB treatment of wastewater leads to their purification from various pollutants. It is caused by the decomposition of pollutants as a result of their reactions with highly reactive species formed from water radiolysis: hydrated electron, OH free radical and H atom [Pikaev (1986)]. Sometimes methods such as EB with biological treatment, adsorption and others improve the effect of EB treatment of the wastewater purification. In the process of EB treatment of wastewater there are utilized chemical transformations of pollutants induced by ionizing radiation. At sufficiently high absorbed doses these transformations can result in complete decomposition (removal) of the substance. Under real conditions, i.e., at rather high content of pollutants in a wastewater and economically acceptable doses, partial decomposition of pollutant takes place as well as transformations of pollutant molecules that result in improving subsequent purification stages, efficiency of the process being notably influenced by irradiation conditions and wastewater composition [Woods and Pikaev (1994)].

1. Introduction

One of the important environmental problems is the reuse of wastewater to industrial and agricultural applications. on-site pilot scale treatment of wastewater from municipal plant will be applied to optimize the operation parameters by a skid mounted Mobile Electron Beam Plant (MEB) mounted in a 40' box metal cargo shipping container.To compare EB technology with other advanced oxidation processes (AOP) such as UV and Ozone technology, in regard to costs and effects for different application cases and local situations.The objectives of this study are optimization of the EB process for minimizing energy loss and absorbed dose upon the water thickness optimization of pre-treatment and post-treatment design parameters and development of design criteria to construct commercial scale re-use plant. Also the evaluation of alternatives to address unforeseen problems resulting from the actual use of proposed treatment processes and characterization and quantification of the raw water and finished water will be conducted.

2. Objective of the research

The treatment of industrial wastewater with EB is one of the actively studied subjects for the environmental application in Korea. The use of alternative disinfectants to chlorine for the liquid stream has garnered increasing attention in recent years. Besides the production of disinfection by-products (DBPs), chlorine poses safety hazards for operational staff and shipping hazards. In addition to health and public welfare risks, chlorine has a minimal

attenuation on TOrCs. Although several technologies have come to the forefront as an alternative to chlorine (e.g., ultraviolet [UV] and hydrogen peroxide), the majority of these technologies are chemically based, with the exception of UV. An attractive physical disinfection approach is by EB irradiation.

One of the important environmental problems is the reuse of wastewater to industrial and agricultural applications. The objective of this research evaluates the efficiency of electron-beam disinfection to treat either liquid or solids streams within wastewater treatment plants for pathogens and trace organics (TOrCs). TOrCs refer to endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and other trace constituents. The rationale behind targeting both streams relates to the notion that EB lends itself toward either medium. In this proposal, on-site pilot scale treatment of wastewater from municipal plant will be applied to optimize the operation parameters by a skid mounted Mobile Electron Beam Plant (MEB) mounted in a 40' box metal cargo shipping container.

3. Previous works

When wastewater is irradiated with high energy electron, the energy absorbed is deposited in water molecules, and the ionization and excitation of water molecules result in formation of free radical and molecular species. The use of such free radicals as disinfectant for effluents from municipal wastewater treatment plants could be state-of-the-art and eco-friendly disinfection processes. EB has the following advantages over chemically based and UV approaches: operates at ambient temperatures and pressure; requires no additional chemicals that could further pollute downstream; has the capacity to mineralize persistent compounds; and its performance is not affected by solids since the EB easily penetrate particles/solids.

The treatment of industrial wastewater with EB is one of the actively studied subjects for the environmental application in EB TECH Co., Ltd (EB TECH). The wastewaters investigated are from textile dyeing companies, petrochemical processes, papermill, leachates from sanitary landfill areas, explosive productions and so on. Those are summarized in Table 1.

TABLE 1 WASTEWATER INVESTIGATED AT EB TECH CO., LTD

Wastewater(from)	Purpose of investigation	Results
Textile dyeing companies[a]	Removal of color and organic impurities	Industrial plant constructed Improved removal efficiency
Papermill[b]	Decrease in COD, color Increase in re-use rate	Reduction in COD, color Commercial plant designed
Leachate from landfill[c]	Removal of organic pollutants	Bio-treatment efficiency improved
Heavy metals[d]	Decrease in the contents in water	Removal of Cd(II), Pb(II), Hg(II), Cr(VI)
Power plant clean-up[e]	Decrease in the contents of organic acid in water	Decrease in the contents of organic pollutants
Explosive production[f]	Decrease in COD, T-N Re-use for production	

a Han et al. (2002, 2005)
b Shin et al. (2002)
c Pikaev et al. (1997a)
d Kartasheva et al. (1997, 1998), Pikaev et al. (1997b), Ponomarev et al. (1997), Yurik and Pikaev (1997)
e Kim et al. (1999)
f unpublished results

4. Materials and Methods

To confirm the use of EB as an alternative disinfectant to chlorine for the liquid stream, a bench scale experiments were conducted in EB TECH with samples from the Municipal Wastewater Treantment Plant in Daejeon City which has the capacity of 900,000m^3/day equipped with the conventional physical and biological treatment system. This plant has been in operation, but to face the control of TOrCs. Typical operation data of influent and effluent of this plant is in Table 2.

TABLE 2 WASTEWATER IN MUNICIPAL WASTEWATER TREATMENT IN DAEJEON CITY

	BOD (mg/l)	COD (mg/l)	SS (mg/l)	T-N (mg/l)	T-P (mg/l)	E-coli [a] (#/ml)
Influent (avg.)	15.1	127.4	201.8	34.2	4.5	N/A
Regulation	<20	<40	<20	<60	<8	<3,000
Designed	<14	<14	<15	<25	<1.5	<1.5
Actual	8.9	11.2	7.2	16.2	4.3	28,000

(a) effective from 2003 in Korea

In this experiments, electron accelerator of 1 MeV, 40kW with the dose rate of 40kGy/s is used with the laboratory unit, schematically shown in FIG. 1, was constructed for irradiation under continuous flow conditions. The initial samples are placed in storage vessel, which serves as an equalizing basin. Wastewater from the vessel is delivered to injection nozzle by pump. Thickness of injected was equal to 4 mm; it is equal to the range of 1 MeV electrons in water. The rate of wastewater moving at the exit of the nozzle was controlled within the range of 2-4 m/s. The wastewater injected along horizontal part of their flight was treated by EB, then irradiated wastewater was collected into the special container. The experiments were conducted with the doses up to 1kGy at atmospheric temperature (20~25℃).

The number of microorganisms decreases 10^2 times with 0.2 ~ 0.5 kGy and 10^4 times with 1kGy without any changes in other water quality indices. From the obtained results, it is clear that 0.2 ~ 0.5 kGy is enough to control the number of E-coli below 1,000CFU/ml. It is observed at low doses (below 0.2kGy), most of the microorganisms have decreased, but there still exist a large amount of microorganisms, however the numbers are not increased after the irradiation since they were inactivated.
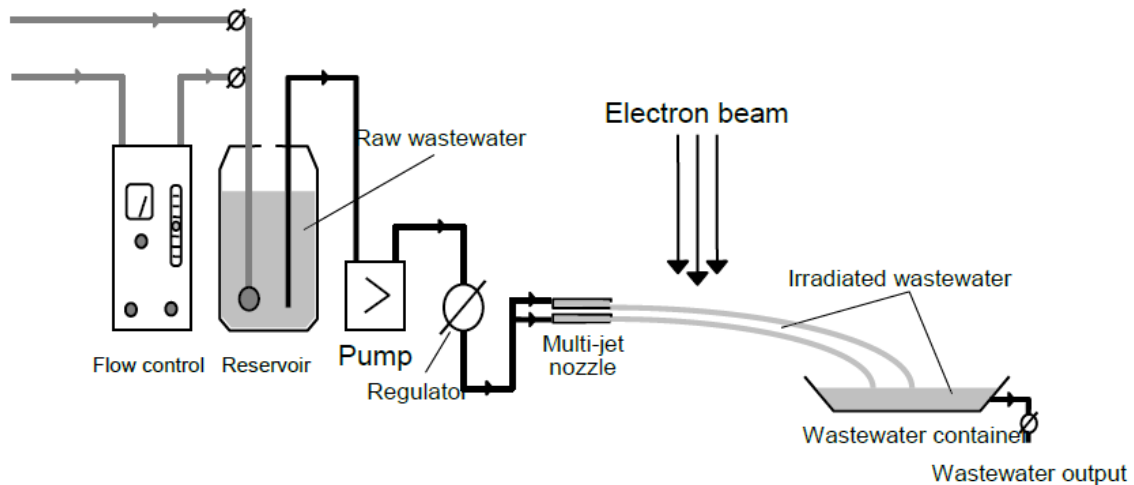
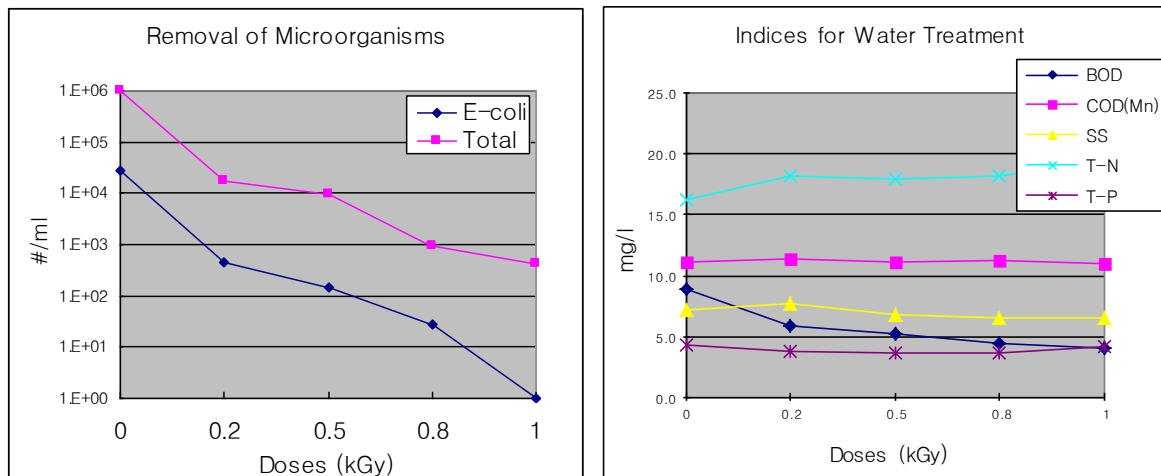Fig. 1. Laboratory electron beam unit; 50m3/day up to 2kGy at continuous operation mode.

FIG. 2. Removal of indicator microorganisms and variation of other indices with doses up to 1kGy.

4.1. Mobile Electron Beam Plant (MEB)

On-site pilot scale treatment of wastewater from municipal plant will be applied to optimize the operation parameters by a skid mounted Mobile Electron Beam Plant (MEB) mounted in a 40' box metal cargo shipping container as shown in below figure.

with water/air cooling system are the main constituents of the plant. Also the wastewater treatment facilities (pumps, gauges, reservoirs etc.) are included. This plant can treat up to 500m^3/day with 2kGy at continuous operation mode.
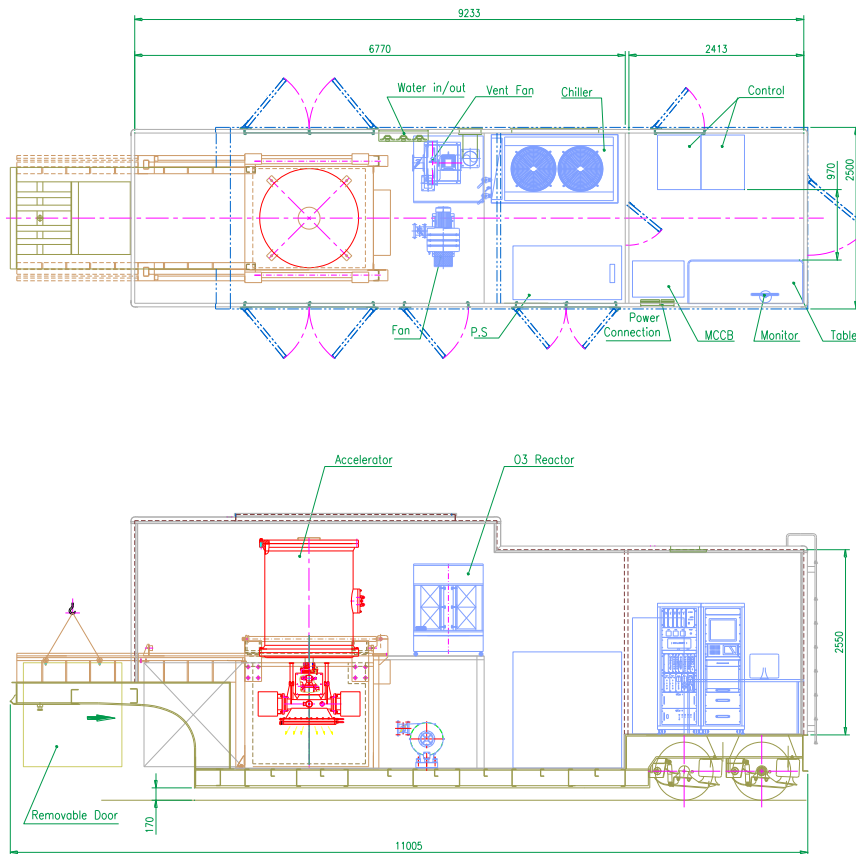
Fig. 3. Mobile Electron Beam Plant (MEB); 500m3/day with 2kGy at continuous operation mode.

This Mobile Electron Beam Plant (MEB) has proved its on-site daptability as operating for a pilot scale demo plant for flue gas treatment from power plant in Jeddah, Saudi Arabia.

Fig. 4. Mobile Electron Beam Plant (MEB) in flue gas treatment in Jeddah, Saudi Arabia.

4.2. Analytical Aproaches

The approach addresses the fate of not just conventional indicator organisms (*E. coli*, *Enterococcus*, coliforms, and total coliforms), but also provides a framework to track and monitor the fate of alternate indicator organisms like the *Bacteroidales*, which are anaerobic and hence decay faster in ambient waters. Unlike traditional indicators, because they are host-

associated, a given *Bacteroidales* genetic marker can be used in the differentiation between human and nonhuman pollution and in the identification of specific animal sources – important information for source control and treatment programs. Both *Enterococcous* and *Bacteroidales* are currently being considered by U.S. EPA in their epidemiological studies to update existing ambient water quality criteria using quantitative PCR (qPCR) methodology.

For technologies entering the market place, it is crucial to have results for the inactivation of both conventional and alternate indicators since alternate indicators are beginning to enter the permitting arena. Although not currently permitted, TOrC removal is gaining momentum as a concern for many municipalities. Our approach investigates the efficacy of e-beam technology to remove TOrCs at doses used for indicators removal, as well as at environmentally relevant TOrC levels.

As describe above, with the on-site operation of mobile electron beam plant, the basic parameters to implement commercial scale disinfection plant for municipal wastewater treatment plant could be achieved. And the optimization of pre-treatment and post-treatment design parameters and evaluation of alternatives to address unforeseen problems resulting from the actual use of proposed treatment processes could be also expected.

4.3. On-site operation of mobile electron beam plant

The mobile plant will be operated continuously to obtain parameters for collecting data with various conditions to secure consistency and reliability of EB process despite fluctuating external environmental variables like day versus night operation, weather and seasonality. Evaluation of obtained data for optimization of the EB process for municipal treatment and alsd the evaluation of energy loss and absorbed dose upon the water thickness will be conducted to optimize the pre-treatment and post-treatment design parameter. In order to develop the design criteria to construct commercial scale re-use plant, evaluation of alternatives to address unforeseen problems resulting from the actual use of proposed treatment processes will also be conducted.

5. Anticipated Results

Anticipated outcomes are:

1. Guidelines of design parameters for constructing commercial scale re-use plant.

2. Achievement of the necessary data to claim the disinfection standards (for example in U.S. as stipulated by California Department of Health Services' Title 22')

3. Effectiveness of EB processing, i.e., consistency and reliability despite fluctuating external environmental variables like day versus night operation, weather and seasonality

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A DEMONSTRATION STUDY ON DECOMPOSITION OF ANNTIBIOTICS AND ENDOCRINE DISRUPTERS CONTAINED IN SEWAGE EFFLUENT BY MOBILE ELECTRON BEAM ACCELERATOR

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Abstract

This report described a work plan on advanced sewage treatments focusing on reduction of antibiotics and endocrine disruptors and sterilization by radiation in Korea. It included a demonstration study on decomposition of antibiotics and endocrine disruptor contained in sewage effluent by MEB(Mobile Electron Beam accelerator). According to the KAERI's national research plan, basic radiation application working on sterilization, decomposition of antibiotics and endocrine disruptor contained in effluent by using radiation were conducted in KAERI's laboratory for three years. In 2011, a field study on advanced sewage treatment with a MEB was conducted and the results obtained from study played an important role in the acquiring a certification on advanced treatment of sewage effluent by radiation, NET(New Environmental Technology), which is issued by Korea ministry of environment. 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. In a future, achievements from the field demonstration study will be transferred to industry. Research on by-products from irradiated antibiotics and toxicity before and after irradiation of antibiotics will be continued in the field with MEB. This information will be useful for the project by radiation treatment of wastewater for reuse, particularly focused on the wastewater containing organic pollutants.

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 nonbiodegrable chemicals into water streams. Therefore, it is very important to control the toxic and nonbiodegrable chemicals before those are discharged to water stream. Limited technologies, such as AOPs(Advanced Oxidation Processes), for the control of these toxic and nonbiodegrable chemicals have been applied into the wastewater treatment plants. However, the control efficiencies of existent technologies are not high enough.

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 study for demonstration of new technology is very important for securing both confidence of the technology and public acceptance on radiation.

The irradiation studies conducted for the decomposition of toxic chemicals and evaluation of toxicity reduction must be helpful for the studies on conservation of water quality and provision of water resources. The field demonstration research is also surely more helpful for the commercial approach in a view of completion of its technological development.

This report introduces several research results carried out with MEB in a Korea sewage treatment plant.

2. Working Program in KAERI

KAERI set a national plan for the development of the advanced sewage treatment using radiation in 2007. During the first three years, basic research on sterilization, decomposition of antibiotics and endocrine disruptors contained in sewage effluent by using radiation were conducted in KAERI's laboratory. In 2007, other basic studies, such as analysis of chemicals in each unit process of sewage treatment, analysis of pathogenic microbes in effluent and sterilization by electron beam and gamma rays were also conducted. In 2008, a study on radiation treatment of organic toxic chemicals and evaluation of eco toxicity were carried out together researches on mineralization of antibiotics and trace amount of organic toxic chemicals by radiation and evaluation of eco safety for irradiated effluent by toxicity evaluation. In 2009, studies on mineralization of endocrine disruptor and evaluation of genetic safety by radiation treatment were conducted. A mobile electron beam accelerator with 0.6 MeV of energy and 20 kW of output power was constructed for the field study and demonstration of radiation application for environmental conservation in that year. In 2010, a field study on treatment of chemicals and sterilization in effluent with MEB was carried out for feasibility test on treatment of organic toxic chemicals and sterilization in effluent, and for comparing the eco safety before and after MEB treatment. NET titled as "electron beam treatment for advanced sewage treatment", which is issued by Korea ministry of environment was acquired using the field demonstration with MEB. In 2011, NET was verified in the field.
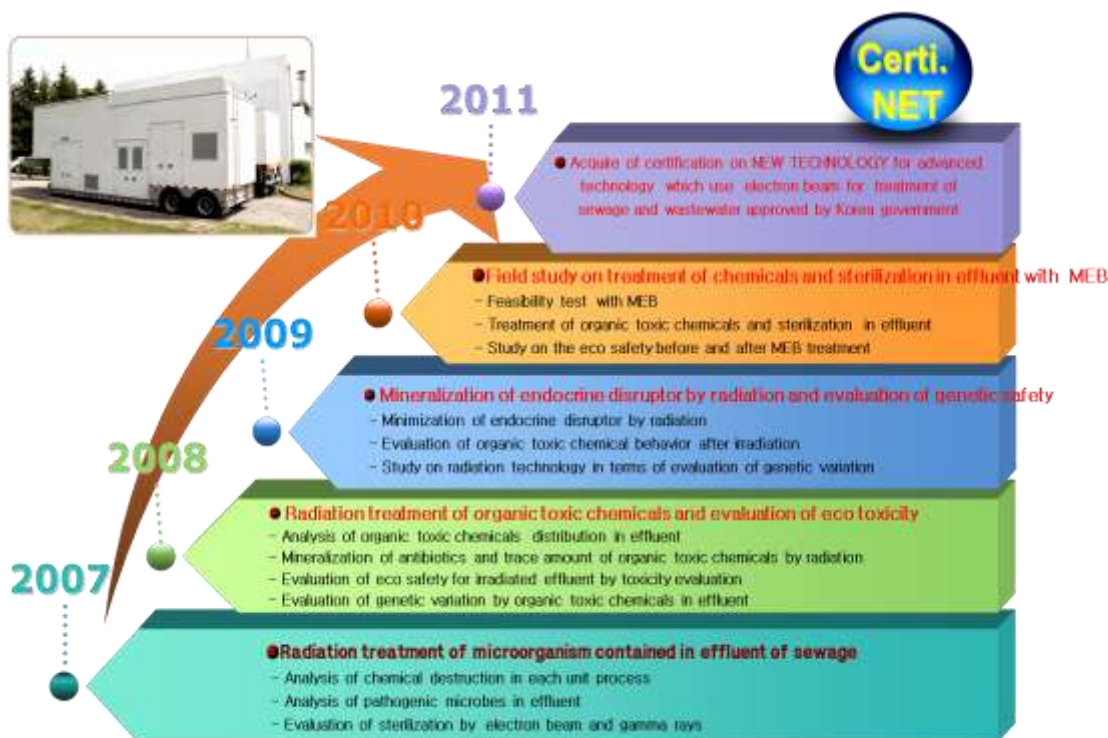

Fig.1. Current research program related to advanced sewage treatment with radiation in KAERI.

3. Preparation of Field Demonstration

3.1. Installation of MEB

MEB was installed at 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 mucipal 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 2 shows the view of MEB installed in sewage treatment plant.

Fig.2. View of MEB installed in sewage treatment plant

3.2. Sample Preparation

In order to study on 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 their concentration after mixing was adjusted to 0.5 mg/l, respectively.

3.3. Irradiation

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. Figure 3 shows the view of irradiation in MEB. Samples were obtained before and after irradiation

Fig.3. View of irradiation of effluent

3.4. Analysis

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.

4. Result and Discussion

4.1. Characteristics of the effluent

Table 1 shows the characteristics of effluent. Average temperature was 18.5℃ and SS(Suspended Solid) was 2.5 mg/l. This means that nothing affects irradiation of effluent. Antibiotics and endocrine disruptors such as lincomycin, Tetracycline and bisphenol-A were not detected because of very low concentration of those. Coli form was 2.2×10^4 CFU/ml and microorganisms were 7.8×10^4/ml. However, these values were changeable. These results are thought to result from mixing with sewage and live stock wastewater together. Higher concentrations of microorganisms and coli form were observed during mixing with both, while lower concentration of these one were observed without the mixing.

TABLE.1. CHARACTERISTICS OF THE EFFLUENT

(unit : mg/L)

Items	Max.	Min.	Average
Temp.(℃)	11.7	25.7	18.5
pH	6.2	7.7	7.0
DO	3.4	11.4	6.2
BOD$_5$	1.5	10.5	4.2
COD$_{Mn}$	7.5	26.1	11.6
COD$_{Cr}$	13.0	26.5	18.9
SS	0.9	5.0	2.5
T-N	9.0	13.5	11.5
T-P	0.2	1.4	0.8
TOC	6.8	13.7	10.0
Coli form(CFU/mL)	13.0	3.4×10^5	2.2×10^4
microorganism(CFU/mL)	8.0×10^2	5.7×10^5	7.8×10^4

4.2. Operating Condition of MEB

Table 2 and figure 4 show the operational conditions of MEB. MEB was operated with 0.6 MeV and 20.6 mA. Their conditions were not changed during the whole experimental periods.

TABLE 2. OPERATING CONDITIONS OF MEB

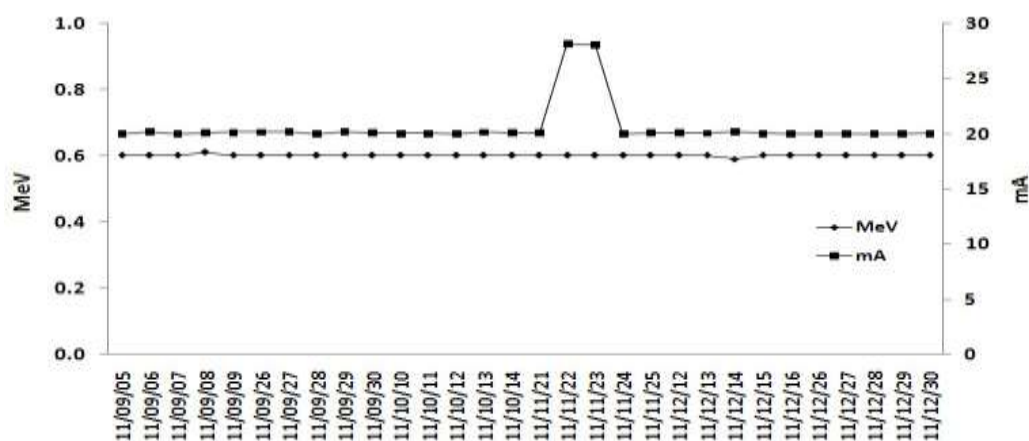| Item	Power of MEB		
	Min.	Max.	Average
Energy (MeV)	0.6	0.6	0.6
Beam current (mA)	20.0	28.1	20.6

Fig.4. Output power of MEB.

4.3. Removal of organic matters, suspended solids and nutrients by MEB

Table 3 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 3. 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

4.4. Removal of Antibiotics and Endocrine Disruptors

Table 4 shows removal of lincomysin before and after irradiation by MEB. Initial concentration of lincomysin with 0.468 mg/l was reduced to 0.001 mg/l at the irradiation condition of 1.5 kGy. It's removal efficiency was 99.8 %. It means that lincomysin can be decomposed at a low value of irradiation dose.

TABLE 4. REMOVAL OF LINCOMYSIN BY MEB

【max~min (average)】

Item	lincomycin (mg/L)		Removal efficient (%)
	Before irradiation	After irradiation	
Concentration(mg/l)	0.468(0.329~0.586)	0.001(0.0~0.005)	99.8(99.0~100.0)

Table 5 shows removal of tetracycline before and after irradiation by MEB. Initial concentration of tetracycline with 0.464 mg/l was reduced to 0.005 mg/l at the irradiation condition of 1.5 kGy. It's removal efficiency was 99.8 %. It means that tetracycline can be decomposed at a low irradiation dose.

TABLE 5. REMOVAL OF TETRACYCLINE BY MEB

【max~min (average)】

Item	Tetracycline (mg/L)		Removal efficient (%)
	Before irradiation	After irradiation	
Concentration(mg/l)	0.464(0.332~0.665)	0.005(0.000~0.008)	98.8(97.9~100.0)

Table 6 shows removal of bisphenol-A before and after irradiation by MEB, which is known as one of endocrine disruptors. Initial concentration of bisphenol-A with 0.437 mg/l was reduced to 0.004 mg/l at the irradiation condition of 1.5 kGy. It's removal efficiency was 99.1 %. It means that bisphenol-A can be decomposed at a low irradiation dose.

TABLE 6. REMOVAL OF BISPHENOL-A BY MEB

【max~min (average)】

Item	Bisphenol-A (mg/L)		Removal efficient (%)
	Before irradiation	After irradiation	
Concentration(mg/l)	0.437(0.410~0.454)	0.004(0.000~0.007)	99.1(98.3~100.0)

4.5. Sterilization of Coli Form and Microorganisms

Table 7 shows sterilization of coli form before and after irradiation by MEB. Maximum concentration of coli form was 3.4×10^5 CFU/ml while minimum was 13 CFU/ml. These results come from mixing with sewage and live stock wastewater together in the sewage treatment plant. No coli form was not 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 7. 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 8 shows sterilization of microorganisms before and after irradiation by MEB. Average value of microorganisms was 7.8×10^4 CFU/ml. These microorganisms reduced to 1.1×10^2 CFU/ml . This means that sterilization of microorganisms is also well conducted with less than 1.5 kGy of irradiation dose.

TABLE 8. REMOVAL OF MICROORGANISMS BY MEB

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)

4.6. Reduction of toxicity

Table 9 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 the irradiation of 1.5 kGy. Figure 5 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 9. REDUCTION OF TOXICITY

	Before irradiation	After irradiation
Toxicity (TU)	15.0	1.8

Fig.5. Algae growth with and without irradiation (left: with irradiation, right: without irradiation).

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 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 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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RADIATION TREATMENT FOR RECYCLING OF INDUSTRIAL WASTEWATER FOR INDUSTRIAL USAGE - BIOLOGICAL AND IRRADIATION TREATMENT OF MIX INDUSTRIAL WASTEWATER IN FLOOD MITIGATION POND AT PRAI INDUSTRIAL ZONES

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Abstract

In this researched, activated sludge system and E-Beam was used to treat mixed industrial waste water from mitigation pond A. The objectives are to study the effect of hydraulic retention time (HRT) in activated sludge and effect of absorbed dose, current and energy to the characteristic of mix industrial wastewater and Di(2-ethylhexyl) phthalate(DEHP) added in the wastewater . DEPH is a type of plasticizer and quantified by GC-MS. Microbe identification in activated sludge was also carried out in this study. At 48hrs HRT, percentage reduction for COD, color, suspended solid were 62.3%, 36.7% and 67.1% respectively. While at 24hrs HRT, COD, color and suspended solid were reduce by 26.0%, 14.9% and 61.3% respectively. Microbial analysis showed six bacteria present in the activated sludge based on 16SrRNA gene sequences. Mixed industrial wastewater was irradiated using electron beam at 1Mev, 5mA and 10mA in a batch system with 3, 6, 8,10 and 12kGy doses. COD, color and suspended solid reduced with the increasing of absorbed dose. Mixed industrial wastewater added with DEPH in the second batch was irradiated with dose up to 300kGy. Concentration of DEHP also reduced with increasing of dose and more effectively decreased in acidic and aerated condition.

1. Introduction

Mixed industrial wastewater in holding pond pumping station A in Seberang Perai was derived from the treated effluent from various industries in the vicinity. The main industries that release their treated effluent into the holding pond are textiles, plastic, chemical/fertilizer and oleochemical. It can contain up to 1,500 m^3 per day. The holding pond A is a flood mitigation step in the industrial area and as an immediate receiving water body prior to the release of the effluent into the sea. Effluent in the pond A was not treated with any treatment and the characteristic of wastewater differs from every time. In this study, sample was collected in September and December 2011 and also in January and April 2012. Another sample collected in July 2012 was treated with activated sludge only.

A lot of research activities on radiation application for wastewater treatment has been done especially in textiles industrial wastewater (B.Han et al.,2002; Kim et al., 2007). Gamma radiation for sewage treatment was also studied by (J.G.Graino, 2001;M.R.Shah et al.,2001). In this study, electron beam radiation was applied for treatment of mixed effluent industrial wastewater. Wastewater was irradiated with the same irradiation conditions(3,6,8and 12kGy) in previous study conducted in 2011. By doing this, effect of radiation on the characteristic of wastewater for the rest of the year can be identified. Additionally, wastewater was spiked with DEPH in different batch and irradiated with the same irradiation conditions. The purpose is to study the effect of e-beam irradiation on DEHP concentration. Di(2-ethylhexyl)

phthalate(DEPH) is widely used as a plasticizer in flexible vinyl products. Plastics may contain from 1 to 40% DEPH by weight and are used in consumer products such as rainwear, footwear, flooring wire and cable food packaging material and children's toys. DEHP was expected to have leached into Pond A because there are companies producing the above mentioned products nearby.

Mixed industrial wastewater was also treated using activated sludge system. This system consists of three basic components which are;

1. reactor in which the microorganisms responsible for treatment are kept suspended and aerated;
2. solid liquid separation, clarifier tank; and
3. a recycle system for returning sludge from clarifier back to the reactor.

Flow rate of the influent into the reactor was varied to obtain different hydraulic retention time. Identification of microbe present in the reactor was done by private laboratory.

2. Materials and Method

2.1. Sample preparation

Mixed industrial wastewater was collected from the centre pump house A, as shown in fig.1. Mixed industrial wastewater was screened to segregate solid material such as sand, rubbish and grass prior to the treatment. Samples pH was adjusted to pH 6.5 to pH 8.5 prior to biological treatment. The pH for samples treated with radiation will not be changed.

2.2. Radiation Treatment

In order to irradiate, the samples were filled in a tray and placed on a trolley and transported into the irradiation chamber. Irradiation of samples was conducted using EPS3000 EB machine in a batch system. The first batch consists of mixed industrial wastewater only and second batch consists DEPH in mixed industrial wastewater. Speed of conveyor and beam current (mA) were adjusted according to irradiation dose required. The irradiation doses selected for this study were 3kGy, 6kGy, 8kGy and 12kGy for the first batch while doses were increased to 50kGy, 100kGy, 150kGy, 200kGy and 300kGy for the second batch. The current used for dose 3kGy was 5mA and current used for 6-12kGy was 10mA whereas 30mA current was used for dose 50-300kGy. The variations in current were to ensure compatibility of the conveyor speed with irradiation dose acquired.

2.2.1. Extraction of DEPH

The procedure in this method involves the use of separating funnel (1000ml). n-Hexane (purity 97%) purchased from Merck Chemicals was used for extracting DEHP from water samples. 1:4 ratio was used for water sample and hexane for extraction. After mixing, the funnel was gently turned from vertical to a horizontal position and shaken vigorously. The stopcock was opened and closed quickly to release the pressure built up from solvent vapor. This process was repeated until no further vapor is released when the stopcock is opened. The funnel was placed in the holder (ring on ring stand) and left overnight to allow the liquids to stand until the layers were completely separated. The lower layer was drawn out followed by upper layer into two beakers. The upper layer which consists of hexane and DEHP was filtered to remove the dirt from the water samples. A small amount of sodium sulphite, anhydrous (Na_2SO_3) was placed on the filter paper to absorb any element of water that might

be present in the extracted solvent. Water is capable of destroying the GC-MS column. The filtered solvent was dried in a fume chamber to obtain DEPH.

2.2.2. GC-MS Analysis

DEHP was analyzed using Finnigian Trace GC Ultra with flame ionization detector (GC/FID) equipped with auto-sampler, an on-column, splitless capillary injection system with Finnigian Trace GC Ultra capillary column (30m x 0.25mm x 0.25μm film thickness). The operating condition is as follows:

— the column was maintained at a temperature of 50^0C for 1.5 min
— the temperature was increased to 270^0C with an incremental rate of 20^0C /min.
— the temperatures of the injector and detector were maintained at 260^0C and 280^0C respectively.
— Helium was used as a carrier gas at a flow rate of 1.0 mL/min
— and the injection of sample was 2.0μL.

2.2.3. MS Condition

1. Ion Source Temperature: 200^0C
2. Interface Temperature: 300^0C
3. Start m/z: 5.00
4. End m/z: 30.00

2.3. Biological Treatment

The Lab scale activated sludge system was made with acryl. It consisted of equalization tank(10L), aeration tank(4L) and clarifier(4L). Wastewater was fed into aeration tank and transferred into clarifier with a peristaltic pump. The water was aerated with diffusers that were connected to small aquarium pump to maintain dissolved oxygen (DO) concentration above 4mg/l in the aeration tank. The dissolved oxygen was monitored daily by a DO meter in the aeration tank. Parameters such as pH, and mix liquor suspended solid were controlled in this system to ensure that the system worked. The process run continuously in order to determine steady state condition.

2.3.1. Microbe identification

One ml sample was taken from reactor tank and diluted with sterile distilled water. Tryptonesoyar agar (TSA) acts as medium for the growth of the microbes. Then, a loop was used to transfer small amount of sample onto the petri dish containing TSA medium. The petri dishes were placed in the incubator at temperature of 30°C. The plates were incubated about half a day. Isolation of single colony was done using the same technique and repeated until single colony appeared. Petri dishes containing single colony were sent to other lab for microbial analysis and identification using 16S rRNA Gene Sequences.

2.4. Analysis

Samples were analysed before and after irradiation. COD is equivalent to the amount of oxygen required to chemically oxidize the organic matter contained in wastewater. To determine the COD, sample was first digested using dichromate (HR range plus) in Hach reactor and COD value was determine by Hach-2400 spectrophotometer. pH of the sample

was analyzed using pH meter (WTW Multi 340i). Hach DR 5000 spectrophotometer was used for color measurement. Turbidity was measured by turbidity meter and suspended solid was analyzed according to APHA method.

Fig 1. Inlet of a Pump A house.

4. Result and discussion

4.1. Mixed-industrial Wastewater Characteristics in the Holding Pond Pumping Station A

The results indicated that the nature of the water changed every month as expected. These changes depended on the activities surrounding the plant and climatic factors such as rain and sunshine. Table 1 shows the compliance or non compliance to Malaysia Standard Environment Quality Act (Industrial Effluent) Regulation 2009. The pH for all the samples complied to the Act (pH5.5-pH9.0). Whereas only samples taken in September 2011 complied to the COD standard value of 100mg/l. Table.1, also shows significant difference between the values of COD and BOD_5. It seemed that the wastewater may contain substances that are quite difficult to treat such as chemicals. Properties of wastewater in Dec. were higher as compared to other months and this is normal scenario during rainy season, where industries discharged untreated effluent into drain and flow into the Pond A. From the overall result, it shows that there is a need to lower the COD value to comply with the set standard.

TABLE 1: WASTEWATER CHARACTERISTICS IN THE HOLDING POND PUMPING STATION A.

Parameters	Sept.11	Dec.11	Jan.12	Apr.12
pH	6.48	8.05	7.22	6.98
COD(mg/l)	45	135	124	106
BOD(mg/l)	-	6	12	11
Suspended solid(mg/l)	37	237	55	46
Color (ADMI)	14	74	19	77
Turbidity (NTU)	7.8	25.3	4.8	26.2

4.2. Effect of radiation on characteristics of effluent (holding pond pumping station A)

4.2.1 Effect of irradiation on COD

Figure 1,2 and 3, show the COD, suspended solid and color were higher in sample collected in December as compared to other months. December is rainy reason, and this result showed similar trend to the study conducted by (Norli 2003) due to the wash out from all over factories flowing into the holding pond. Other reason was that all substance raised from the bottom of the pond caused turbulence during rain and illegal discharged of untreated wastewater from premises.
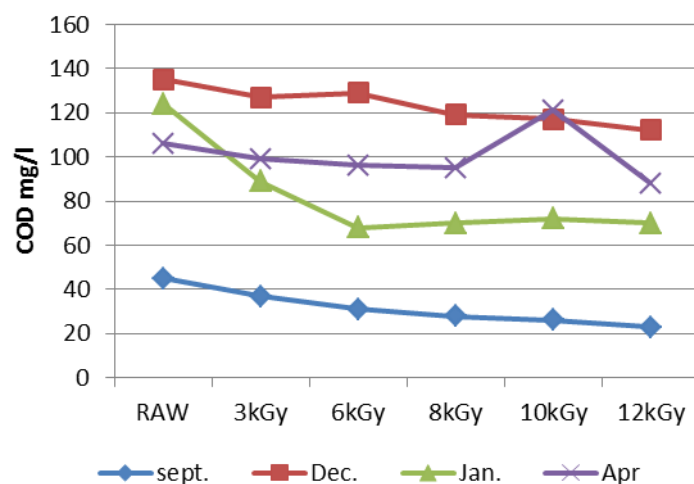
Fig.2. Effect of radiation on COD sample in specific months.

In general, the value of COD decreased when dose is increased for samples collected at different months (Fig.1). This is due to the degradation of organic pollutant with active radical produced in the water during irradiation. The average reduction in COD is 35.6% for sample in September, 10.5% for December, 40.5% in January and 43.4% for sample in April, as the samples were exposed to the doses between 3kGy to 12kGy. Sample in December with highest COD value showed less percentage reduction. This indicated that COD removal efficiency was dependent on the initial concentration of COD.(Teo Ming 2008).

4.2.2 Effect of Beam current on COD

Effect of beam current on characteristic of wastewater can be seen by comparing the properties of wastewater at dose 3kGy and 6kGy. This was because 5mA beam current was used to irradiate sample at 3kGy dose while 10mA beam current was applied to obtain 6kGy dose. The average reduction in COD is 14.6% for all samples irradiated with 5mA beam current at 3kGy. The COD value reduced by 22.5% for sample irradiated with 10mA beam current at dose 6kGy. More electrons were produce at higher beam current that will react with the wastewater to form more reactive species such as OH., H.and e_{aq}^{-} through radiolysis of water. More reactive species at higher beam current had improved the efficiency of COD removal compare to lower beam current.
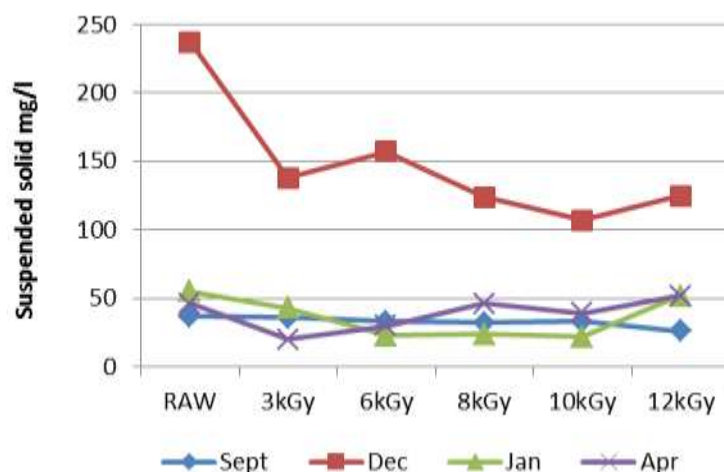
Fig.3. Effect of radiation on suspended solid sample in specific months.

4.2.3. Effect of radiation on suspended solid

Suspended solid in mixed industrial wastewater shows inconsistence trend when it is subjected to e-beam radiation as shown in figure 2. Significant reduction of suspended solid is shown by sample collected in December 2011. The average reduction for this sample is 45.1%. Inconsistent trend of suspended solid as the dose increased may be due to transformation of pollutant degradation. Many organic pollutants can be transformed into insoluble or sparingly soluble compounds upon irradiation, to form higher weight product [Ponomarev et.al1999; Pikaev et.al. 1977]. Normally, organic compounds having a molecular weight of more than 200 amu have low solubility. Statement above may explain the inconsistent trend of suspended solid for sample in September, January and April.

4.2.4. Effect of radiation on Color removal

Significant reduction of color occurred for the December 2011 and April 2012 samples [Fig.3]. The average reductions are 56.8% and 59.5% for December 2011 and April 2012 respectively. Destruction of chromophore bond and benzene ring contribute to decoloration (Cs.M.2009). No changes of color occurred after irradiation at dose between 3kGy and 12kGy for samples in January 2011 and September 2012. This was possibly because the color causing-compound does not present in the mixed industrial wastewater. Generally, the molecule of organic compound in the wastewater was in the simple form, without chromophore bond or benzene ring in the molecules. This explains the process of mineralization that occurs directly without the process of degradation and resulting in COD reduction in Fig.1.
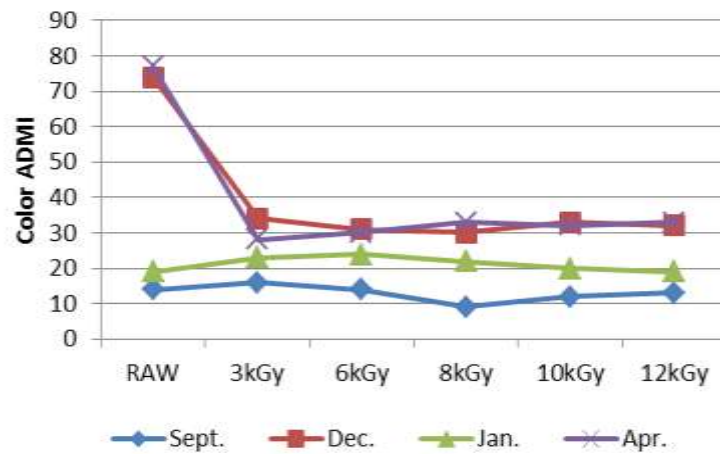
Fig.4 . Effect of radiation on suspended solid sample in specific months.

4.2.5. Effect of irradiation on DEHP concentration.
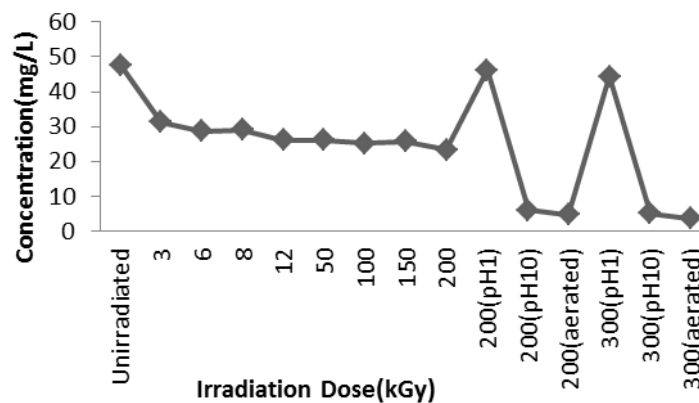

Fig.5. DEHP concentration at various dose and conditions.

The initial DEHP found in industrial wastewater was 47.62mg/L. After irradiation the concentration of DEHP depletes gradually especially when irradiation doses increases. The highest percentage of reduction was found in the sample aerated overnight before irradiation at 300kGy. The reduction percentage was 84%. Hydroxyl radical (reactive species) formed through radiolysis of water is responsible for decomposition of pollutants. Hydroxyl radical produced will attack the aromatic molecules and produce intermediates (Getoff, N., 2002). The higher the dose, more OH radicals are produced and hence there is an increase in the reduction of DEHP concentration. Aeration will provide more oxygen to the water samples. The oxygen molecules make the radiolysis process more effective during irradiation. Significant reduction was observed in the peak area as dose of irradiation increases.

4.3. Characteristic of mixed industrial wastewater after treatment in activated sludge

4.3.1. Effect of 48 hours hydraulic retention time on water properties for 14 days in the biological treatment.

Hydraulic retention time in the reactor was 48 hours and the process was continued for 14 days to determine the steady state condition which means the effluent showed constant value

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of COD, suspended solid and color. Within 48 hours retention, there were reduction of 62.3%, 67.1% and 36.7% for COD, suspended solid and color respectively. These values more or less become constant on the eighth day. This means, the microbes that used, was able to mineralize some of the organic material within 48 hours. The COD and suspended solid removal further increased to 65.8% and 89.0% on day ten to fourteen. This may be due to the destruction of complicated molecule structure of organic compound at the beginning (2,4,6 and 8 day) to form simple molecule on the day ten. Destruction of complicated molecule structure may be described as high color removal rate occurred on the second day to day eight as compared to day ten to fourteen.
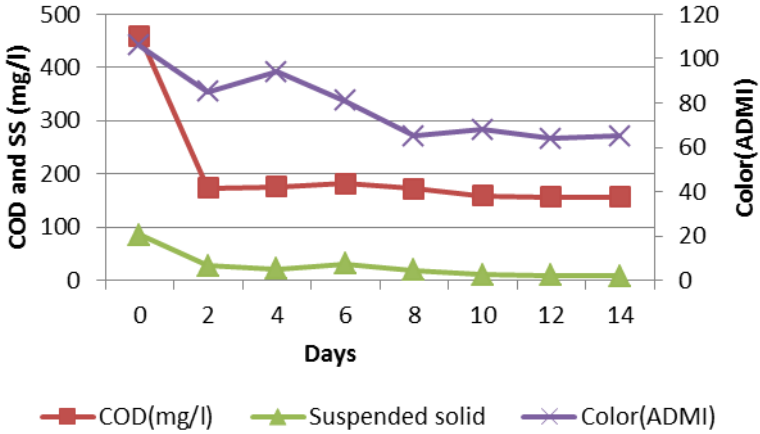
Fig.6.Water characteristics of sample after 14 days treatment in biological treatment.

4.3.2. Effect of 24 hours hydraulic retention time on water properties for 14 days in the biological treatment

Fig.7 (a), (b) and (c) show the COD, suspended solid and color of the effluents after the activated sludge process. There are little significant reduction for COD(a) and color((c) except for suspended solid. The average reduction of COD, suspended solid and color were 26.3%, 62.3% and 17.0% respectively. Although the results show a small reduction of COD, suspended solid and color, it was observed that a steady stage for parameter tested was obtained on day twelve onwards.

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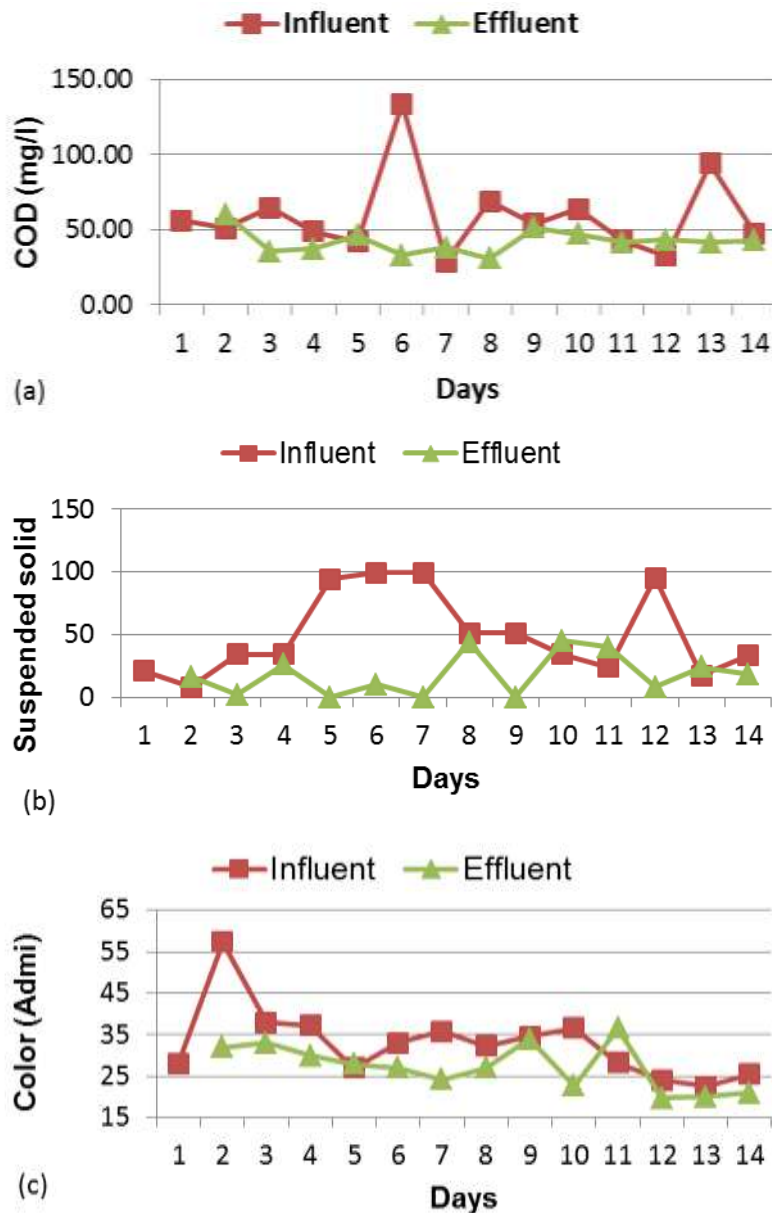
Fig.7. Effect of HRT on COD, suspended solid and color of mix industrial wastewater during 14 day treatment in activated sludge system.

4.3.3. Effect of HRT on characteristic of effluent in activated sludge process.

From Table.2, it is shown that the removal efficiency was lower for tested conditions when the HRT is at 24 hours. As the HRT decrease from 48 hours to 24 hours, the COD removal efficiency decreased from 62.3% to 26.3%. A decrease of HRT for the activated sludge process means an increase in substrate loading for the microbes. At the HRT 48h, the substrate loading is low and the retention time is enough to treat the substrate in the wastewater.

TABLE 2 SHOWS THAT REMOVAL EFFICIENCY OF COD, SUSPENDED SOLID AND COLOR FOR TWO DIFFERENT HRT

Hydraulic Retention Time (HRT) Hour	COD %	Suspended Solid %	Color %
48	62.3	67.1	36.7
24	26.3	62.3	17.0

4.4. Microbe Identification.

Bacteria identification was carried out once during the 15-days activated sludge operation where the sample was taken on day 8th. There are six bacteria presented in the reaction tank. However this research did not identify which bacteria that is responsible for pollutant degradation in activated sludge process.

TABLE 3. TYPES OF BACTERIA PRESENT IN THE REACTOR TANK DURING THE ACTIVATED SLUDGE PROCESS.

No.	Bacteria Name
1.	*Microbacterium ginsengisoli*
2.	*Rhizobium* sp
3.	*Azotobacter vinelandii*
4.	*Agromyces* sp.
5.	*Aeromonas caviae*
6.	*Shinella granuli*

5. Conclusion

E-beam radiation is capable of reducing COD in mixed industrial wastewater at lower dose, however the removal efficiency is dependent on the initial concentration of COD. Irradiation is also able to reduce DEHP concentration in wastewater and the reduction is better when aeration was introduced into wastewater prior to irradiation. In activated sludge treatment, the removal efficiency was lower for COD, suspended solid and color at HRT of 24 hours as compared to the HRT of 48 hours. Steady state was obtained earlier (day 8) for the 48 hours HRT, compared to day 12 for 24 hours HRT.

Acknowledgement

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LABORATORY AND FEASIBILITY STUDY FOR INDUSTRIAL WASTEWATER EFFLUENTS TREATMENT BY RADIATION

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Abstract

The study of wastewater treatment by radiation regarding chemical processes contribution and physical-chemical separation of highly concentrated non-organic pollutants deposited in specific industrial waste are proposed. Laboratory stand should be build and the study should be performed to confirm possible mechanism of the sedimentation process of nonorganic pollutants during separation initiated by ionizing radiation. Evaluation from technical and economical point of view of this specific radiation technology and feasibility study preparation for industrial facility will be the main output at the final stage of the project.

1. Introduction

Different hazardous wastes are produced as the results of mankind activity, what creates serious impact on environment, especially in industrialized countries. The radiation processing method may offer unique possibility for wastes recycling, when common processes are too expensive or not offering required efficiency. The suitable evaluation procedure should be applied regarding development status, technical feasibility, retrofitability, process reliability, energy consumption, resources requirements and economical aspects of the radiation process.

Institute of Nuclear Research and Technology (INCT) is involved in number of projects related to environment protection over several decades. Radiation process of wastes from acrylonitrile manufacture degradation was investigated more than 30 years ago [1], when the conditions of effective cyanide ions decomposition were established. A lot of experiments were performed at INCT to confirm that sewage sludge is sanitary safe after suitable electron beam treatment process. It was found that the dose 6 kGy inactivate all parasite eggs and decrease total bacteria content by 3 logs. The feasibility study for municipal sewage sludge was prepared [2, 3]. The capital cost of the radiation facility based on 10 MeV electron accelerator with capacity 70 t/day and dose 6 kGy was estimated on 4 M US$.

Gaseous pollutants like NO_x and SO_2 are emitted when fossil fuels that contain sulfur (coal, oil and natural gas) are burned. Strict control of pollutants emission was forced in many countries. The technology for flue gas treatment by radiation was found as one from few so called second generation methods which can provide simultaneous NO_x and SO_2 removal and those pollutants conversion to usable byproduct with presence of ammonia. Laboratory study was performed in facility located at INCT with a gas flow up to 400 m^3/h. Pilot plant experiments were performed in Poland [4, 5] and in several other countries. The Polish Pilot Plant of capacity 20000 m^3/h has been built at EPS located in Warsaw. The positive results of the tests performed on laboratory and pilot installations in Poland has led to decision concerning design and construction of the industrial demonstration facility for electron beam flue gas treatment.

Industrial demonstration facility for electron beam flue gas treatment was designed and constructed at EPS Pomorzany in Szczecin. This flue gas purification installation treats

exhaust gases coming from a block which consists of two Benson type boilers of power 56 MWe each, supplying additional steam for heating purposes up to 40 MWth each. The 270 000 Nm^3/h flue gases (half of produced by the block) can be treated with efficiency 90% for SO_2 and 70% for NO_x to meet Polish regulations which are imposed since 1997. Four electron accelerators constructed by Nissin High Voltage, Kyoto has been installed to provide 1000 kW of total beam power with electron energy 0,7 MeV. Solid particles formed during technological process salts are separated in ESP with amount of 700 kg/h [6-9].

The other gaseous pollutants emitted by industry to the atmosphere are volatile organic compounds (VOC). The laboratory facility for investigation of toxic gases removal from gaseous streams has been built on the base of ILU 6 electron accelerator at INCT. The number of projects were initiated to cover different subject related to mechanism of 1,1-dichloroethylene decomposition in humid air under, reduction of VOCs in flue gas from coal combustion by electron beam treatment, NO_x and PAHs removal industrial flue gas by using electron beam technology with alcohol addition, chloronaphthalene decomposition in different gas mixtures under electron beam irradiation [10-14].

Study on radiation decomposition of selected pesticides (herbicide, fungicide) was performed at INCT regarding their presence in industrial wastes and groundwater because their common use in agriculture. Except yield of degradation the number of parameters was examined like toxicity changes, irradiation dose and dose rate influence, pH and initial concentration of the target compounds and scavengers presence. The mechanism of radiation process was proposed and verified by computation modeling in certain cases [15-18].

Research on the application of radiation technology for conventional wastewater treatment has mainly dealt with sewage sludge to be used in agriculture, and involved study on the effect of radiation on the sanitary condition of sediments and their technological properties. The latter case mainly dealt with the sedimentation capabilities initially only sewage sludge with low percentage of dry mass. Usually the concentration of the pollutants in industrial wastewater is high wich requires higher doses to achieve suitable removal efficiency. Laboratory and feasibility study for wastewater effluents treatment by radiation was proposed to describe chemical contribution and physical-chemical separation of nonorganic pollutants deposited in industrial waste. The formation of sediments from suspensions and chemical reaction involvement initiated by electron beam will be studied. The evaluation of the radiation process of nonorganic pollutants separation, decomposition and removal will be evaluated from technical and economical point of view.

2. Industrial wastewater with high calcium carbonate concentration

The important feature of any combined method involved chemical, thermal, flotation mechanism is efficiency of wastewater purification from non biodegradable pollutants. It was found that the sedimentation capabilities of sediments had been significantly improved by non-selective radiation induced processes based on free radical reactions and surface effects in adsorption on solids and systematic interaction of sedimentation and electrical field [20,21], 20]. The substantial research evidence collected over the years has confirmed that radiation technology can be successfully used in effective and feasible process this type.

Industrial waste generated during soda ($NaHCO_3$) fabrication based on Solvay process can be divided on nonorganic solid particles and liquid phase. It was recognized that in conventional process conditions solid particles amounts up to 200 kg per 1 t of suspension. The solid particles consists of calcium carbonate ($CaCO_3$) 70% and silica 30%. Liquid phase is

dominated by NaCl presence (300 g/l) with some quantities of other compounds like KCl, $CaCl_2$, $CaSO_4$, $MgCl_2$, $Ca(HCO_3)_2$ with concentration in the range of 0.3 – 3.0 g/l.

Sediment separation with limited chloride content (<0.5% of dry mass) could be the main task of treatment process. Liquid phase will be reuse in industrial process after conventional treatment. It should be mentioned that coagulating agent application is excluded to avoid distortion of main industrial process. On the other hand separated sediment can be recognized as market product and practically applied as component of agriculture fertilizers or building materials. Fig. 1 illustrates flow sheet of waste processing plant equipped with electron accelerator, two sedimentation tanks and filter for sediment separation. The necessary process water recirculate in close system equipped with conventional treatment technology.
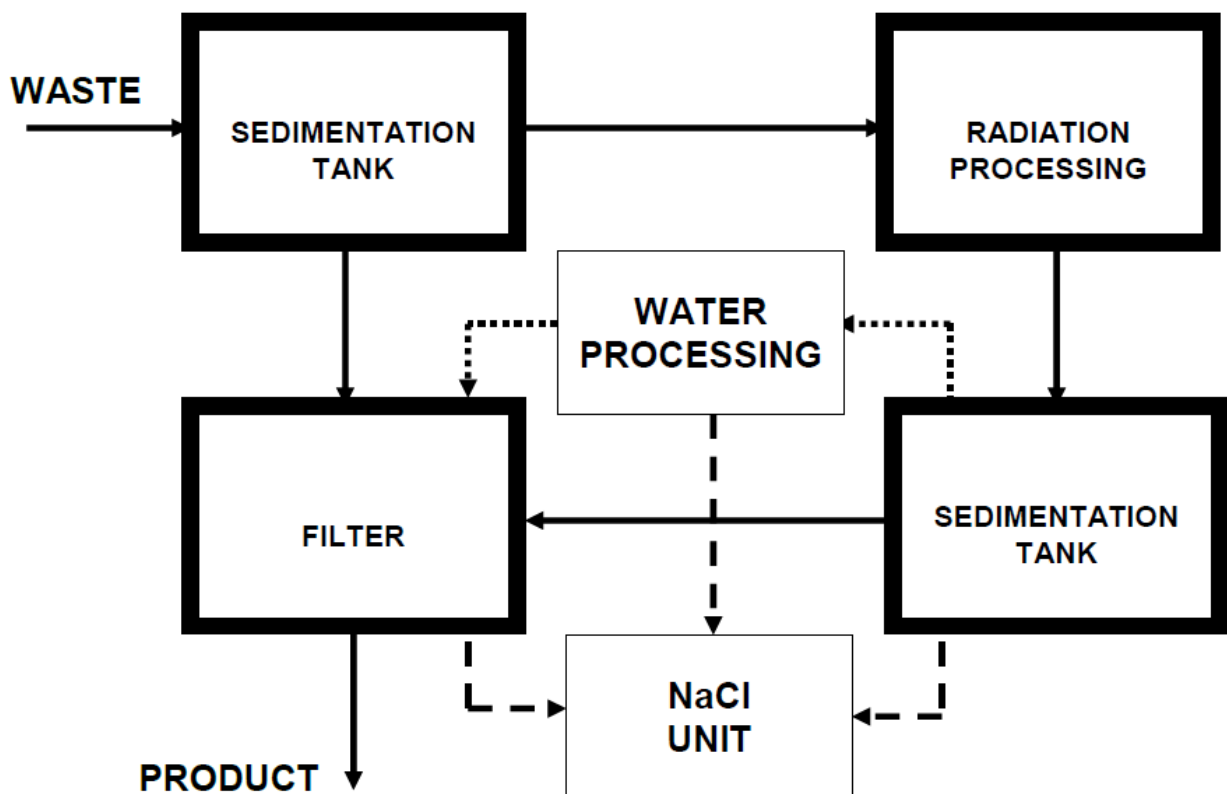
Fig. 1. Flow sheet of the waste processing plant.

3. Laboratory stand for experimental investigation of sedimentation process

Laboratory stand for experimental investigation of sedimentation process will be established. Electron accelerator ILU 6 located at INCT will be applied. The basic accelerator parameters are presented in Table 1. Fig. 2. shows flow sheet laboratory stand with basic components like electron accelerator (1); reaction vessel (2); pressurized air system (3); NaCl unit (4); sedimentation tanks (5-6); pump (7); filter (8); valves (Z1-3).

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TABLE 1. TECHNICAL PARAMETERS OF ELECTRON ACCELERATOR IŁU 6 TYPE

Range of electron energy	0,5 – 2 MeV	
Nominal electron energy	1 MeV	2 MeV
Nominal beam power	20 kW	20 W
Energy instability	< 2 %	< 2 %
Average beam current	20 mA	10 mA
Beam current instability (nominal power)	< 2 %	< 3 %
Pulse current (max)	1 A	0,6 A
Pulse duration	400 μs	400 μ
Pulse repetition rate	2 – 60 Hz	2 – 50 Hz
Power line (AC 3x380 V)	< 100 kW	
Width of beam scanning	30 – 80 cm	
Electron energy (max with beam power 16 kW)	2,4 MeV	
Beam power (max with electron enegy do 1,7 MeV)	24 kW	
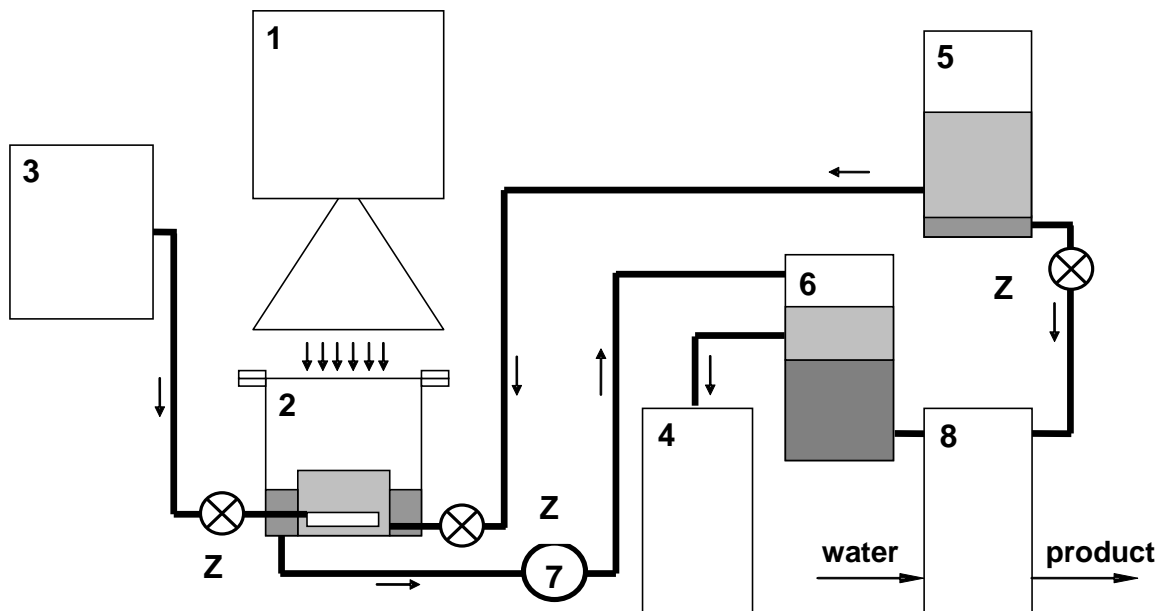
Fig. 2. Flow sheet laboratory facility: 1 – electron accelerator; 2 – reaction vessel; 3 – pressurized air; 4 – NaCl unit; 5-6 – sedimentation tanks; 7 – pump; 8 – filter; Z1-3 – valves.

Sedimentation and coagulation processes initiated by electron beam treatment will be investigated according to:

—   Surface properties of irradiated solid particles,
—   Radicals formation and their involvement in sedimentation process
—   Interaction of sedimentation and electrical field,
—   Efficient solid particles filtration process.

4. Feasibility study of sediment separation process initiated by radiation

Feasibility study of sediment separation process initiated by radiation is the principal objective of the described project. It should include detailed investigation of the wastewater radiation facility for capacity of the waste flow in the range of 200 000 m^3/y. Electron accelerator is usually the most expensive part of the radiation facility. Table 2 illustrates the most significant indicators which describe different accelerators which could be applied in the facility for wastewater treatment. The accelerator selection depends on necessary electron energy (penetration range) and beam power (productivity). As can be easily noticed from presented data the economically feasible selection suggests accelerator with low energy and high beam power. The final accelerator selection will be the significant part of optimization radiation facility type and size.

TABLE 2. THE MOST SIGNIFICANT INDICATORS WHICH DESCRIBE DIFFERENT ACCELERATORS WHICH COULD BE APPLIED IN RADIATION FACILITY FOR WASTEWATER TREATMENT

Manufacturer	Energy [MeV]	Current [mA]	Power [kW]	Price* [M$]	Cost [$/W]
IBA, Belgium	10	20	200	8.1	40.5
INP, Russia	5	10	50	1.2	24.0
RDI, U.S.A.	5	50	250	4.9	19.6
INP, Russia	1	400	400	2.0	5.0

* Estimated price level

The objectives of feasibility study will be focused on determination:

—   - if the proposed project is capable to perform its intended functions,
—   - optimum radiation facility type and size,
—   - electrical energy consumption of the technological process,
—   - if the product has sufficient market value,
—   - if the host institution is ready and capable to such investment,
—   - if a government agency's may have intention to support such project.

5. Conclusion

The study of wastewater treatment by radiation regarding chemical processes contribution and physical-chemical separation of highly concentrated nonorganic pollutants deposited in specific industrial waste are proposed. Laboratory stand should be build and the study should

be performed to confirm possible mechanism of the sedimentation process of nonorganic pollutants during separation initiated by ionizing radiation. Evaluation from technical and economical point of view of this specific radiation technology and feasibility study preparation for industrial facility this type will be the main output at the final stage of the project.

Results obtained

In the preliminary studies on radiation induced sedimentation process number of experiments were performed. The first set of data was obtained when raw waste were irradiated (before sedimentation tank). Results are displayed on Fig. 2.
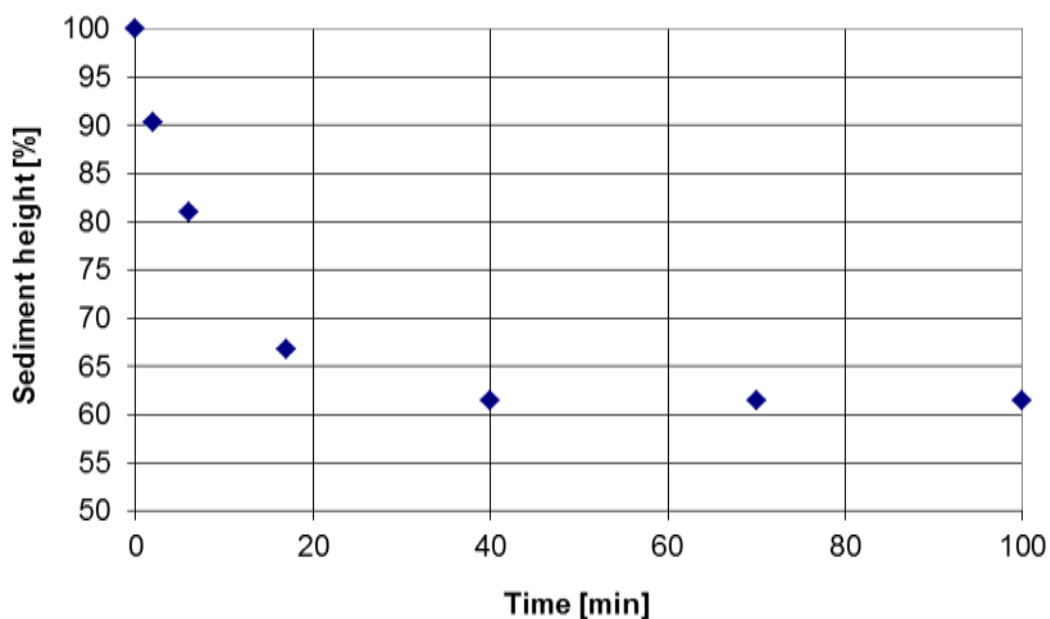
Fig. 2. Formation of layers with different volume fraction upon sedimentation of raw waste for dose level 2.5 kGy.
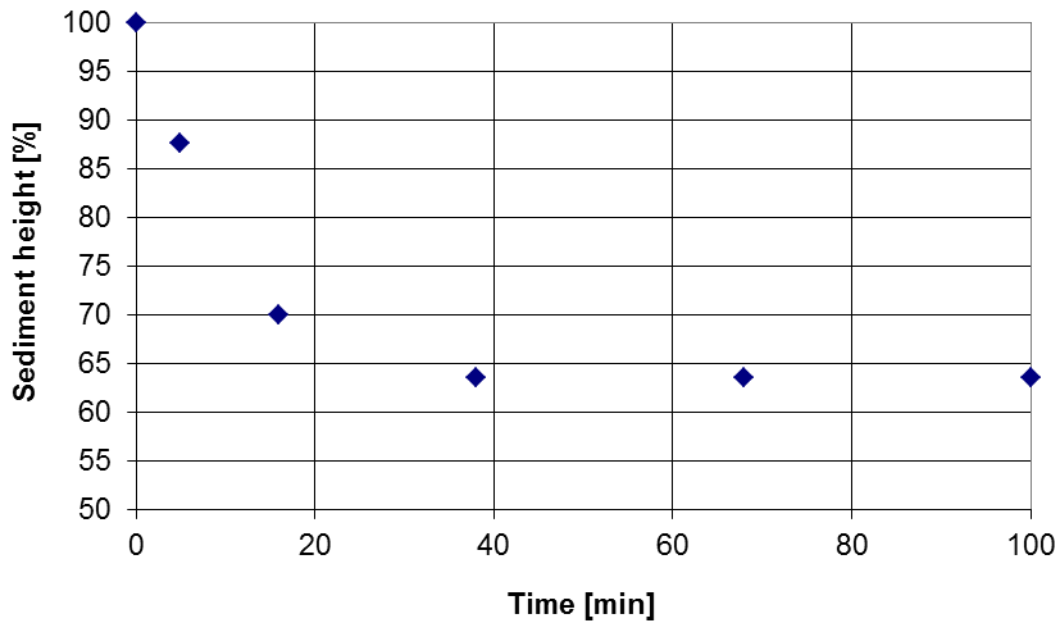
Fig. 3. Formation of layers with different volume fraction upon sedimentation of raw waste.
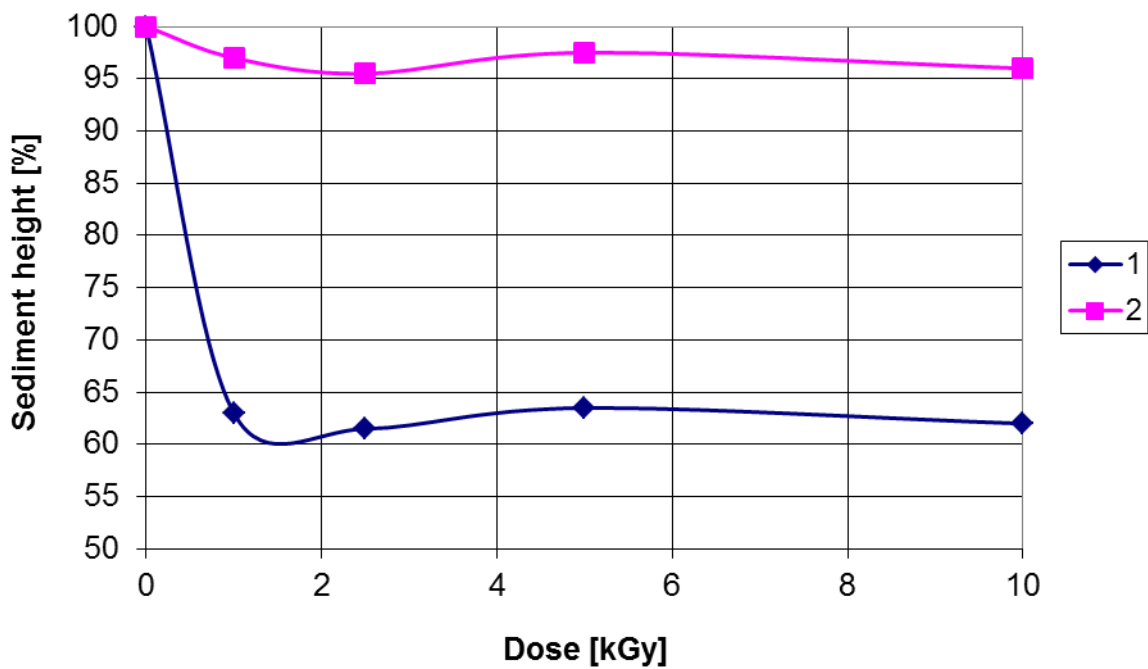
Fig. 4. Formation of layers with different volume fraction upon sedimentation of raw waste for different dose: 1 – overall effect, 2 – irradiation implementation.

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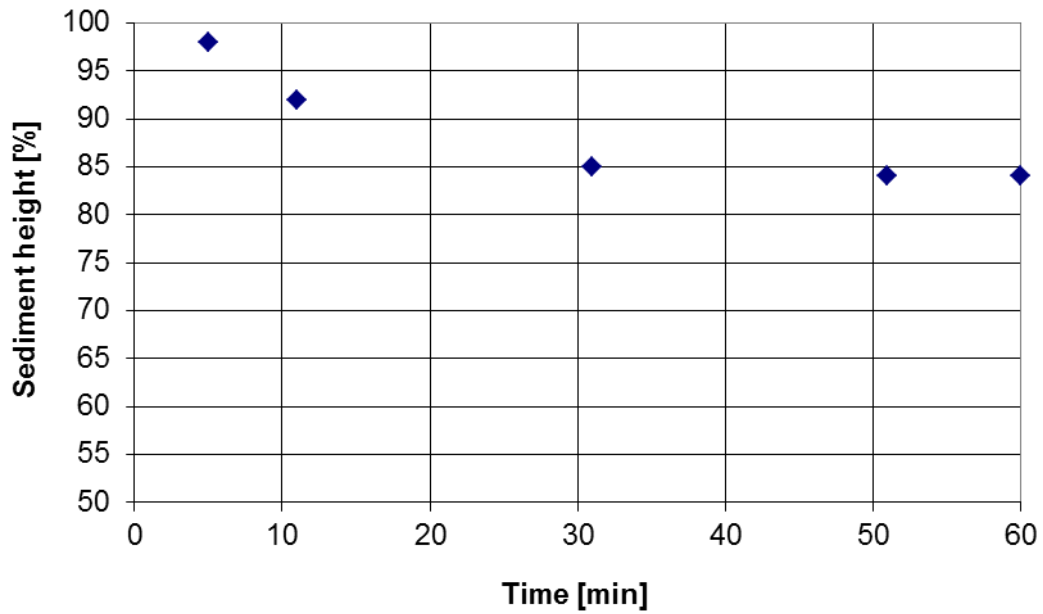
Fig. 5. Formation of layers with different volume fraction upon sedimentation of sediment after sedimentation tank for dose level 2.5 kGy.
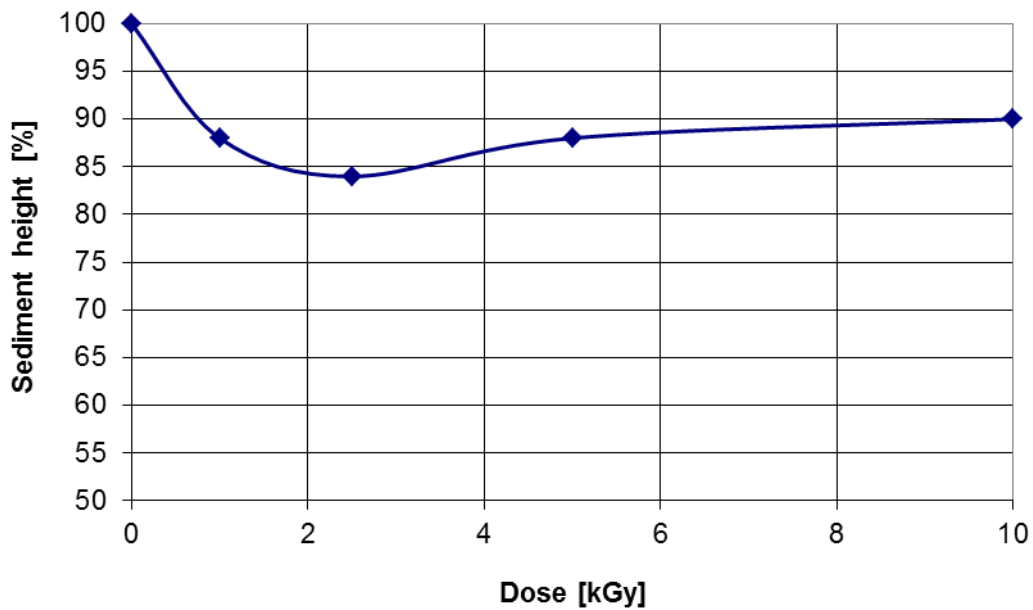
Fig. 6. Formation of layers with different volume fraction upon sedimentation of sediment after sediment tank for different dose: 1 – overall effect, 2 – irradiation implementation.

Economic aspects of industrial wastewater effluents treatment by radiation

Estimated cost analysis of industrial wastewater effluents treatment by radiation was performed to establish basic parameters and pilot plant cost-effectiveness.

Total capital investment:

Accelerator (100 kW; 1 MeV):   1.0 M$

Reactor, design, building: 1.0 M$

Transport, tax, insurance: 0.5 M$

Total: 2.5 M$

Annual fixed cost:

Interest (6%):   0.15 M$

Depreciation (20 years):   0.12 M$

Total: 0.27 M$

Annual operation cost:

Electricity (200 kW):   0.08 M$

Labor (3 shifts):   0.1 M$

Maintenance (2%):   0.05 M$

Total: 0.23 M$

Total annual cost: 0.5 M$

Calculation of mass productivity:

$M[kg/s] = P[kW] \times F / D[kGy]$

M – mass productivity

F – efficiency of beam energy transfer (0.6)

D – absorbed dose

$M = 100 \times 0.6 / 2.5 = 24$ kg/s = 86.4 t/h

Total annual production (6000 h; 2.5 kGy):

Unit cost: 1 $/t

Conclusions

It has been confirmed that wastewater treatment by radiation regarding chemical processes contribution and physical-chemical separation of highly concentrated nonorganic pollutants deposited in specific industrial can be successfully performed. The sediment after sediment tank should be irradiated to obtain the highest process efficiency. The dose 2.5 kGy was found to be optimal from point of view process economical effectiveness. Laboratory stand based on electron beam utilization should be build to to confirm possible mechanism of the sedimentation process of nonorganic pollutants during separation initiated by ionizing radiation. Evaluation from technical and economical point of view of this specific radiation technology and feasibility study preparation for industrial facility this type will be the main output at the final stage of the project.

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APPLICATION OF IONIZING RADIATION ON THE CORK WASTEWATER TREATMENT

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Abstract

In the framework of the CRP on "Radiation treatment of wastewater for reuse with particular focus on wastewaters containing organic pollutants" Portuguese team is been developed studies on the implementation of ionizing radiation technology as a complementary treatment for industrial effluents and increase the added value of these wastewaters. Based on these assumptions, preliminary studies of the gamma radiation effects on the antioxidant compounds present in cork cooking water were carried out. Radiation studies were performed by using radiation between 20 and 50 kGy at 0.4 kGy/h and 2.4 kGy/h. The radiation effects on organic matter content were evaluated by Chemical Oxygen Demand (COD). The antioxidant activity was measured by Ferric Reducing Power (FRAP) assay. The total phenolic content was studied by Folin-Ciocalteau method. Results point out that gamma radiation increases both the amount of phenolic compounds and antioxidant capacity of cork cooking water. By the other hand, the radiolytic degradation by ionizing radiation of gallic acid and esculetin as models for recalcitrants were studied. The objective of this study was to find out if radiolytic degradation, followed by microbial degradation could increase the treatment efficiency. A natural cork wastewater bacterium was selected from the irradiated wastewater at 9 kGy. The applied methodology was based on the evaluation of growth kinetics of the selected bacteria by turbidimetry and colony forming units, in minimal salt medium with non-irradiated and irradiated phenolic as substrate. The overall obtained results highlights the potential of this technology for increase the add value of cork waters and raised some issues to explain by new methodological setup on biodegradation studies.

1. Objective of the research

The main goal of the research to be developed by the Portuguese team is the implementation of ionizing radiation technology as a complementary treatment for industrial effluents. The current research studies are based on two fields: 1) to find out if radiolytic degradation, followed by microbial degradation could increase the wastewater treatment efficiency and 2) to study the potentialities of ionizing radiation to increase cork wastewaters added value.

2. Introduction

Cork production and transformation process are important sectors of activity in Portugal. This is the raw material that feeds an industry of great importance to the national economy [1]. In cork processing, after the stabilization period of the cork planks (3-12 months), the planks are immersed in water at 100ºC to cook. The water is reused (3 labor days) and, at the end of each cycle, there is a filtration step to minimize the organic load and solid waste of the cooking water.

The cork cooking waters are complex mixtures of plant extracts turning water to dark brown liquor. These waters have a high organic load and considerable toxicity due to hot extraction that occurs in cooking process. Among other natural compounds, these waters have a high

concentration of polyphenols such as phenolic acids, tannins, 2,4,6-trichloroanisole, benzoic acid and cinnamic acids[2]. Some of these polyphenols are known for their high antioxidant activity. According to Minhalma and Pinho [3], the main phenolic acids in these waters are gallic, protocatechuic, vanillic, ferulic and ellagic acids.

Advanced oxidation processes are being studied as potential technologies to reduce the organic matter content as phenolic compounds, increasing the biodegradability of wastewaters [4, 5, 6]. The Fenton oxidation process is one of the most recognized technology where the generation of highly reactive hydroxyl radicals (HO•) through catalytic decomposition of hydrogen peroxide reduces the amounts of organic matter [7]. However, the reagent and catalyst (ferrous iron) added to generate the HO• radicals are expensive and potential pollutants and it would be desirable to reduce its use. Ionizing radiation has the same mechanism of Fenton oxidation, i.e., the generation of free radicals to promote compounds degradation but without adding any chemical. Therefore, ionizing radiation seems to be a potential technology to be applied in order to increase the biodegradability [8, 9, 10]. In addition, the use of natural bacteria from wastewater as degraders could be a promising approach to remediation of wastewaters [11].

3. Materials and Methods

3.1. Gamma irradiation of cork cooking wastewater, gallic acid and esculetin solution

Cork boiling wastewater was collected from Fabricor, S.A., the cork industry used as case study in this project. The sampling procedure had three purposes:1) irradiation of raw cork wastewater collected in the end of cooking process before the discharge to the wastewater treatment plant in order to assess the gamma radiation effects on organic matter and antioxidant activity; 2) the characterization of natural cork wastewater microbiota and 3) the isolation of the survivor population after irradiation. Therefore, the cork wastewater sample was irradiated at 2 kGy up to 50 kGy and for the radiolytic degradation of tested phenolic compounds, pure solutions of 1 mmol/dm^3 gallic acid (>99%; Sigma-Aldrich) solution and a 0.1 mmol/dm^3 esculetin solution (>99%; Sigma-Aldrich) were also irradiated at 9 kGy absorbed dose. The gamma irradiations were carried out at the Co-60 facility in the Radiation Technology Unit located at Nuclear and Technological Institute [12]. The dose rate used was 2.5 kGy/h and the measured absorbed doses by routine dosimeters [13].

3.2. Isolation and morphological characterization of cork boiling wastewater microbiota

The characterization of cork wastewater microbiota was made using conventional microbiological techniques (e.g. microscopic observation; gram staining; catalase and oxidase tests) and, after microrganims growth, colonies with distinct macroscopic morphologies were isolated by sub-culturing on the same medium. The most frequent isolate from irradiated sample was identified by API system (Biomérieux, France) according to manufacturer instructions. This microorganism was selected to be used in the growth evaluation studies.

3.3. Growth evaluation on synthetic medium

A minimal mineral medium [1.28% Na2HPO4.7H2O, 0.3% KH2PO4, 0.05% NaCl and 0.1% NH4Cl] was supplemented separately with three carbon sources for gallic acid: i) 200 mg/L of gallic acid solution (GA); ii) 200 mg/L of irradiated gallic acid solution at 9 kGy (GA9) and iii) 200 mg/L of irradiated gallic acid solution at 38 kGy (GA38); and with two carbon sources for esculetin: i) 200 mg/L of esculetin solution (E) and ii) 200 mg/L of irradiated esculetin solution at 9 kGy (E9). Addition of each of the tested compounds to the growth

medium caused no change in pH. For both studied compounds, Tryptic Soy Broth (TSB) was used as growth positive control (C) and minimum mineral medium without carbon source as negative control (B). The selected isolate was inoculated in all culture medium at an initial concentration approximately 107 cfu/mL (initial Optical Density (O.D.610nm) approximately 0.06 for gallic acid and 0.2 for esculetin) and incubated at 30 ± 2 ^{o}C in an orbital shaker (100 rpm). The bacterial growth for each culture assay was monitored at regular time intervals by: 1) turbidity measurement at 610 nm (Shimadzu spectrometer UV-1800) and 2) CFU counts by direct plating into Tryptic Soy Agar of aliquots of serial decimal dilutions.

3.4. Chemical Oxygen Demand (COD) and Total Phenolic Content (TP)

COD was measured by Titrimetric method accordingly to the Standard Methods for the Examination of Water and Wastewater [14]. Samples were diluted 10-fold. The TP was determined based on Folin-Ciocalteau method (Singleton at al., 1999) using gallic acid as standard. Samples were diluted 5-folds and 0.5 mL of the diluted sample was added to 35 mL of water and 2.5 mL of Folin-Ciocalteau reagent (FC). After shaking and incubating 5 minutes at room temperature, it was added 7.5 mL of sodium carbonate solution and water to the 50 mL line. The solution was incubated at room temperature for 2 hours and after that the absorbance of the reaction mixture was measured at 765 nm using a Shimadzu UV 1800 spectrophotometer. Results were expressed as mg of gallic acid equivalents per liter of sample.

3.5. Evaluation of antioxidant activity by Ferric Reducing/Antioxidant Power (FRAP)

The assay was carried out according to the method described by Benzie and Strain[15]. FRAP reagent was freshly prepared by mixing 300 mM of acetate buffer (pH 3.6), 10 mM of 2,4,6-Tris(2-pyridyl)-s-triazine (TPTZ) and 20 mM FeCl3.6H2O in a ratio of 10:1:1 at 37°C. One hundred microliters of sample diluted 10-folds in ultrapure water were added to FRAP reagent (3 mL) in a test tube. After 15 minutes of incubation at 37°C, the absorbance was measured at 593 nm. The antioxidant potential of the sample was determined from a standard curve using FeSO4.7H2O solution between 0 and 1.0 mM.

4. Results and Discussion

The natural cork wastewater mesophilic bacterial population was isolated before and after irradiation. A total of 27 isolates in non-irradiated and 11 in irradiated samples at 9 kGy were phenotyped according to microscopic morphology and biochemical characteristics. The relative frequency of each phenotype is presented in Figure 1.
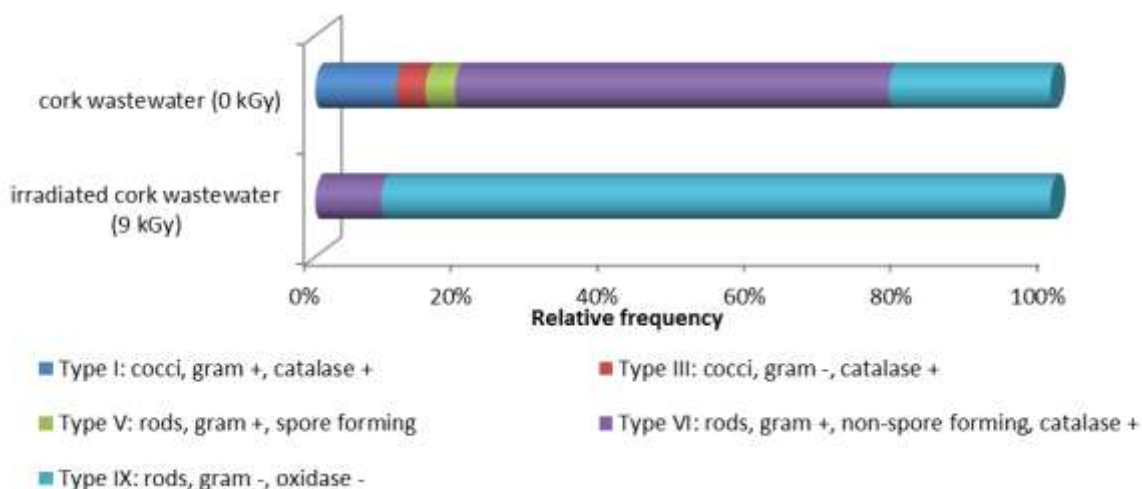
Fig. 1. Relative frequency (in percentage) of the phenotypes of the isolates from non-irradiated cork wastewater and irradiated cork wastewater at 9 kGy.

The isolates from non-irradiated wastewater sample were grouped into five morphological types, being the most frequent the gram positive rods non-spore forming (59%). After irradiation at 9 kGy the diversity decreased, only two of the initial morphological types had persisted. The most frequent was the gram negative oxidase negative rods (91%). The major isolate from this group was identified as *Stenotrophomonas malthophilia* (%id = 92.4). Although it was an environmental isolate, strains from this microorganism are known to metabolize a broad range of aromatic compounds [16, 17]. Based on that assumption, this isolate was used as test strain to evaluate the degradation of target compounds before and after irradiation. This evaluation was made by inoculation of the microorganism into a mineral medium with 200 mg/L of non-irradiated or irradiated gallic acid (GA) and esculetin (E) solution, separately, as sole carbon and energy source. As growth positive control TSB medium was used and as growth negative control, mineral medium without carbon source was used.

4.1. Standard phenolic compounds

The bacterial growth monitoring by turbidity at 610 nm for both gallic acid and esculetin is represented in Figure 2.
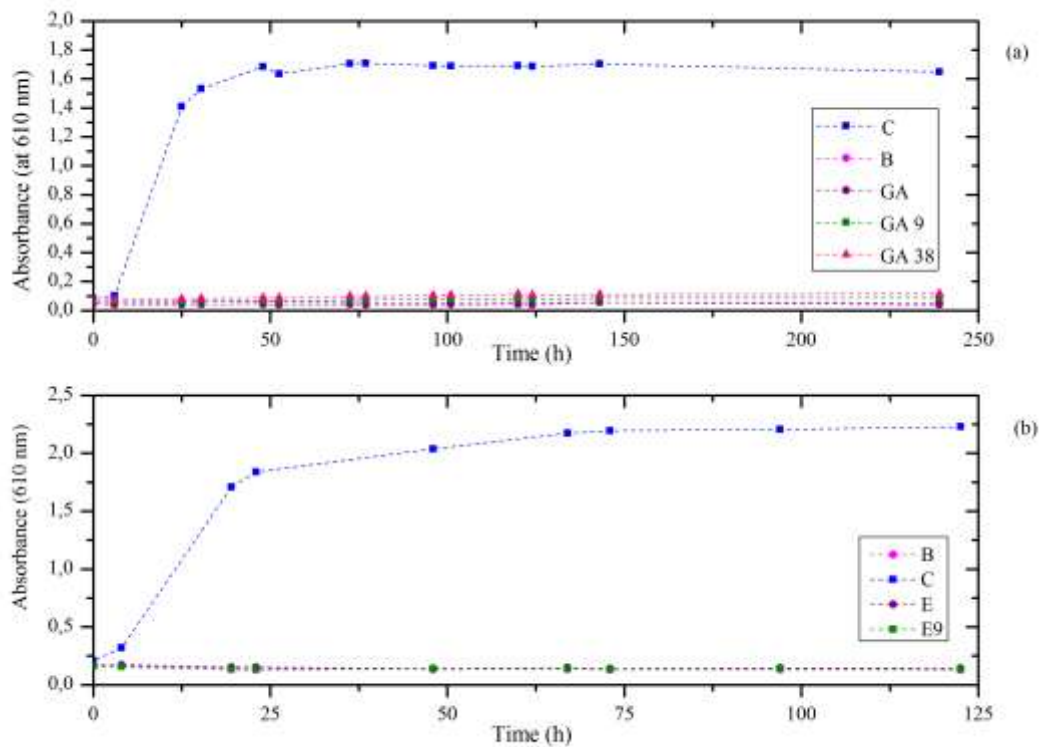
Fig. 2. Turbidity results monitored as Optical Density (O.D.) at 610 nm for each different carbon source culture medium for both studied compounds: (a) (C) positive control (TSB medium); (B) negative control (mineral medium without carbon source); (GA) GA sol., 0 kGy; (GA9) GA sol. 9 kGy and (GA38) GA sol., 38 kGy; (b) C) positive control (TSB medium); (B) negative control (mineral medium without carbon source); (E) E sol., 0 kGy and (E9) E sol. 9 kGy.

The presented turbidity growth results suggested that the test strain was not able to metabolize as sole carbon source either gallic acid solution (irradiated and non-irradiated) and esculetin solution (irradiated and non-irradiated) at the used concentration. The positive growth control indicated the viability of the inoculum denoted by the obtained well defined growth curve and negative control indicated that selected bacteria was not capable to growth in the minimal mineral medium.

The other method used to monitored growth, the cfu counts, also failed to detect bacterial growth in gallic acid cultures (see Figure 3).
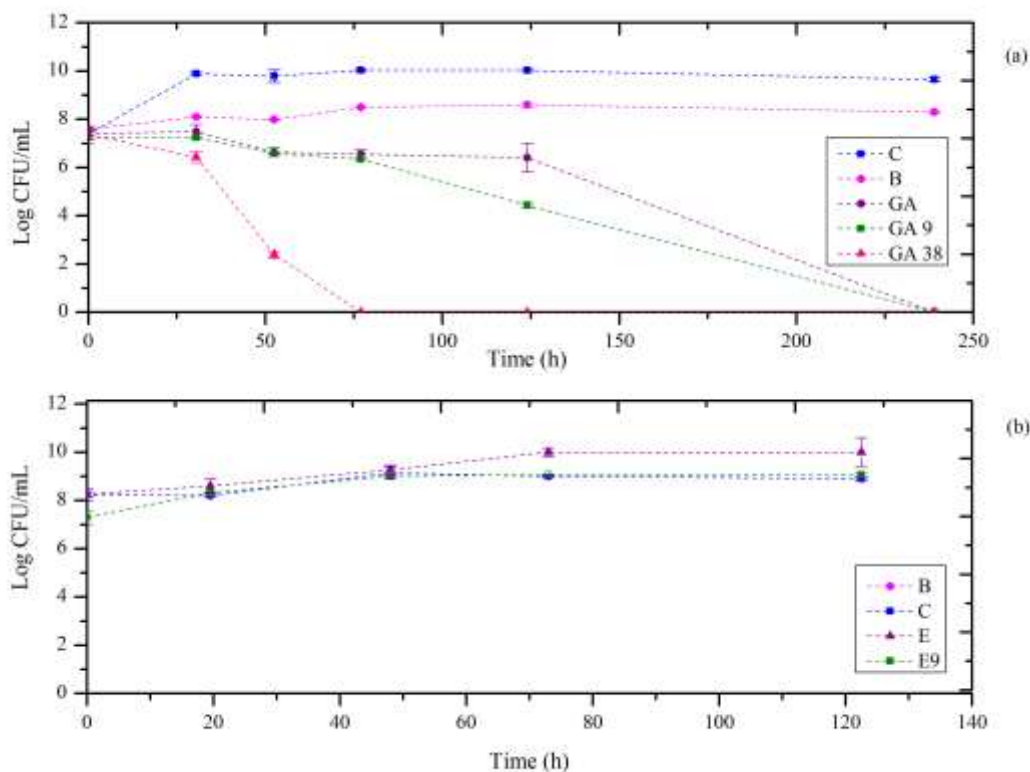
Fig. 3. Average CFU counts of Stenotrophomonas maltophilia *strain in both gallic acid and esculetin different cultures: (a) (C) positive control (TSB medium); (B) negative control (mineral medium without carbon source); (GA) GA sol., 0 kGy; (GA9) GA sol. 9 kGy and (GA38) GA sol., 38 kGy; (b) (C) positive control (TSB medium); (B) negative control (mineral medium without carbon source); (E) E sol., 0 kGy and (E9) E sol. 9 kGy. Error bars correspond to 95% confidence intervals about mean values (n= 6; α = 0.05).*

In agreement with turbidity measurements, the CFU counts of the positive control (C) increased during the initial incubation hours, indicating the adequacy of methods to evaluate the growth of the test strain either gallic acid and esculetin medium cultures. As expected, for the negative control (B) it was not observed substantial variations in growth during incubation time.

As presented in Figure 3(a), the results point out to a decrease in CFU counts in GA solution with absorbed dose. Therefore, the radiolytic by-products seem to have higher negative effect on *S. malthophilia* growth then the parent compound. The antimicrobial activity of phenolic acids, namely gallic acid, have been demonstrated against gram negative bacteria in planktonic state [18, 19]. Phytochemical products (e.g. gallic acid) are routinely classified as antimicrobials on the basis of susceptibility tests that produce growth inhibitory effects in the range of 100 to 1000 μg/mL [20]. Since the GA concentrations used (non-irradiated and irradiated) in cultures medium were 200 μg/ml it is reasonable to assume an antimicrobial action of gallic acid against the tested strain.

Melo et al. [21] reported that at 9 kGy the gallic acid radiolytic byproducts are mainly fragments from gallic acid degradation with aromatic ring opening, connected to some still resilient gallic acid structures. This fact could explain the low biodegradability of irradiated gallic acid solution. However, irradiated gallic acid solution at 38 kGy showed that not only gallic acid,

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but also the aromatic intermediate products, tend to disappear [21] meaning that even non-aromatic byproducts present an antimicrobial action against the tested strain. Besides the bacterial growth assessment, it was also important to determine the quantity of gallic acid present in the cultures supernatant.

Concerning esculetin solution, Figure 3(b) shows that there is no gamma radiation effect on esculetin solution. The radiolytic products of esculetin were identified in our lab (submitted) and are mainly aliphatic compounds since esculetin structure degrades at low absorbed doses. As for gallic acid biodegradation assay, the tested strain point out to be not able to use either irradiated or non-irradiated esculetin as carbon source, denoting a growth inhibition. Although, must be noticed that the test strain was maintained viable in esculetin supplemented cultures with unchangeable counts during almost 6 days. This fact could suggest a bacteriostatic effect of esculetin against *S. maltophilia* strain. A study performed by Dürig et al. [22] demonstrated that esculetin abolish biofilm formation but have no effect on planktonic growth of a *S. aureus* strain at the concentration of 128 µg/ml. Other authors [23] have stated the antimicrobial activity of esculetin against several microorganisms.

To our knowledge, this is the first study that tries to associate the metabolic capacities of cork natural microbiota along with a radiolytic process, in order to promote the recalcitrant compounds degradation. Besides the obtained inconclusive results and not comparable with the literature, this preliminary bench scale approach have raised some issues to explain by a new methodological setup. Briefly, a detailed organic content characterization will be performed in order to select the main recalcitrant compounds for the studied cork wastewater and a mixed natural wastewater microbial population will be tested. The well-known potentialities of gamma radiation as complementary wastewater treatment technology will be carried on to a future scale up on a Portuguese cork Industry.

4.2. Chemical Oxygen Demand (COD)

COD is a routine parameter used to reveal the total organics in wastewaters as well as the extent of wastewater treatment [24, 25]. This parameter reflects a global oxygen capability uptake that can be due to a large variety of compounds including the phenolic compounds. The COD results are presented in the Figure 4.
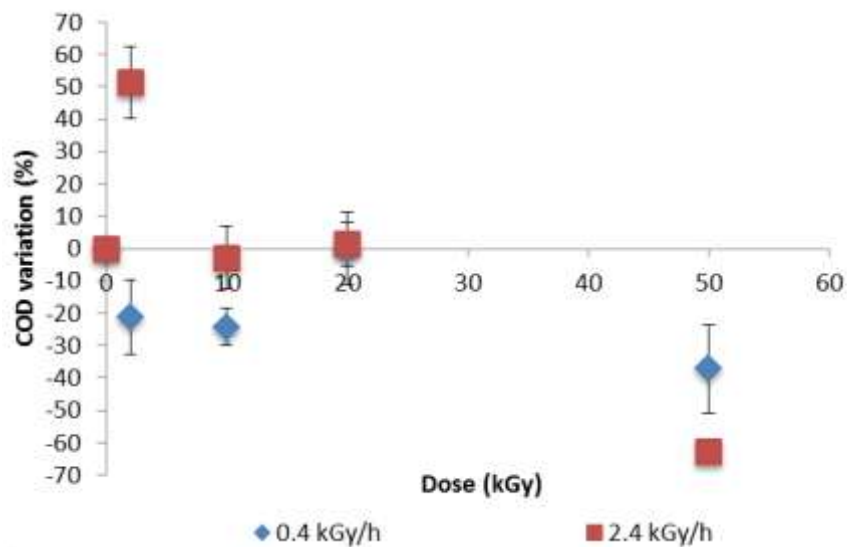
Fig. 4. COD vs. Absorbed dose (n=5; α=0.05).

Figure 4 shows that for a 50 kGy absorbed dose the % COD variation decreases (average 37±14% at 0.4 kGy/h and average 63±0.01% at 24 kGy/h) for both dose rates. With the exception of 2 kGy absorbed dose at high dose rate (2.4 kGy/h) the gamma radiation effect is associated with a decrease of COD and therefore indicates that there is a chemical degradation of organic matter [26] . Other authors [27, 28] also reported that the COD decreases with gamma irradiation in industrial wastewaters. At low absorbed doses (2 kGy) and high rate (2.4 kGy/h) the momentary increase of COD value can, probably, be done to the degradation of some heavy mass compounds in a large number of lower mass compounds that actively contribute to that increase. However, for larger doses, also these smaller compounds are degraded leading to a final decrease of COD value.

4.3. Correlation between antioxidant activity by Ferric Reducing/Antioxidant Power (FRAP assay) and Total phenolic compounds (TP)

Figure 5 shows the correlation found between FRAP and TP and showed that the main responsible for the antioxidant activity are the phenolic compounds, as expected. The Pearson coefficient (r) for the both doses rates is strong and positive (r=0.902 for 0.4 kGy/h and r=0.998 for 2.4 kGy/h) that indicates a strong correlation between TP and the antioxidant activity. The higher antioxidant activity increase at 2.4 kGy/h dose rate could be related to a greater amount of radical species generated that tend to for a higher number of antioxidant active compounds.
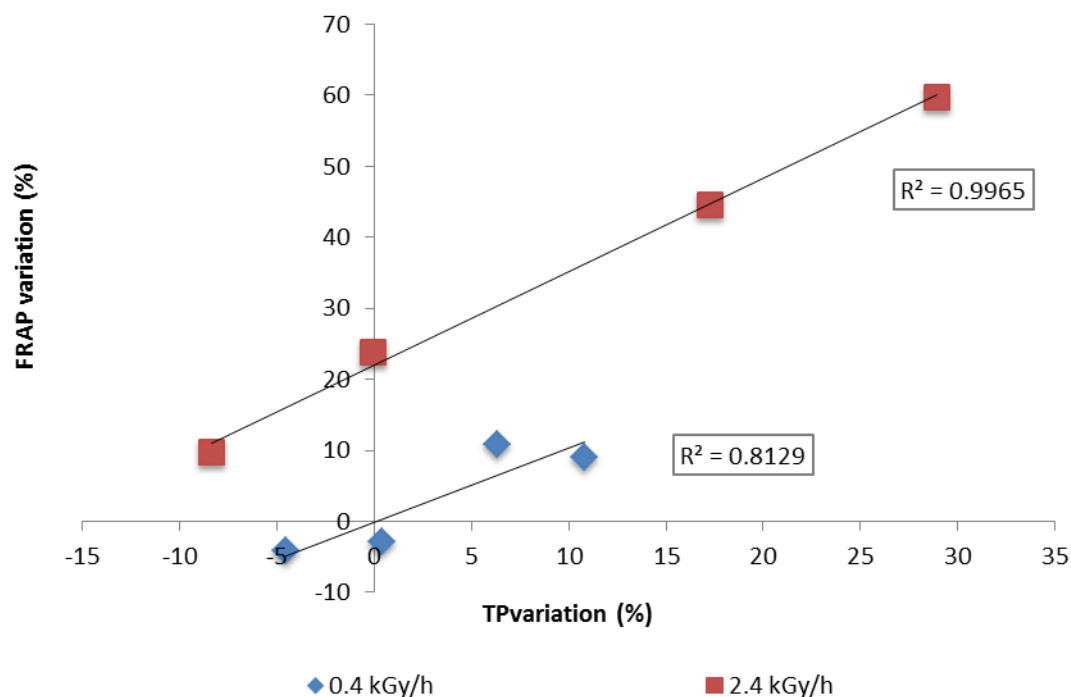
Fig. 5. Antioxidant activity vs. total phenolic compounds.

These results could be explained by hydroxyl radical attack to large molecules (eg. tannins and other complex phenolic compounds) but without breaking most of the phenyl groups. The breaking of those compounds leads to an increase of the concentration of smaller phenolic structures with a global higher antioxidant activity.

In conclusion, gamma radiation was applied as a pretreatment for cork cooking water. High dose rate (2.4 kGy/h) and low dose rate (0.4 kGy/h) were applied and the obtained results point out that there are significant differences between dose rates. COD results, together with FRAP and TP results, show us a picture where larger molecules are degraded producing a lot of small phenol compounds. This is a very important result to cork industry since a treatment like this one increases dramatically the added-value compounds (antioxidants) in the cooking water while decreases other organic matter leading to a much more valuable solution as raw material for other industries. To our knowledge, there are no studies about gamma irradiation effects on antioxidant activity of cork cooking water. Further studies have to be performed to access the technical viability of extraction, identification, purification and reuse of now detected antioxidants.

5. Ongoing activities and further work

Ongoing studies are focusing on two main fields:

1) extraction of potential antioxidants: activated carbon (olive seeds); the economic viability of these techniques; toxicity tests and repetition of experiments with electron beam

2) As mentioned above, the application of a new methodological setup for biodegradation will be performed and a new microbial population will be selected in order to optimize the biological treatment as a complement with ionizing radiation.

3) The understanding of the mechanisms of different antioxidant activity methodologies in cork wastewater irradiation. These studies could be helpful to better understand the oxidation mechanisms in radiolytic reactions. Analytical techniques (e.g.: High Performance Liquid Chromatography (HPLC) and ionization by electrospray (ESI-MS)) will be used to characterize and quantify the radiolytic products produced in irradiated wastewaters. In addition, modulation tools will be used to develop kinetic models and calculate reaction rate constants to understand the reaction mechanism of these compounds after irradiation that will be applicable to several free-radical based technologies.

The synergy between both studies will allow the optimization of the irradiation parameters (e.g. type of energy, geometry, absorbed doses and dose rates) to be implemented in a pilot plant on cork industry.

Acknowledgments

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EXTENSIVE USE OF GAS CHROMATOGRAPHY – MASS SPECTROMETRY FOR THE CHARACTERIZATION OF THE EFFECTS OF RADIATION TREATMENT OF WASTEWATER

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Abstract

An ongoing radiolytic study is currently carried out on model wastewater samples spiked with organochlorine insecticides (e.g. hexachlorobenzene (HCB)) and polychlorinated byphenils (PCB, e.g. PCB 52). To identify the most convenient irradiation conditions for wastewater treatment, samples were irradiated at different doses: 1.3, 4.5 and 13 kGy (1.3 kGy/h dose rate).

The dependence of organochlorine insecticides and PCB's concentration of the absorbed dose was monitored by gas chromatography (GC) with simultaneous micro electron capture detection (ECD) and mass spectrometric detection (MS, in single ion monitoring (SIM) mode); using ISO 6468:1996 protocols for sample preparation. The molecular structure confirmation of target compounds and possible persistent organic pollutant (POP) radiolysis products was also performed with the mass spectrometric detector in SCAN mode.

A molecular modelling study is developed to predict the most probable radiolysis products and it is correlated with the GC/MS results to suggest some preferential radiolysis pathways.

1. Objectives of the research

To improve the knowledge on irradiation treatment of wastewater and its side-effects and to prepare the conditions for a large experiment eventually using a mobile e-beam, by:

— assessing GC/MS, GC-ECD and GC-FID as analytical methods for pollutants, radiation by-products and microbiological characterization of wastewater before and after irradiation;
— dose optimization of radiation treatment at laboratory scale and small-pilot scale using a gamma research irradiator;
— to identify most convenient situations for wastewater radiation treatment.

2. Introduction

Other part of the world water crisis is the issue of water availability in the required quantity and quality of life. In Romania, only 80% of all surface water bodies assessed in 2011 meet the environmental objectives (have good ecological status/good ecological potential). Regarding the assessment of groundwater bodies, in 2011, only 82% of groundwater bodies achieve quality objectives. Although Romania is not on a map of the water crisis, water resources of our country are relatively poor and unevenly distributed in time and space. In theory, these amount 134.6 billion m^3 (bcm) (consisting of surface water-rivers, lakes, the Danube - and groundwater), from which the usable resource, according to the degree of

watershed planning is about 40 bcm. Specific endogenous resources of Romania reported to the population number are 1894 m³/year/inhabitant, Romania being one of the countries with the lowest water resources in Europe.

If exogenous water resources (representing the contribution of rivers that form in other countries and then enters the country) are also taking into account (in Romania's case will consist of Danube and the higher streams of Siret basin, about 170 km³/year), Romania's total water resources rise to 212 km³/year. Therefore, Romania depends very largely on water resources coming from different countries upstream. These water resources are not fully usable. Unlike the countries of Western and Northern Europe, the lack of sufficient water resources are likely to become a limiting factor for economic development, if not promoted a strict policy of rational use of water by stakeholders.

For 2011, the volume of water required by businesses is 7.7 bcm of water, down from the previous year and almost three times lower than in 1990. Broken down by categories, total water requirement for 2011 is as follows: 1.22 bcm of water (16%) for the population, 1.32 bcm of water (17%) for agriculture and 5.16 bcm of water (67%) for the industry (http://www.rowater.ro).

In Romania, the degree of connection to sewerage equivalent population is 57%, and the degree of connection to wastewater treatment plants is 46%. In the last 4 years (2007-2011), ca. 2,997,173,000 Eur were invested nationwide for the expansion and rehabilitation works of water infrastructure (http://www.rowater.ro).

Following the accession of Romania to the European Union, have resulted in a number of commitments involving significant investment in water and wastewater sector, over relatively short periods of time. Thus, in accordance with the Accession Treaty, Romania obtained following transition periods for compliance with EC Directive no. 91/271/EEC concerning urban wastewater:

- until 2015, for 263 agglomerations of more than 10,000 inhabitants;
- until 2018, for 2,346 agglomerations between 2,000 and 10,000 inhabitants.

The planned work in these projects aim to achieve a number of about 170 new or rehabilitated wastewater treatment plants and an increase in the volume of treated wastewater, respectively, from 35% to 60%. It is also anticipated an increase in people connecting to water the regional system from 52% to 70% (http://www.rowater.ro).

While several countries worldwide have started feasibility studies for establishment of demonstration plants to treat wastewater for reuse in urban irrigation and some industrial uses. This studies show that the treated municipal and industrial wastewater effluents are still contaminated with persistent organic pollutants (POP), such as pesticides and endocrine disruptors in low concentration and there is a need for optimized and validated analytical methods to fully characterize and evaluate effects of by-products in treated wastewaters.

Another important problem arising is the increasing presence of pharmaceuticals and endocrine disruptors compounds in municipal wastewater entering into the receiving stream, for which new treatment techniques and procedures are needed to remove excreted drugs before releasing the effluent into public waterways or reuse.

We aim to investigate the utilization of ionizing radiation (gamma or accelerated electrons) as an alternative advanced water treatment technology for reuse, with particular focus on wastewaters containing organic pollutants. The research is focused simultaneously on two directions:

—— the degradation of POP and

— - the bioburden reduction in wastewater.

Gas chromatography coupled with mass spectrometry (GC/MS) was chosen, because is able to identify and measure small molecules resulted from POP's irradiation treatment.
In the same time GC/MS is able to identify microorganisms (bacteria) in the frame of a modern molecular biology method, recently introduced in European Pharmacopoeia. This method is based on the identification of a specific pattern of fatty acids from the microorganism cell membrane, by using a large interactive data-base and multivariate data analysis [1, 2].

Organochlorine pesticides and polychlorinated byphenils (PCB) are groups of toxic compounds, most of them being included in the Stockholm convention list of persistent organic pollutants. They are characterized by high chemical stability and may lead to marked changes in the aquatic ecosystem via bioaccumulation and biomagnification. Gamma radiolytic degradation is thought to be a promising treatment for their decomposition to more environmental friendlier compounds.

3. Materials and Methods

The experimental part was focused on optimization and extension of applicability of ISO 6468:1996 standardized analytical method for the validation of radiation treatment of wastewaters containing certain organochlorine insecticides or PCB. The analytical methods used were gas chromatography (GC) coupled with mass spectrometry (MS) and micro electron capture detector (ECD). The decomposition of organochlorine insecticides or PCB from spiked sewer wastewater samples was achieved with gamma irradiation. A GC/MS screening in correlation with a molecular modelling study were also performed for the identification of possible POP radiolysis products.

Two sets of irradiation experiments were performed: one with acetone or methanol as POP's solvents miscible with water; and other with the model wastewater samples used in the irradiation experiments, which had a spiked concentration of 1 ppb POP and 0.1% solvent (methanol).

3.2. Samples and sample preparation

Spiked samples, positive and negative quality controls were prepared as follows:

— sampling: real treated sewer wastewater samples (UN-WW) were taken from the IFIN-HH wastewater treatment station, compact type (in prefabricated container, installed by EDAS EXIM, www.edas.ro), with membrane biological reactor (MBR), and a maximum treatment capacity of 100 m^3/day. Samples were taken in 2.5 l brown glass containers with polytetrafluoroethylene (PTFE) caps (thus avoiding contact with other plastic materials which may serve as adsorbent materials for POP), and stored overnight in a freezer at 4 °C. Next day, samples were decanted and diluted 1 part wastewater at 9 parts deionised water and further used at spiked test specimens preparation.

— negative quality controls (QC-BK) preparation: 1 ml of acetone or methanol (HPLC purity, Sigma-Aldrich) were transferred in 1 l Berzelius graduated beakers and filled with deionised water. High dose Co^{60} gamma irradiation experiments (with absorbed doses of 65 and 130 kGy, 1.3 kGy/h dose rate) were conducted and methanol was selected over acetone, because acetone produced flocculation after irradiation.

— positive quality controls (QC-HCB or QC-PCB52) preparation: 1 ml of methanol with 1 ppm hexachlorobenzene (HCB) or 2,2',5,5'-tetrachlorobiphenyl (PCB 52) were transferred in 1 l Berzelius graduated beakers and filled with deionised water. The final POP's concentration was 1 ppb HCB or PCB 52 in water.

— spiked test specimens (QC-WW-HCB or QC-WW-PCB52) preparation: 1 ml of methanol with 1 ppm HCB or PCB 52 were transferred in 1 l Berzelius graduated beakers and filled with diluted real treated sewer wastewater (wastewater : deionised water = 1 : 9). The final POP's concentration was 1 ppb HCB or PCB 52 in water. The spiked test specimens were stored at 4 °C until analysis.

Standard solutions preparation for GC quantitative analysis: 10 mg of HCB or PCB 52 (reference standards for GC purity) were transferred into volumetric flasks of 100 ml, further filled with n-hexane (for GC-MS & GC-ECD calibration curves) or methanol (for preparation of QC-HCB or QC-PCB52 and QC-WW-HCB or QC-WW-PCB52), thus obtaining stock standard solutions of 100 ppm (POP's concentration, stable for maximum one year at 4 °C). Standard solutions of 1000 ppb, 100 ppb, 10 ppb, 1 ppb and 0.1 ppb of HCB or PCB 52 were prepared, according to the GC-ECD method linearity range (between 0.1 ppb & 1000 ppb, the detector commonly exhibiting a 10,000-fold linear range).

3.3. Irradiation experiments

To identify the most convenient irradiation conditions for experimental model sewer wastewater treatment, samples were irradiated at IRASM Multipurpose Irradiation Facility (IFIN-HH, Bucharest-Magurele), a SVST Co-60/B tote-box, wet storage (max. 2 MCi) industrial gamma irradiator (360 kCi in Jan 2012). The absorbed doses were 1.3, 4.5, 13, 65 and 130 kGy (1.3 kGy/h dose rate). The dosimetry was performed with ethanol-chlorobenzene (ECB) dosimeters ($\pm$ 2% standard deviation) [4].

Two consecutive irradiation experiments were carried out:

— first, for establishing the stability of spiking solvents (acetone versus methanol, with a concentration of 0.1% in deionised water) to irradiation treatment, after an intriguing initial irradiation experiment which led to solution colouring into white-yellow and decantation of yellowish deposits (fig. 1). The absorbed doses of 65 and 130 kGy were 100 times higher than doses usually used in industrial applications for wastewater treatment. At high dose acetone reacted with water intermediates, which produced colloidal particles. Methanol was more stable (fig. 2), no significant turbidity was observed, and for this reason it was selected for the POP's irradiation decomposition experiments.

— second, for establishing the absorbed dose which will reduce 10 times the target POP's concentration in sewer wastewater for our experimental irradiation geometry (fig. 3). The purpose of the experiments was to develop a validation protocol for radiation decomposition of target POPs in sewer wastewater. The experimental absorbed doses were 1.3, 4.5 and 13 kGy (1.3 kGy/h dose rate). The irradiated samples consisted in deionised water (QC-BK) and sewer wastewater spiked with HCB (QC-WW-HCB) or PCB 52 (QC-WW-PCB52) (POP's concentration of 1 ppb) and methanol (0.1%).

Fig. 1. The initial irradiation experiment of acetone (0.1% in deionised water) as spiking solvent for PCB 52 and HCB (having a concentration of 1 ppb in deionised water, obtained by adding 1 ml of acetone with 1 ppm of POPs to 1 l of deionised water): a) - f) unirradited & irradiated positive quality controls before and after liquid-liquid extraction; g) & h) organic phase collected after liquid-liquid extraction before and after separation from interfering matrix by freezing at – 20 ºC.

Fig. 2. First irradiation experiment for establishing the chemical stability of spiking solvents when subjected to irradiation treatment.

Fig. 3. Second irradiation experiment for establishing the absorbed dose which will reduce 10 times the target POP's concentration in sewer wastewater.

3.4. Sample processing

3.4.1. Liquid – liquid extraction

1 litre of test specimen (water sample) is transferred into a separation funnel of 1 l (figures 1 and 3). 100 ml of n-hexane (GC purity, e.g. "pestiscan") is added and mixed for 20 min, followed by phase separation for 10 min (depending on residual wastewater interfering matrix). The aqueous phase is recovered into 1 l Berzelius graduated beaker (the same used for sample preparation and irradiation) and the organic phase is transferred into a 0.5 l Berzelius graduated beaker. The liquid-liquid extraction is repeated 2 times with fresh volumes of n-hexane into the same separation funnel and the organic phases are collected and reunited in the same 0.5 l Berzelius graduated beaker.

3.4.2. Separation from interfering matrix

The organic phase collected after liquid-liquid extraction was cooled down to -20 °C, and kept for 2 hours (figure 1). Depending on the interfering matrix (which can appear sometimes as a foam into the organic phase) a number of freezing cycles between room temperature and -20 °C can be applied, until transparent liquid organic phase is separated from the frozen solid decanted phase. The transparent liquid organic phase is transferred into a glass round-bottom flask for rotary evaporators.

3.4.3. Sample extract concentration

Sample extract was concentrated to a small volume of 0.5 - 1 ml in a constant vacuum of 340 mbar, obtained with Heidolph Laborota 4002 rotary evaporator with vacuum pump. The glass round-bottom flask was thermostated during evaporation on a water bath at 40 °C. The concentrated sample extract was further quantitatively transferred (using an automated micro pipette with disposable PTFE 1000 µl tip) into a 2 ml GC vial. Small volumes of clean solvent were used to wash the evaporation vessel twice for completing the extract volume to 1 ml, and immediately seal the GC vial with a PTFE-silicon-PTFE septum.

The recovery efficiency was calculated based on the nonirradiated spiked quality controls and samples which were processed in the same batch with the irradiated ones.

3.5. The chromatographic analysis GC-ECD&MS

The dependence of organochlorine insecticides and PCB's concentration of the absorbed dose was monitored with gas chromatography (GC) with simultaneous micro electron capture detection (ECD) and mass spectrometric detection (MS, in single ion monitoring (SIM) mode). The molecular structure confirmation of target compounds and possible POP radiolysis products was also performed with the MS detector in SCAN mode.

Agilent GC 6890N was used with the following configuration: auto sampler (with 10 µl Hamilton syringe), programmable temperature vaporizer cold injection system (Gerstel PTV CIS4 with Peltier cooling option) with a straight liner (150 µl, packed with deactivated glass wool), a 1 m x 0.25 mm retention gap connected at one end with the PTV injector and to the other end with a quartz "Y" capillary connection, from which emerge two identical HP-5ms columns, 30 m x 0.25 mm (with 0.25 µm film of (5%-phenyl)-methyl-polysiloxane non-polar, bonded and cross linked stationary phase). Each HP-5ms column was further connected with a detector: one with the Agilent micro electron capture detector (ECD); and the other one with Agilent 5975 inert MSD. The MSD had the following configuration: electron ionisation

source; quadrupolar mass analyser (m/z 2 Da to m/z 1050 Da); and high energy dynode (HED) detector.

The software applications used for GC-ECD & GC/MS data acquisition and data analysis were: Agilent Enhanced Chemstation software (version D.02.00.275); NIST 2005 GC/MS mass spectral library; NIST MS 2.0 library search software and AMDIS (version 2.62) automated mass deconvolution and identification system.

Injection of 1 μl of n-hexane (target POP's concentration of $1 \div 10^{-3}$ ng/μl) was performed in hot (280 °C) splitless mode (1:1) for 1 min, followed by inlet purge at 100 ml/min for 7 min, and inlet purge at 50 ml/min for the rest of chromatographic method and inlet standby mode. Helium (99.9999 % purity) has been used as carrier gas, with a capillary constant flow of 3 ml/min through the retention gap, further divided approximatively into 2 ml/min through the MSD column and 1 ml/min through de ECD column.

Column temperature programming consisted in the following profile: isothermal for 8 min at 80 ℃, ramp with 12 °C/min to 310 °C and isothermal (column conditioning) for 3 min.

3.5.1. Quantitative GC-ECD&MS

The ECD detector had the following parameters: constant makeup flow mode (nitrogen, 60 ml/min, 99.9995% purity), thermostated at 350 °C, data acquisition rate of 50 Hz.

The MSD detector had the following parameters: transfer line set at 280 ℃; electron ionisation source set at 230 ℃; mass analyser set at 180 ℃ and used in single ion monitoring mode (SIM, e. g. for PCB 52 were monitored 5 fragment ions with m/z: 220, 222, 290, 292 and 294 Da), in low mass resolution mode ($0.7 \div 0.9$ Da) with a dwell time of 50 ms (3.65 cycles/sec).

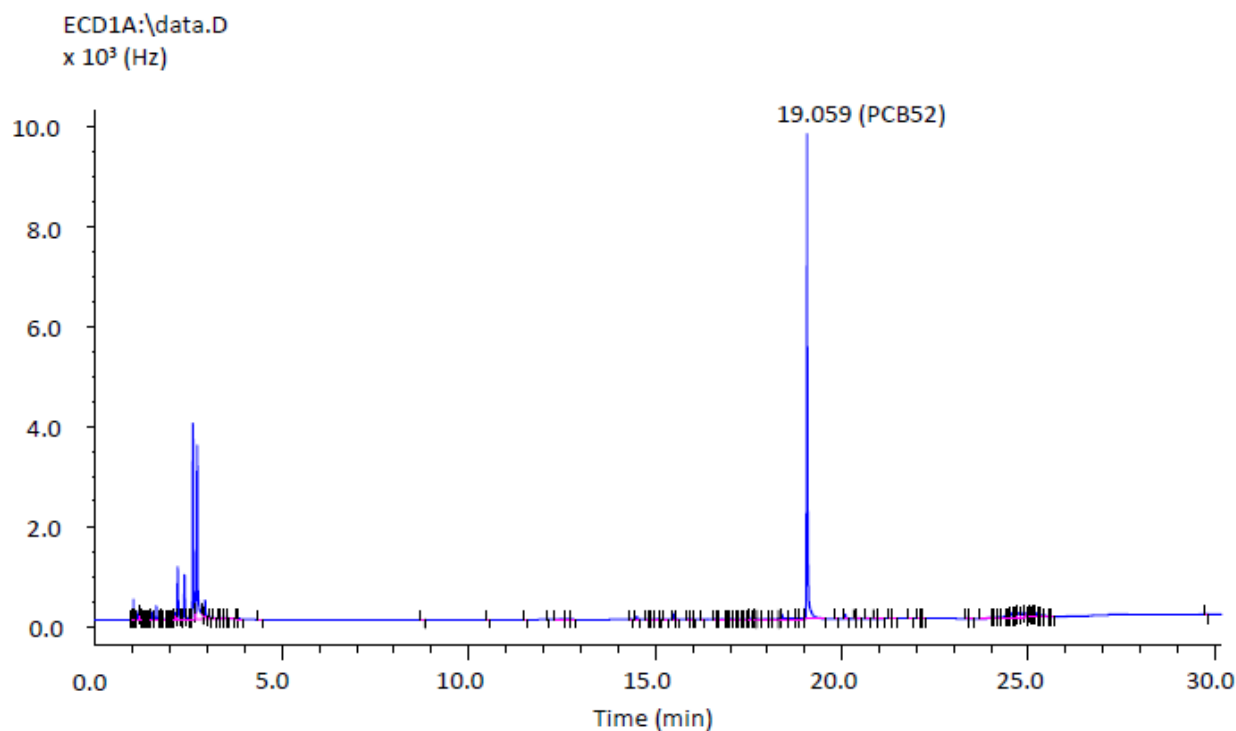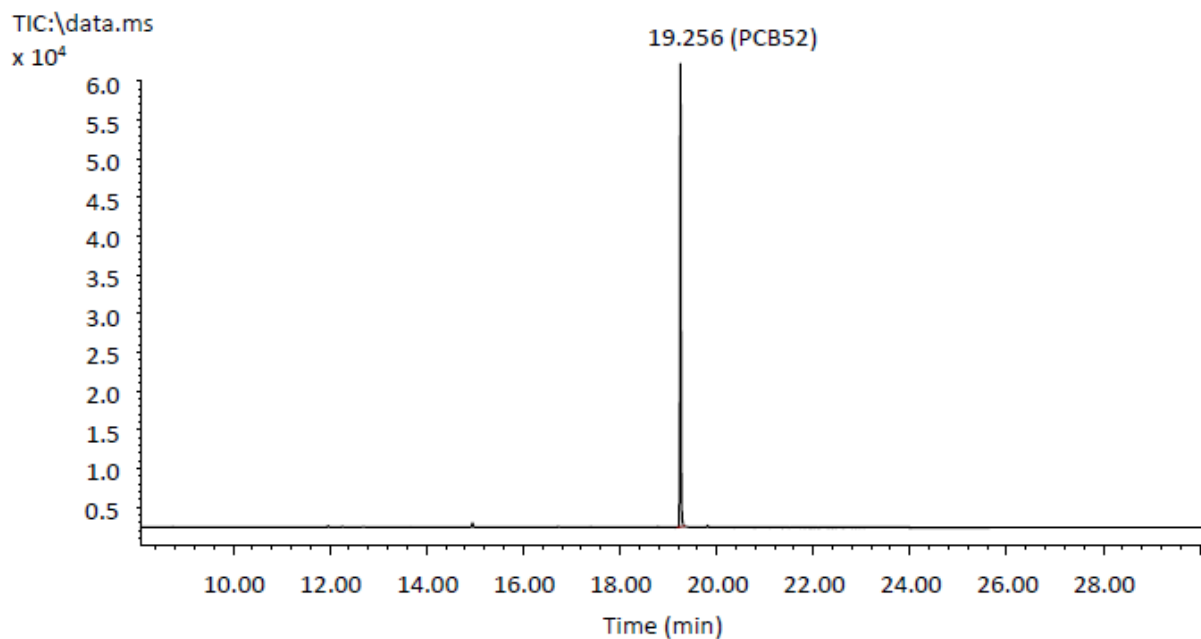The resulting GC-ECD&MS chromatograms for PCB 52 are shown in figure 4.

Fig. 4. Total Ion Chromatogram (TIC, SIM mode) and ECD chromatogram, for the nonirradiated positive quality control with 700 ng/l of PCB 52.

Calibration curves were made for HCB and PCB 52 (see figures 5 and 6) for the concentrations between $0.1 \div 1000$ µg/l of n-hexane, equivalent to $0.1 \div 1000$ ng/l of water.
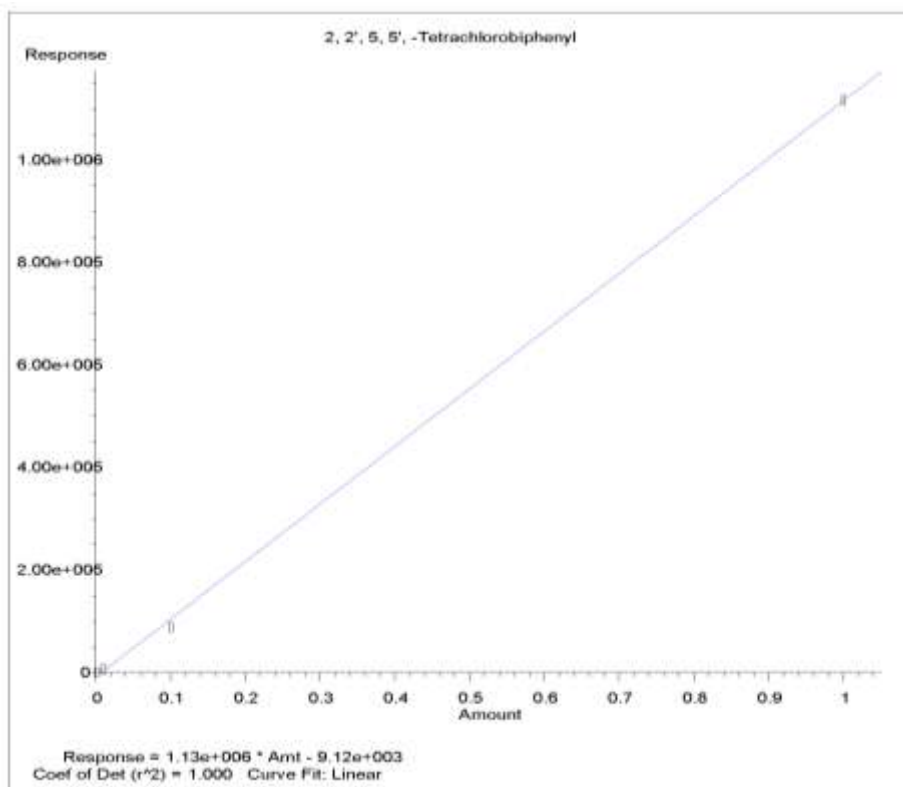
Fig. 5. GC/MS calibration curve for PCB 52 (0.1 ÷ 1000 μg/l of n-hexane, equivalent to 0.1 ÷ 1000 ng/l of water) is best described by a linear fit.
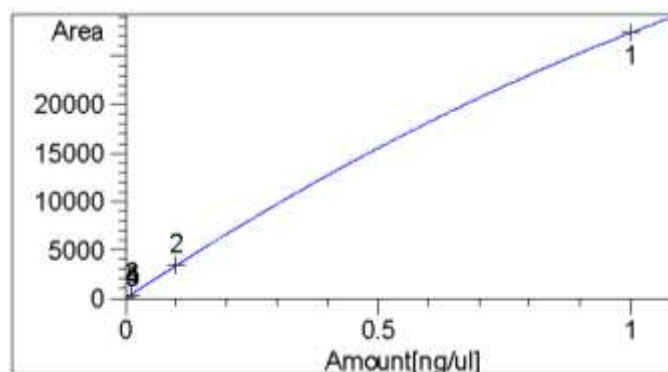

Fig. 6. GC-ECD calibration curve for PCB 52 (0.1 ÷ 1000 μg/l of n-hexane, equivalent to 0.1 ÷ 1000 ng/l of water) is best described by a polynomial regression, as follows: $y = ax^2 + bx + c$; $a = -7109.2$; $b = 34487.1$; $c = 20.4$; y is the peak area; and x is the concentration.

The data analysis of the samples from the second irradiation experiment showed that an absorbed dose of 1.3 kGy reduces 10 times the concentration in water of PCB 52 from 700 ppt to approximatively 70 ppt (see also figure 7).
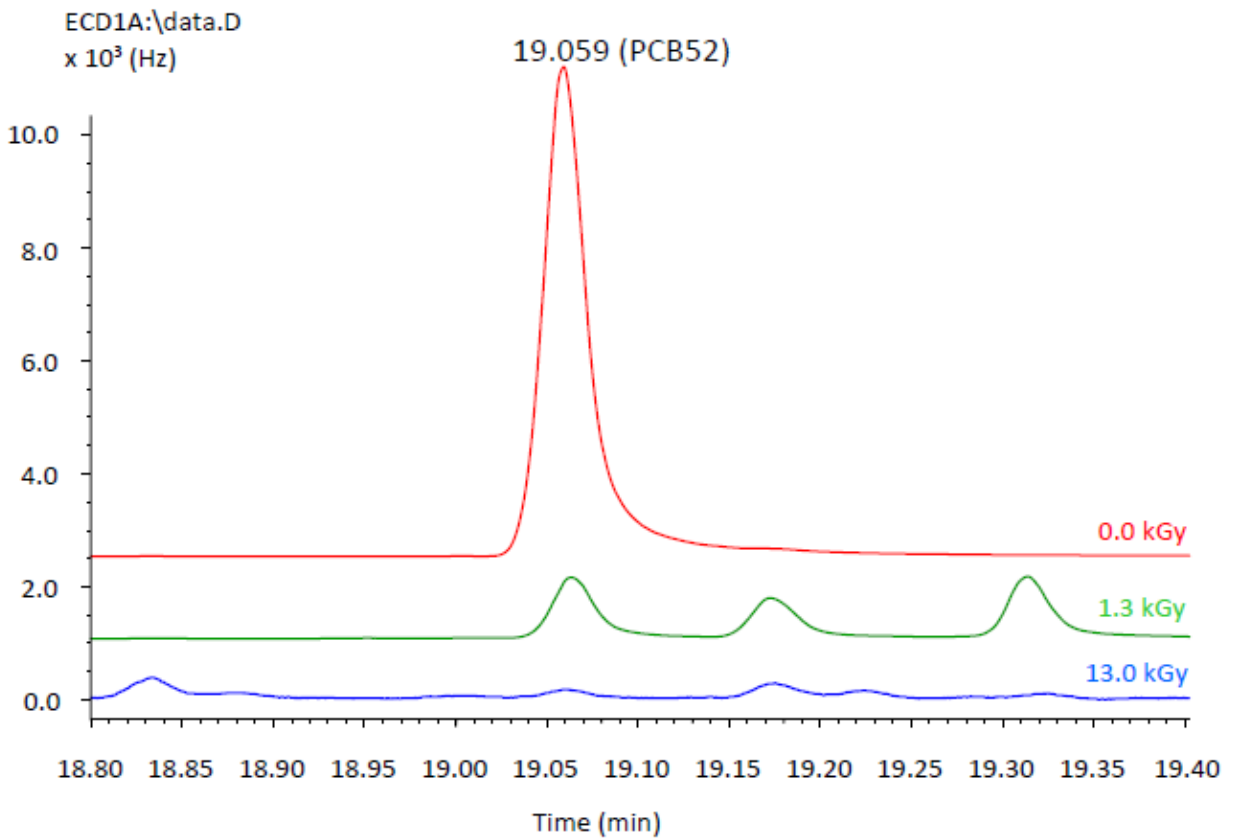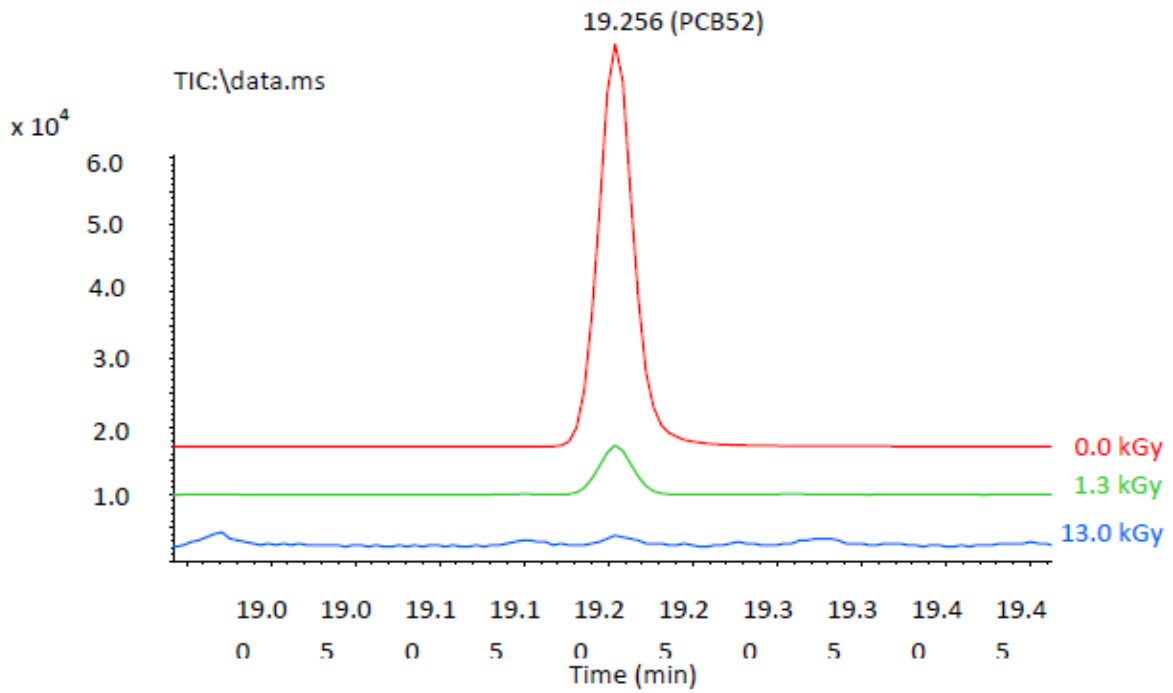
Fig. 7. Total Ion Chromatogram (SIM) and ECD chromatogram, for the nonirradiated (700 ng/l) and irradiated positive quality control spiked with PCB52.

3.5.2. GC/MS screening

The MSD detector had the following parameters: same temperatures on transfer line and MSD zones, except the detector has been used in SCAN mode, screening for fragment ions with m/z between 50 and 550 Da, with 1 Da mass spectral resolution, corresponding to an data acquisition rate of 2^3 scans/Da or 1.5 scans/sec. Noise was minimized by using a threshold of 100 cps/Da. The mass spectral data acquisition parameters were similar with the ones used for MSD tuning (for both mass axis and spectral intensity) with PFTBA (PerFluoroTriButylAmine), thus making the identification of deconvoluted experimental mass spectra in NIST 2005 GC-MS library more reliable, especially when combined with retention time or retention index in AMDIS.

The molecular structure confirmation of target compound in irradiated samples has been done with the MSD in SIM detection mode, based on the relative abundances of the five specific fragment ions, in comparison with experimental mass spectra acquired in SCAN mode and the one from NIST 2005 GC/MS library (e. g. PCB 52 – see figure 8).
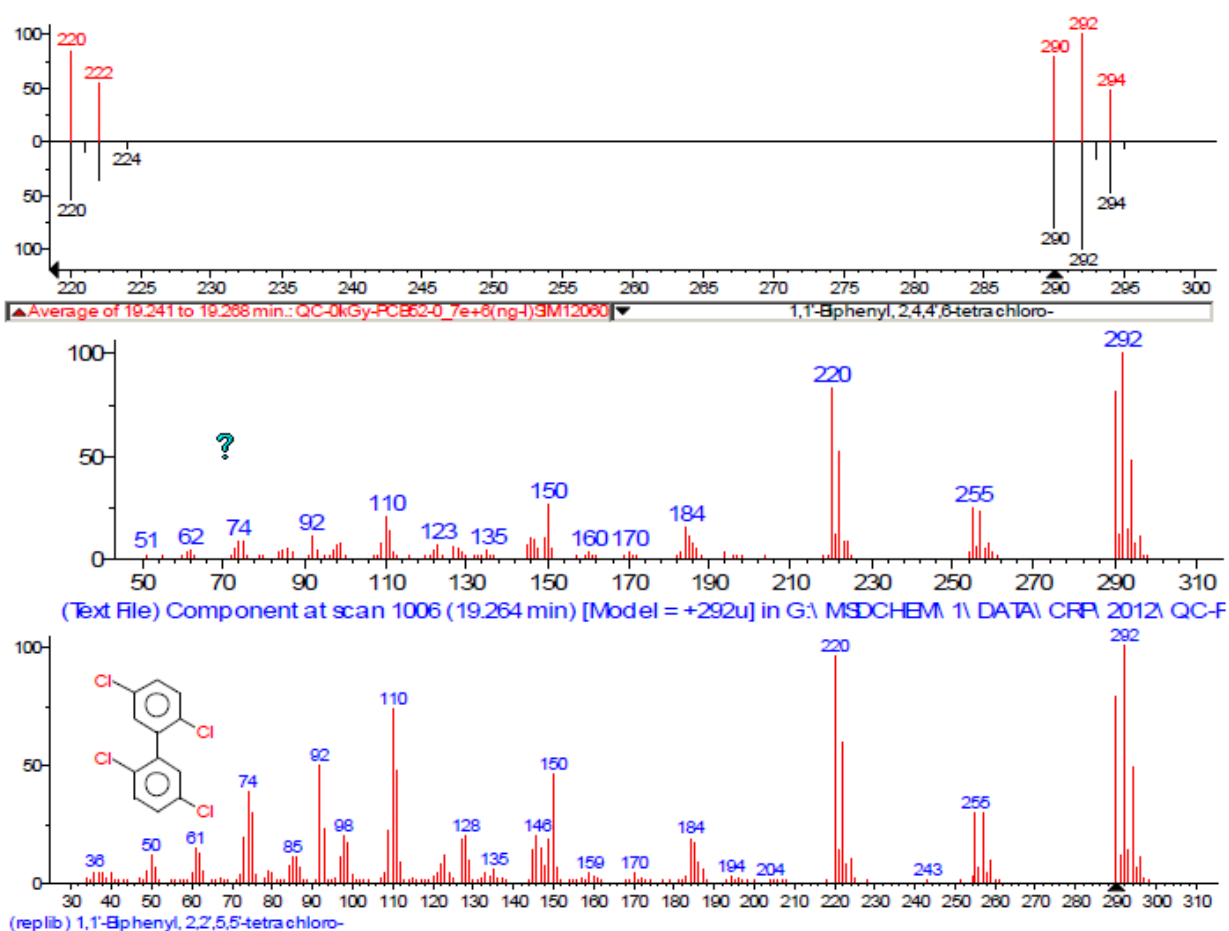

Fig. 8. PCB52 target compound molecular structure confirmation, experimental SIM and SCAN spectra versus NIST 2005 GC/MS library spectra for the nonirradiated (0 kGy) positive quality control water sample.

The GC/MS screening in SCAN mode was unable to evidence the presence of proposed persistent organic pollutants radiolysis products formed by successive attacks either with solvated electron (figure 9, proposed molecular structures $A_1 \div A_4$), either with hydroxyl

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radical (figure 9, proposed molecular structures $B_1 \div B_4$). This may be also because the mass spectrometer sensitivity in SCAN mode is almost 100 times lower than in SIM mode, or because of further degradation competing processes. Other studies in correlation with molecular modelling may be performed in order to determine the order of magnitude for the concentration of possible POP radiolysis products, whether it is significant or not when compared with the concentration of parent molecules and with the detection limits of the current available instrumentation.
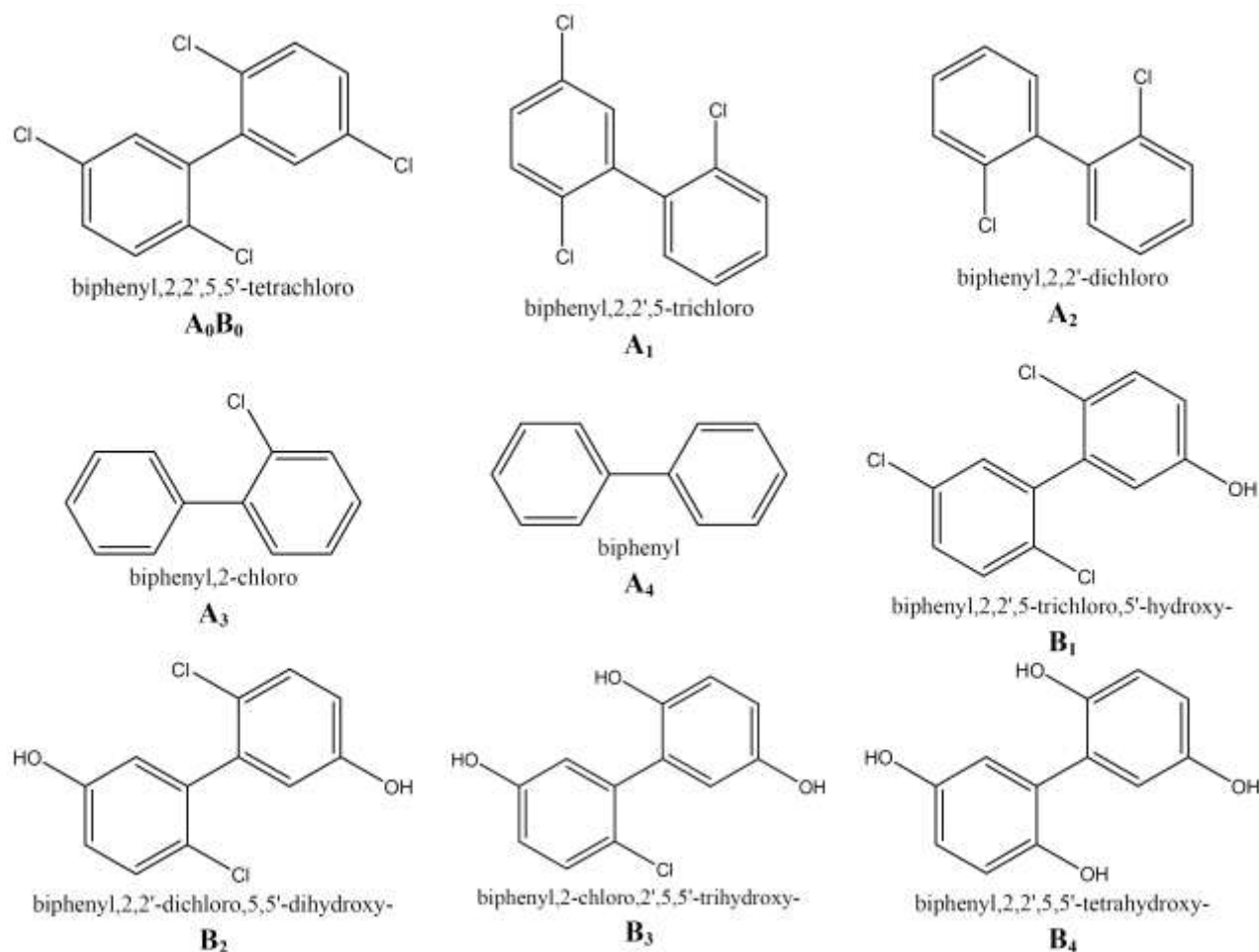
Fig. 9. Molecular structures of proposed radiolysis products formed by reaction mechanisms: A) with solvated electron (A1 ÷ A5); and B) with hydroxyl radical (B1 ÷ B4).

3.6. Molecular modelling

A molecular modelling study is developed to predict the most probable radiolysis products and it is correlated with the GC/MS results to suggest some preferential radiolysis pathways. Modelling of the reactants, transition states and products was done with quantum semi-empirical AM1 and PM3 methods, included in Hyperchem (and Ampac) program(s). Starting geometry of POP and theirs derivatives was obtained from the 2D manual drawing of the molecule and from the 3D automatic builder molecular model. To obtain an accurate structure, geometry optimization with Polack-Ribiere algorithm, Restricted and Unrestricted Hartree Fock approximations and gradient of 0.01 kcal/mol·Å was done. Heat of formation, activation energy, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest

Unoccupied Molecular Orbital) frontier orbitals energy and shape, were obtained and correlated with the compounds reactivity.

4. Conclusions

The above methods and procedures will help to better assess the usefulness and limitations of GC-ECD and GC-MS for routine monitoring and screening of organochlorine insecticides or PCB in municipal wastewater after gamma irradiation treatment for biological bioburden decrease and POP decomposition.

Gamma irradiation experiments on spiked wastewater with PCB 52 enabled us to calculate the dose necessary to decrease 10 times the concentration of PCB 52. The GC/MS screening in SCAN mode was unable to evidence the presence of POP radiolysis products. Other studies in correlation with molecular modelling may be performed in order to determine the order of magnitude for the concentration of possible POP radiolysis products, whether it is significant or not when compared with the concentration of parent molecules.

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RADIATION INDUCED TREATMENT OF ORGANIC POLLUTANTS

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Abstract

In this period of the research, aerobic and anaerobic digestion, characterization of alkaloids present and radiolysis products formed after irradiation, under different conditions of ambient and additives, optimization of dose to achieve desired end characteristics for discharge of waste water were aimed. In this regard, unirradiated and irradiated wastewaters were subjected to aerobic and anaerobic digestions. Substrate removal efficiencies of unirradiated and irradiated wastewater with various initial COD values were determined with SBR aerobic digestion treatment method. On the other hand Fenton's advanced oxidation treatment method was also applied for pre-treatment. BMP tests of anaerobic digestion were also completed. LC/MS studies were carried out on unirradiated and irradiated alkaloid standard solutions of morphine, codeine, thebaine, papaverine, and noscapine to determine the degradation mechanisms and byproducts. Dose optimization studies were completed and found to be a lower dose of 5 kGy rather than 40 kGy for ambient irradiation conditions.

1. Objective of the research

The main objective of the research was to investigate the aerobic/anaerobic biological treatability of opium alkaloid industry wastewaters in conjunction with irradiation as a means of pre-treatment and the tasks carried out during frame time of the research are:

— Aerobic and anaerobic digestion studies of the radiation treated waste water.
— Characterization of specific organic pollutants present and radiolysis products formed after irradiation.
— Irradiation of alkaloid industry waste water under different conditions of ambient and additives and study the effect on effluent characteristics
— Optimization of absorbed dose to achieve desired end characteristics for discharge of waste water.

2. Introduction

Opium alkaloid industry produces mainly morphine to be used in medical field. Licensed opium poppy cultivation for medical purposes currently takes place in 12 countries around the world. The four main producers are India, Australia, Turkey and France. Opium Alkaloid Plant in Afyon, Bolvadin produces around 30% of global morphine production. Consequently, alkaloid industry is important for Turkey from financial and prestigious point of view. Effluent generated from alkaloid extraction and processing is on average 480 m^3/day. The average hourly flow rate of the wastewater is about 27.5 m^3/h. The effluent is discharged to Eber Lake through Akarçay River.

The wastewater generated by the opium alkaloid industry is heavily polluted with very high COD and BOD_5 content, and have intense dark brown color. Color causing substances in wastewater are almost totally dissolved and resistant to biodegradation. The pollutant

constituents in alkaloid wastewater mainly consist of morphine, codein, thebain, papaverine, noscapine, protopine, laudonosine, wax-like substances and cellulose.

3. Materials and metods

Each sample was irradiated at ambient atmosphere and temperature with a source of gamma irradiation ^{60}Co at a dose rate of 0,67 kGy/h.

3.1. Aerobic biotechnology

The bacterial seed sludge used in the preliminary batch treatability studies was taken from an aerobic membrane bioreactor (MBR) treating domestic wastewater of ODTUKENT area at Middle East Technical University (METU) campus. Inoculum used in all the later studies, including batch and sequencing batch reactors, was obtained from the return line of the activated sludge unit of the Ankara Central Wastewater Treatment Plant. Prior to use, activated sludge was aerated one day and washed two times with tap water.

3.1.1 Unirradiated Wastewater

Aerobic biological treatability of opium alkaloid wastewater was investigated in batch reactors. Various pre-designated initial concentrations of wastewater (COD between 2,500 and 26,000 mg/L) were added into reactors inoculated with unacclimated culture. It is obvious from the results obtained that the wastewater is not inhibitory to bacteria even at the highest concentrations studied, i.e. there is no substrate inhibition. Results show also that almost all of the COD biodegradation occurs within the first 5 days for batch run 1, and occurs around 10 days for batch run 2. In experiments with high initial organic loads, namely 7,000, 18,000 and 26,000 mg/L, a slight increase in COD values is observed in the first day of experiment. Unacclimated biomass removed 83 – 90 % of the organic carbon, depending on the initial COD values. Overall, these results suggest that the opium alkaloid wastewater has a good biodegradability and therefore it is suitable for aerobic biological treatment.

3.1.2. The effect of Irradiation on Biological Treatability

In order to see the effect of irradiation on the biodegradability of opium alkaloid wastewater, BOD and COD measurements were performed on wastewater irradiated at doses 40 kGy and 140 kGy. Unirradiated and irradiated wastewater samples with various initial COD concentrations were fed to reactors. Substrate removal efficiencies that were achieved with irradiated wastewaters were slightly lower than the case with unirradiated wastewater (Table 1).

Apart from this, another set of batch experiments was conducted with wastewaters, both raw and irradiated (COD around 35,000 mg/L). In order to simulate the conditions in conventional activated sludge systems, reactors were inoculated with higher amount of seed sludge, which was around 3,000 mg/L. COD removal efficiencies obtained were as high as 89, 88 and 84 % for unirradiated, 40 kGy and 140 kGy irradiated samples fed into reactors, respectively.

Initial COD	Substrate Removal %		
(mg/L)	Unirradiated	40 kGy	140 kGy
3,000	82	80	78
5,000	84	81	79
10,000	87	84	82
20,000	94	87	82
30,000	91	87	-

The COD removal efficiency in reactor fed with 40 kGy irradiated wastewater was only
slightly better than the case with raw wastewater. Hourly COD degradation profile for the
reactor fed with 40 kGy irradiated wastewater is shown for one cycle in Figure 1. Profile
suggests that almost all COD removal (corresponding to 99 % of the total COD removal)
occurred in approximately 5 hours as similar to the case with raw wastewater. Other than that,
the application of higher radiation dose, namely 140 kGy, seems to have resulted in lowered
COD removal efficiency.
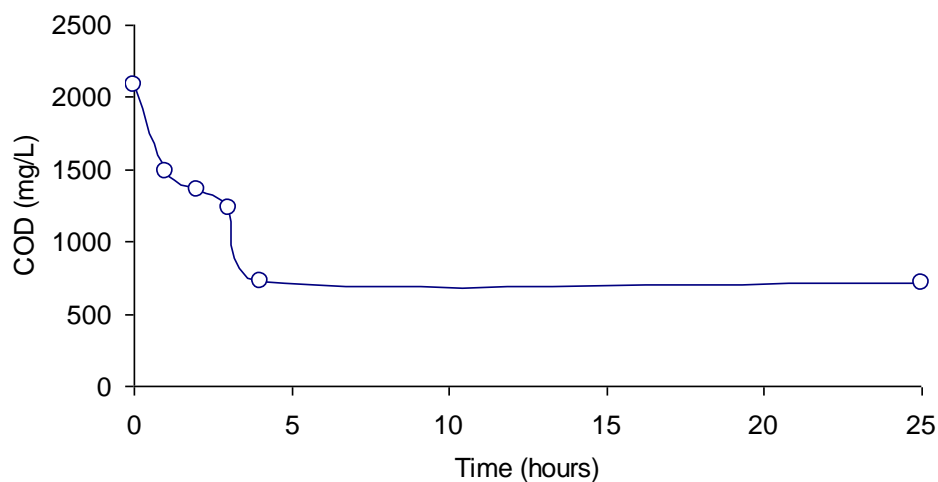
Fig. 1. Degradation of COD over time in SBR reactor fed with 40 kGy irradiated wastewater.

3.1.3. Fenton's Oxidation as a Pre-treatment

In this part, results obtained from the Fenton's oxidation, which was applied as a pre-
treatment alternative process, are presented. Firstly, a preliminary study was conducted in
order to assess the required initial doses of Fenton's reagents to initiate the research. A set of
experiments was conducted in order to examine the effect of hydrogen peroxide dosage at
different reagent ratios. First, hydrogen peroxide concentration was kept constant at 30 g/L
and $FeSO_47H_2O$ dose was varied so as to provide H_2O_2 / Fe^{+2} mass ratios between 0.5 and 5.
Experiment was repeated for 10 and 20 g/L hydrogen peroxide doses respectively providing
the same H_2O_2 / Fe^{+2} ratios. Higher hydrogen peroxide concentrations resulted in better COD

removals due to generation of greater amount of ˙OH radicals. At all fixed dosages of peroxide (10, 20 and 30 g/L) COD removal performances increased with increasing iron dosages. For H_2O_2 dosage of 30 g/L such increase was not as significant in comparison to other oxidant doses. H_2O_2/Fe^{+2} mass ratio of 0.5 provided the best COD removal efficiencies at all H_2O_2 dosages studied. However, it should be noted that, the use of greater amounts of iron should be avoided as the removal of settled iron hydroxide sludge would require an additional treatment step resulting in higher cost[1]. Therefore, in the following experiments optimum concentration of Fe^{+2} was sought keeping the hydrogen peroxide concentration constant at 30 g/L, where better removal efficiencies were obtained, especially at lower iron dosages. The results are shown Figure 2. As it is seen in Figure 2, 6 g/L Fe^{+2} concentration was the optimal dosage resulting in approximately 44 % COD removal efficiency. However, for 480 m^3/day flow rate of Afyon alkaloid factory, this treatment would require very high amounts of both chemicals which would be neither economical nor feasible.

3.2. Anaerobic biotechnology

Mixed anaerobic cultures, which were used in Biochemical Methane Potential (BMP) assays were obtained from anaerobic sludge digesters of the Greater Municipality of Ankara Tatlar Domestic Wastewater Treatment Plant. The digesters have a retention time of 14 to 20 days and pH measured in the digester ranges from 7 to 7.5.
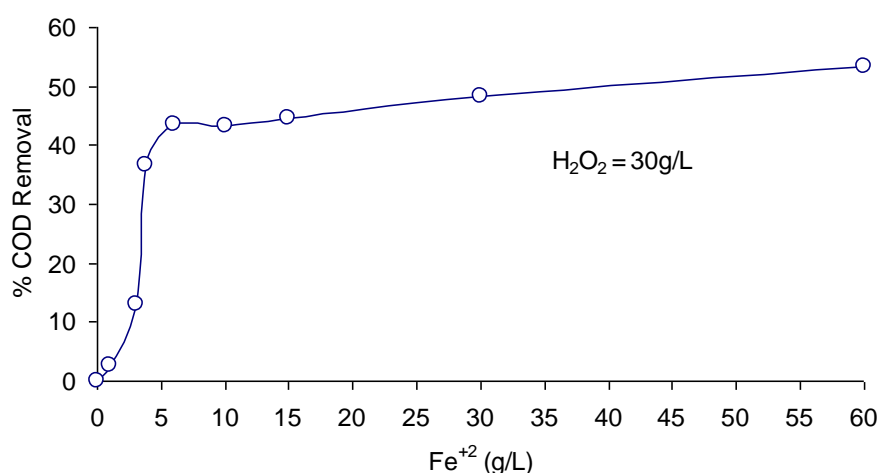

Fig. 2. Effect of Fe^{+2} dosage on COD removal efficiency at constant $H_2O_2 = 30$ g/L.

3.2.1 BMP assay for treatability of opium alkaloid wastewater

Treatability of opium alkaloid wastewater was investigated by means of BMP assay for initial COD concentrations of 2400, 6000 and 9600 mg/L with and without basal medium. The cumulative gas production for these three concentrations and control reactors were given in Figure 3. It can be seen from Figure 3 that no significant gas production was observed for both seed control reactors with and without basal medium (BM) throughout the experimental period of 48 days. This result pointed out that basal medium and seed cultures did not have a significant contribution to the cumulative gas production, although gas produced in the control reactor with BM was slightly higher than gas produced in the control reactor without BM. The difference was due to presence of basal medium. Gas produced in other reactors was emanated from biodegradation of alkaloid wastewater and net cumulative

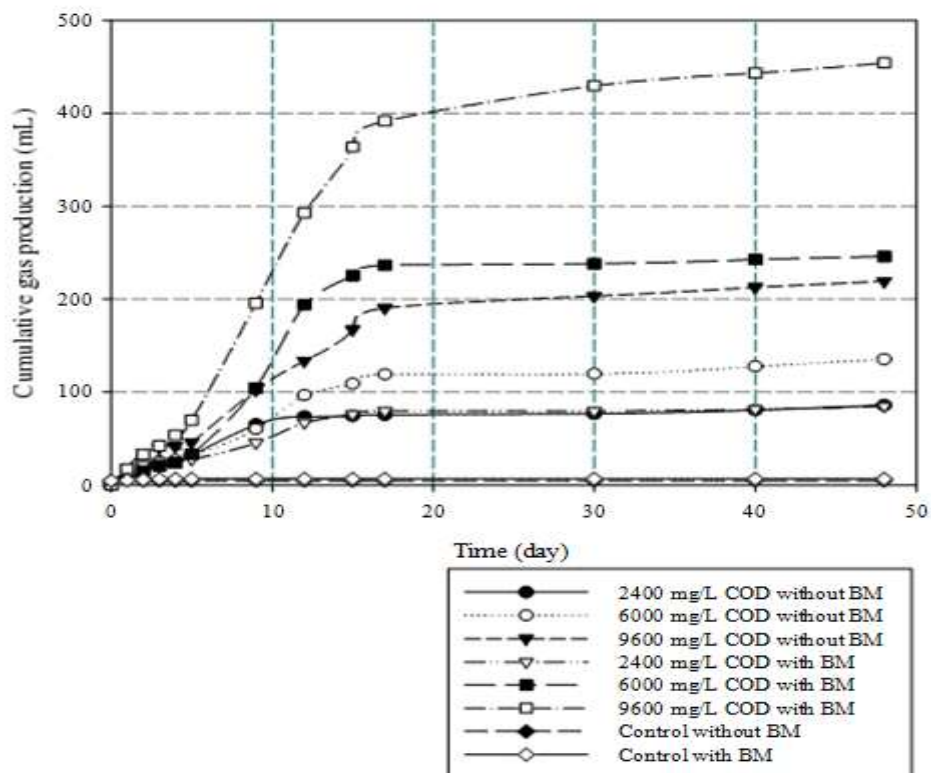gas production (NCGP) for these reactors were calculated by subtracting seed control gas.

Fig. 3. BMP experiment result for opium alkaloid wastewater (2400, 6000 and 9600 mg COD/L) with and without basal medium.

3.3. LC/MS studies of standard solutions of opiates

Irradiated and unirradiated opiate standards solutions were analyzed by high performance liquid chromatography (HPLC:Waters 2695 separation module) coupled with mass spectrometry (Waters Micromass ZQ) using a reverse phase column (INERTSIL ODS 3.3 μm, 15cm×3.2mm i.d.) from Hichrom. The initial HPLC conditions were 5% methanol and 0.5% acetic acid in water, at flow rate of 0.3 mL/min. The column was then developed to 100% methanol over 40 min. The positive mode of electron spray was employed for ionization of the analytes. Parameters were: capillary voltage 4.25 kV, cone voltage, 70 V; source temperature, 150°C; desolvatation temperature, 450°C; cone gas flow, 250 L/h; desolvatation gas flow, 500 L/h. Nitrogen was used as desolvation and nebulization gas.

3.3.1. Characterization of Organic Pollutants and Radiolysis Products

Five opiate standards were disolved in methanol and the solutions were irradiated with γ-ray at different doses. Then both unirradiated and irradiated standard solutions were analyzed with LC/MS in order to examine degradation mechanism and the radiolysis byproducts. Obtained mass spectrum of morphine standard solutions irradiated at 0, 10, 30 and 50 kGy and their fragment ions are given in Figure 4 and Scheme 1, respectively.
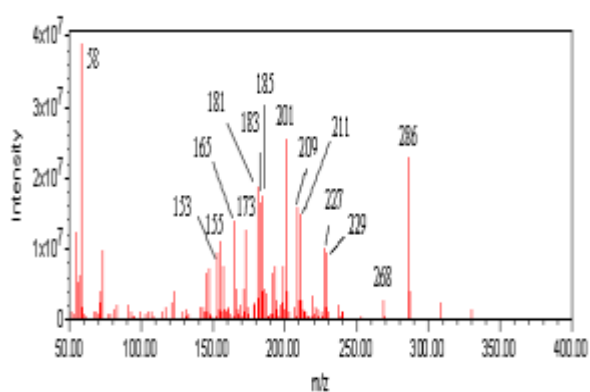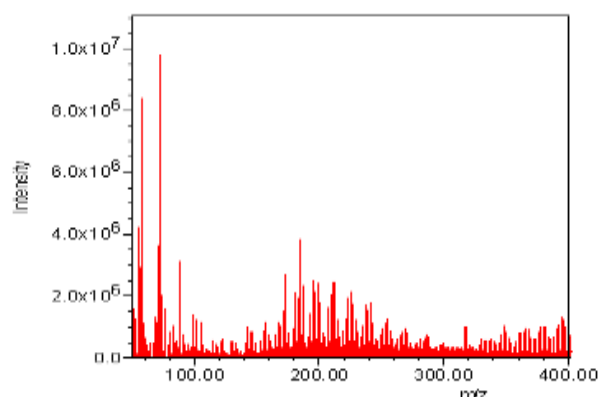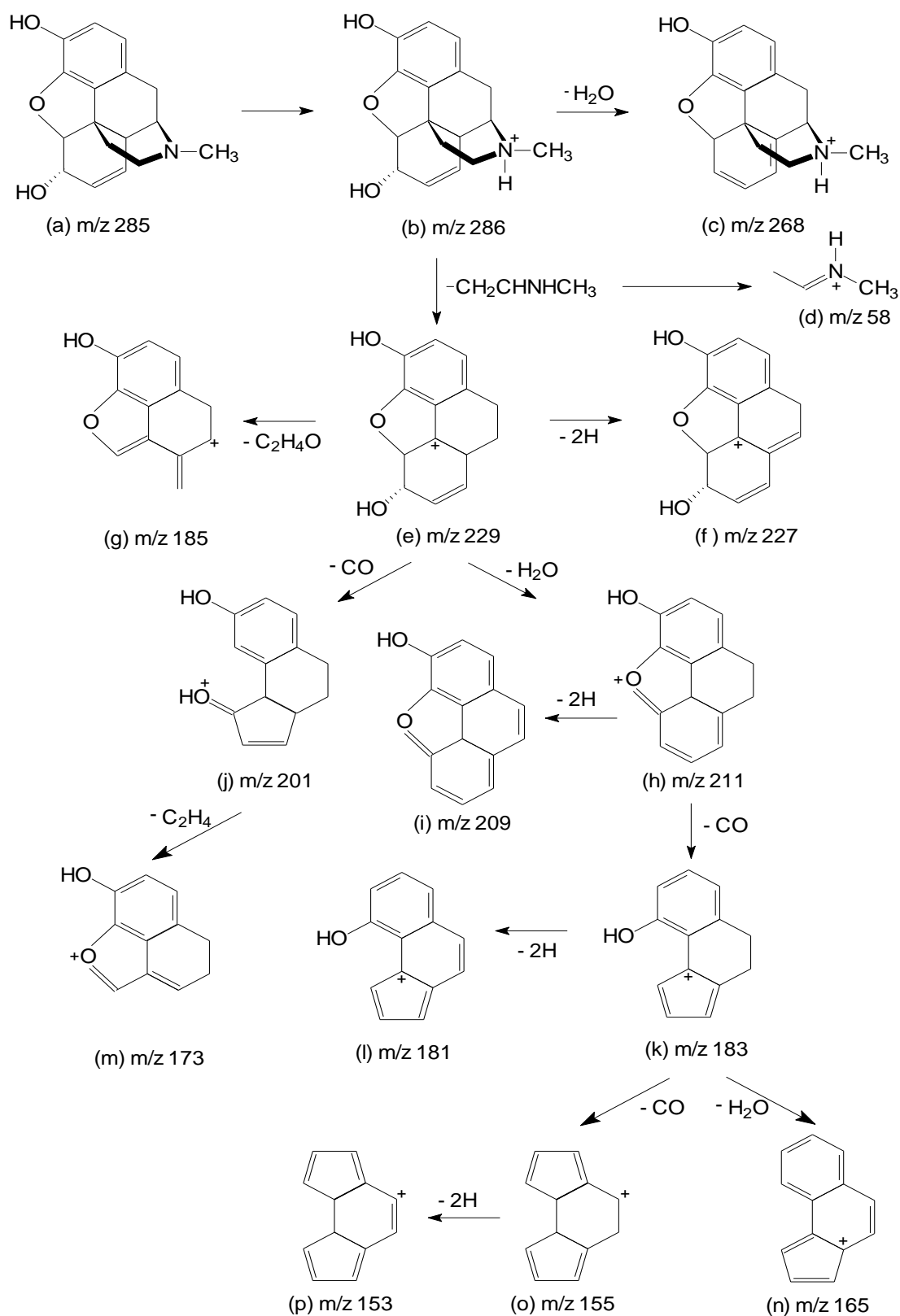
Morphine
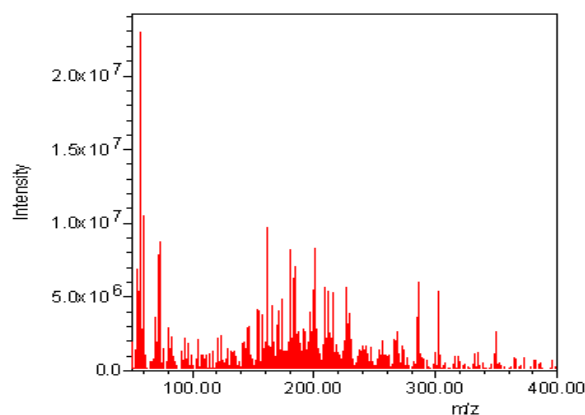
Morphine 10 kGy
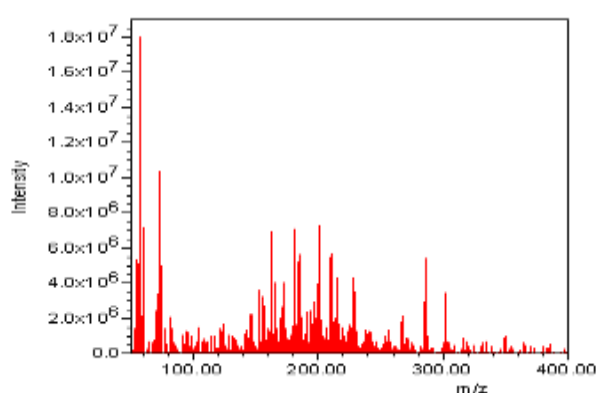

Morphine 30 kGy

Morphine 50 kGy

Fig. 4. Mass spectra of morphine solutions.

Methanol solutions of five opiate standards were irradiated with γ-rays at 10, 20, 30, 40 and 50 kGy and their mass spectra were obtainedwith LC/MS. Concerning the LC/MS analyses of the irradiated sample solutions, following things were found. The intensity of the protonated parent species (m/z 286 for morphine, m/z 300 for codeine, m/z 312 for thebaine, m/z 340 for papaverine and m/z 414 for noscapine) and the fragment ions are decreased with increasing doses. However, after the initial irradiation doses several degradation products are observed for mophine, codeine and thebaine. It is suggested that these products are formed by the addition of the methoxy radical ($CH_3O\cdot$) to the parent molecules[2].

Besides this, oxidation and reduction reactions occur, due to these reactions degradation products which has higher m/z values than the parent species were seen in the spectra. At higher dose values these molecules could not be observed. It is said that the percentage degradation of opiates is higher (less degradation products are formed) in the case of higher dose values. Obtained mass spectrum of irradiated morphine solution and degradation products are given in Scheme 2.

Scheme 1. Fragmentation of protonated morphine, m/z 286 (structure b)
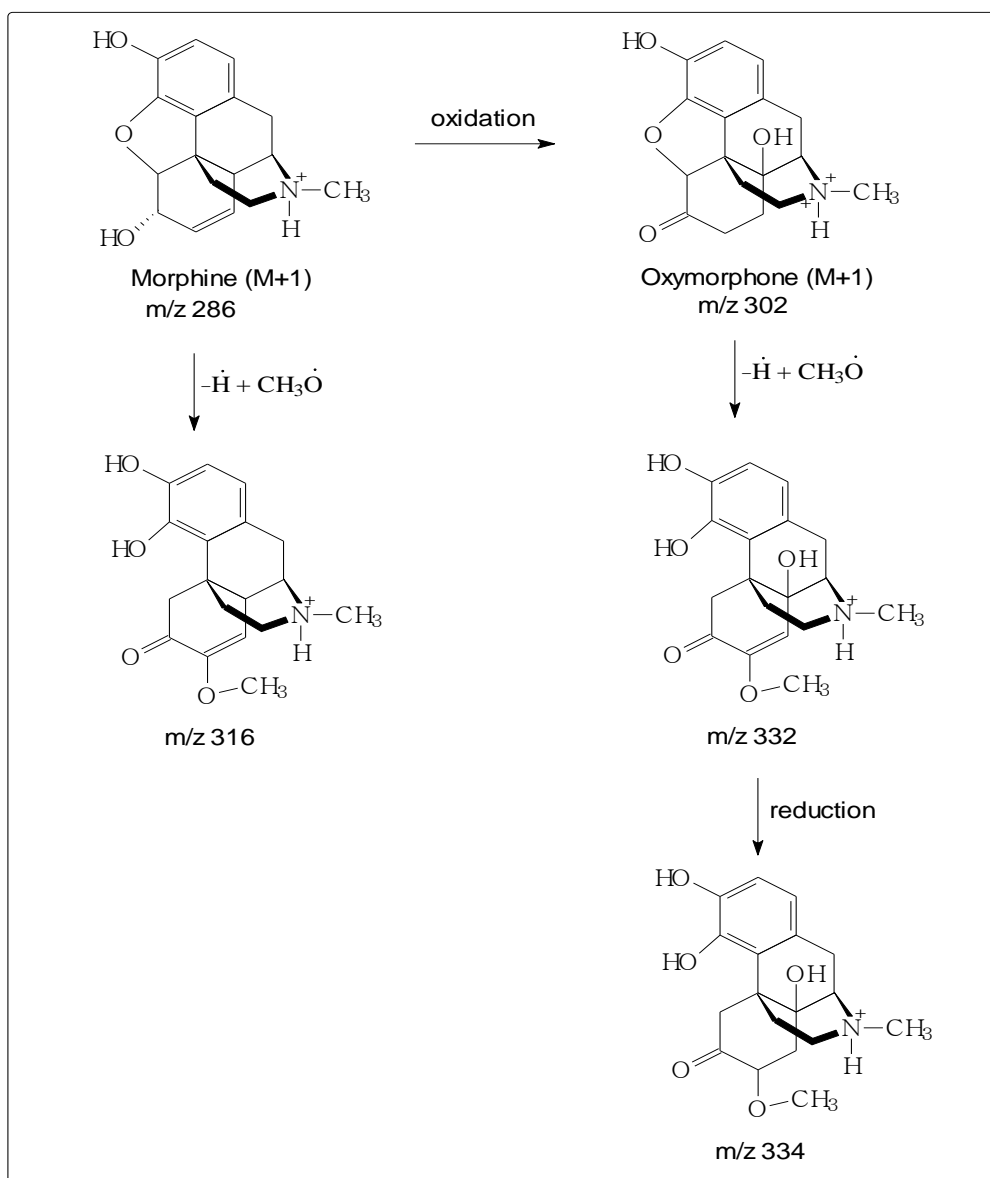
Scheme 2. Mass fragments of irradiated morphine solution.

As it was seen from the mass spectra and degradation mechanisms at low dose values of gamma rays irradiation, an addition reaction of a solvent radical (CH₃O·) was the dominant process. The radical adduct abstracts hydrogen from solvent molecule to reproduce a solvent radical. However, at the higher dose values degradation products could not be observed. Therefore, degradation efficiency of opiates is increased by applying higher dose values (≥50 kGy).

References

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ADVANCED OXIDATION DEGRADATION OF DICLOFENAC

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Abstract

Advanced oxidation/reduction processes (AO/RPs), utilize free radical reactions to directly degrade chemical contaminants as an alternative to traditional water treatment. This study reports the absolute rate constants for reaction of diclofenac sodium and the model compound (2, 6-dichloraniline) with the two major AO/RP radicals; the hydroxyl radical (•OH) and hydrated electron (e^-_{aq}). The bimolecular reaction rate constants (M^{-1} s^{-1}) for diclofenac for •OH was $(9.29 \pm 0.11) \times 10^9$, and, for e^-_{aq} was $(1.53 \pm 0.03) \times 10^9$. Preliminary degradation mechanisms are suggested based on product analysis using ^{60}Co γ-irradiation and LC-MS for reaction by-product identification. The toxicity of products was evaluated using the *Vibrio fischeri* luminescent bacteria method.

Introduction

There is a rising concern about the occurrence and persistence of Pharmaceutical and Personal Care Products (PPCPs) in the aquatic environment, due to their potential impact on the aqueous ecosystems and human health (Schwarzenbach et al. 2006, Kumar and Xagoraraki 2010). The worldwide consumption of medicines provides a continuous release of the substances or their metabolites in the environment. Conventional wastewater treatment systems such as filtration and activated sludge do not efficiently remove many of these PPCPs and as a result they have been found in a wide range of environmental samples including surface water, groundwater and drinking water (Kolpin et al. 2002, Kim et al. 2007). Therefore, advanced treatments technologies need to be evaluated and eventually employed, that are capable of either the complete removal of these chemicals from wastewater or at the very least the destruction of their biological activity (Snyder et al. 2003).

Recently studies indicated that the nanofiltration and reverse osmosis processes guarantee the rejection of PPCPs (Radjenovic et al. 2008). However, biofouling of membrane elements and disposal of retentate are considered major problems in these processes (Snyder et al. 2007, Wintgens et al. 2006, Ben Abdelmelek et al. 2011). Ozonation can destroy some of PPCPs in raw and/or clarified water; unfortunately, the competition between the PPCPs and organic material in the raw water may lead to rapid depletion of ozone, resulting in incomplete oxidation of PPCPs (Ikehata et al. 2006).

Advanced oxidation/reduction processes (AO/RPs) are alternatives to traditional treatment and have recently received considerable attention for PPCPs removal. AO/RPs typically involve the formation of hydroxyl radicals (•OH) as oxidizing species and either hydrated

electrons (e^-_{aq}) as reducing species, both can be utilized in the destruction of organic pollutants present in drinking or wastewater. AO/RPs are effective in the treatment of a variety of anthropogenic pollutants including PPCPs (Song et al. 2009, Song et al. 2008a, Song et al. 2008b). However, to provide a fundamental understanding of the applicability of these processes to degrade PPCPs, it is necessary to determine the bimolecular reaction rate constants and degradation mechanisms, more important, degradation products toxicities.
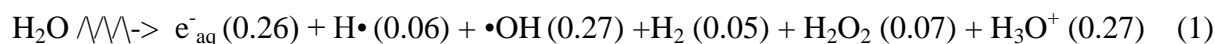
This study focused on the diclofenac, a common nonsteroidal anti-inflammatory drug (NSAID). It is often found as a persistent toxic waste and one of the most widely available drugs in the world. Average concentrations in the low µg L^{-1} range were detected in influents and effluents of municipal sewage treatment plants and surface waters in Austria, Pakistan, Germany and United States (Kolpin et al. 2002, Stülten et al. 2008, Scheurell et al. 2009, Al-Rifai et al. 2007). Even at very low concentrations adverse effects have been observed in different organisms. In rainbow trout, livers, kidneys and gills, the lowest observed effect for cytopathology occurred at 1 µg L^{-1} (Triebskorn et al. 2004). For ecological effect, diclofenac residues have been reported to cause vulture population decline in Pakistan (Oaks et al. 2004). Therefore, it is critical to develop a fundamental understanding of the fate and oxidative and reductive degradation of diclofenac during water treatment processes.
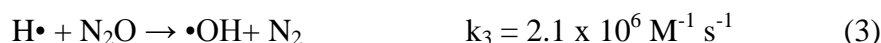
Materials and Methods

Materials. Diclofenac and 2, 6-dichloraniline (DCA) were purchased from Sigma-Aldrich ($\geq$ 99 %) and used without any further purification. Methanol, 2-propanol, and acetic acid (Fisher Science) were of HPLC grade. All solutions were prepared in 5.0 mM phosphate buffer and adjusted to pH 7.0 with NaOH or H_3PO_4, as necessary.

Pulse radiolysis and γ-radiolysis. Pulse radiolysis experiments were performed at the US Department of Energy, Notre Dame Radiation Laboratory using an 8-MeV Titan Beta model TBS-8/16-1S linear accelerator that produces 2 ns electron pulses which generate radical concentrations of 1-3 µM per pulse. All experimental data were taken by averaging 8 to 15 replicate pulses using the continuous flow mode of the instrument. Dosimetry was performed with N_2O-saturated, 1.00×10^{-2} M SCN$^-$ solutions monitored at λ = 472 nm.

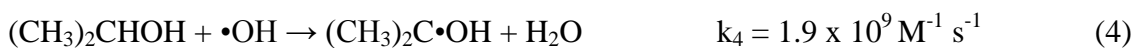The radiolysis of water is described in Eq 1:

$$H_2O \text{ /\\/\\/\\-> } e^-_{aq} (0.26) + H\bullet (0.06) + \bullet OH (0.27) + H_2 (0.05) + H_2O_2 (0.07) + H_3O^+ (0.27) \quad (1)$$

Where the numbers in parentheses are G values (yields) in µmol J^{-1}. To study the oxidative chemistry of the hydroxyl radical solutions were saturated with nitrous oxide (N_2O), which quantitatively converts the solvated electrons and hydrogen atoms (H$\bullet$) to the $\bullet$OH radical.

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + OH^- + \bullet OH \qquad k_2 = 9.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (2)$$

$$H\bullet + N_2O \rightarrow \bullet OH + N_2 \qquad k_3 = 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \qquad (3)$$

Reactions between the solvated electron and diclofenac were studied in N_2-saturated solutions buffered at pH 7.0. These solutions contained 0.10 M isopropanol to scavenge the hydroxyl radicals and hydrogen atoms, to convert them into relatively inert isopropanol radicals.

$$(CH_3)_2CHOH + \bullet OH \rightarrow (CH_3)_2C\bullet OH + H_2O \qquad k_4 = 1.9 \times 10^9 \, M^{-1} \, s^{-1} \qquad (4)$$

$$(CH_3)_2CHOH + H\bullet \rightarrow (CH_3)_2C\bullet OH + H_2 \qquad k_5 = 7.4 \times 10^7 \, M^{-1} \, s^{-1} \qquad (5)$$

A Shepherd[®] 109-86 Cobalt-60 source was used for γ radiolysis with samples of 1.0 mM diclofenac saturated with air before irradiation. The dose rate was 8.14 krad min^{-1} (0.0772 kGy min^{-1}), as measured by Fricke dosimetry.

HPLC and mass spectral analysis. The concentration of diclofenac was analyzed by an Agilent 1260 HPLC using the following conditions: column, Phenomenex Gemini C_{18} 250 x 4.6 mm i.d.; mobile phase consisting of 15 % CH_3OH, 15 % CH_3CN and 70 % 10 mM phosphate buffer solution (pH 3.0). The LC-MS system was an Agilent 1100 HPLC Pump and Waters LCT Classic Mass Spectrometer with electrospray ionization source and a Phenomenex Luna C_{18} (2) column (2.0 x 250 mm). The injection volume of the samples was 10 μL. The mobile phase was A: 98 % H_2O + 2 % CH_3CN +0.2 % formic acid and B: 50 % CH_3OH, 50 % CH_3CN and 0.2 % formic acid. Gradient elution was 0 % of B for 5 min followed by a linear increase to 100 % in 50 min, and then held constant for an additional 10 min. The mass spectra data were obtained in the positive ion mode by scanning from m/z 100 to 350.

Ion chromatography. Chloride ion released by the reaction of diclofenac with •OH and e^-_{aq} was quantified by ion chromatography (DX-120, Dionex) with conductivity detection. Separation was performed on an Ion-Pac AS16 anion column (4 250 mm, Dionex) using 35 mM NaOH eluent solution at a flow rate of 1.0 mL min

Results and Discussion

Kinetic Measurements. Pseudo-first-order growth rate constants for the reaction of hydroxyl radical with diclofenac were determined by fitting exponential growth curves to the time-dependent absorbance of the transient monitored at 330 nm and 370 nm, over a range of different diclofenac concentrations (Figure 1a). At both wavelengths, the initial growth in absorbance was followed by a second, smaller, concentration-independent growth, which was accounted for in the data fitting by using the sum of two exponential growths. The hydroxyl radical bimolecular rate constant for this reaction, k = (9.29 ± 0.11) × 10^9 M^{-1} s^{-1}, was then determined from a plot of these pseudo-first-order rate constants as a function of diclofenac concentration (see Figure 1b). This rate constant is slightly fast than the steady-state competition kinetic based value of (7.5 ± 1.5) × 10^9 M^{-1} s^{-1} recently reported by Huber (Huber et al. 2003) for •OH generated by γ-irradiation. To determine the site of reaction of •OH with diclofenac, the rate constant of •OH reaction with diclofenac was compared with that for several model compounds (Table 1). The rate constant of aniline was slightly higher than DCA, while both were similar with diclofenac. This suggests that •OH attacks both aromatic rings; however, when compared to DCA, the aniline ring is slightly more reactive due to the high electron density on the ring. The •OH radical reaction rate constant of acetic group was ~100 times slower, reflects the fact that •OH abstract hydrogen from alkyl group in the diclofenac plays a minor role.
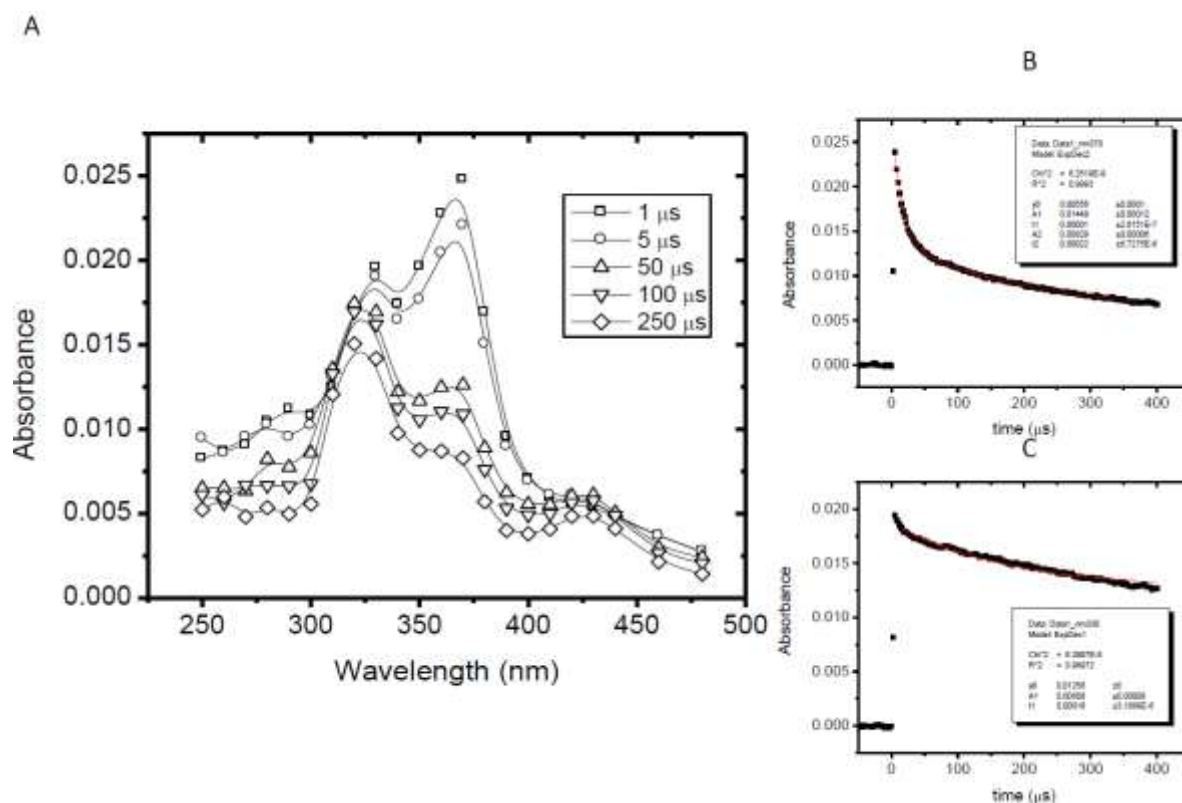
Fig. 1. (A) Transient absorption spectra obtained from electron pulse radiolysis of N₂O saturated aqueous solutions of diclofenac at room temperature and pH 7.0. Transient decay kinetics shown for at 310 nm (B) and 370 nm (C).

TABLE 1. SUMMARY OF SECOND-ORDER RATE CONSTANTS IN THIS STUDY (BOLD) IN COMPARISON TO VALUES FOR ANALOGOUS COMPOUNDS FROM LITERATURE.

Compound	$k_{\cdot OH}/M^{-1}s^{-1}$	$k_{e^-aq}/M^{-1}s^{-1}$
Diclofenac	**(9.29 ± 0.11) x10⁹**	**(1.53 ± 0.03) x10⁹**
2, 6-dichloroaniline	**(6.97 ± 0.14) x10⁹**	**(3.26 ± 0.04) x10⁹**
m-dichlorobenzene	5.7 x10⁹ (Kochany and Bolton 1992)	5.2 x10⁹ (Anbar and Hart 1964)
Aniline	1.0 x 10¹⁰ (Solar et al. 1986)	3.0 x10⁷ (Solar et al. 1986)
Acetic acid	8.5 x10⁷	1.1 x10⁶

The second order rate constant for the reaction of the solvated electron with diclofenac was determined by fitting single exponential decays to the absorbance of e^-_{aq} monitored at 700 nm. Plotting these pseudo-first-order values against diclofenac concentration, a second-order rate constant of k = (1.53 ± 0.03) × 10⁹ M⁻¹ s⁻¹ was obtained (Table 1) in comparison to values for

analogous compounds. Our diclofenac value is considerably faster than for the reduction of aniline (3×10^7 M^{-1} s^{-1}) or acetic acid (1.1×10^6 M^{-1} s^{-1}), nevertheless similar to rate constant for m-dichlorobenzene (5.2×10^9 M^{-1} s^{-1}) or DCA. From these rate constants, it appears that the reduction occurs predominately via dissociative electron attachment at the chlorine moiety in diclofenac.

Degradation efficiency and dechlorination. Steady-state γ irradiation of diclofenac in N_2O saturated solutions (•OH) and N_2 saturated aqueous isopropanol solutions (e^-_{aq}) showed decreasing concentration with increasing dose (see Figure 2a). The curvature of the plot is consistent with previously reported irradiation studies for other contaminants in water (Jeong et al. 2010a, Jeong et al. 2010b, Luo et al. 2012), suggesting competition for the reactive species (•OH and e^-_{aq}) between diclofenac and the reaction by-products at the higher applied doses.

These data allow estimation of the efficiencies of the initial •OH oxidation and e^-_{aq} reduction of diclofenac. From the lowest dose measurement, an estimate of the initial slope was -3.23×10^{-4} M kGy^{-1} for the •OH radical, seen as the straight line in Figure 2a. This predicted line corresponds to the total removal of diclofenac, assuming no interference from stable products occurred. Under these experimental conditions all the produced hydroxyl radicals will initially react with diclofenac and the degradation efficiency was 60 %. The similar assumption has also been applied to estimate the solved electron reaction efficiency and reported as 62 %.

The release of chloride ion from irradiated solutions of diclofenac was measured by ion chromatograph (Figure 2b). The dechlorination by •OH fit a straight line and the formation rate determined was 9.2×10^{-5} M kGy^{-1}, which accounts for only 17% •OH radical attack. The of diclofenac by e^-_{aq} fit pseudo first order growth, and the initial formation rate is 2.7×10^{-4} M kGy^{-1}. This rate was equal to the $G(e^-_{aq})$ value (2.6×10^{-4} M kGy^{-1}), and indicated an efficiency of 100 %.
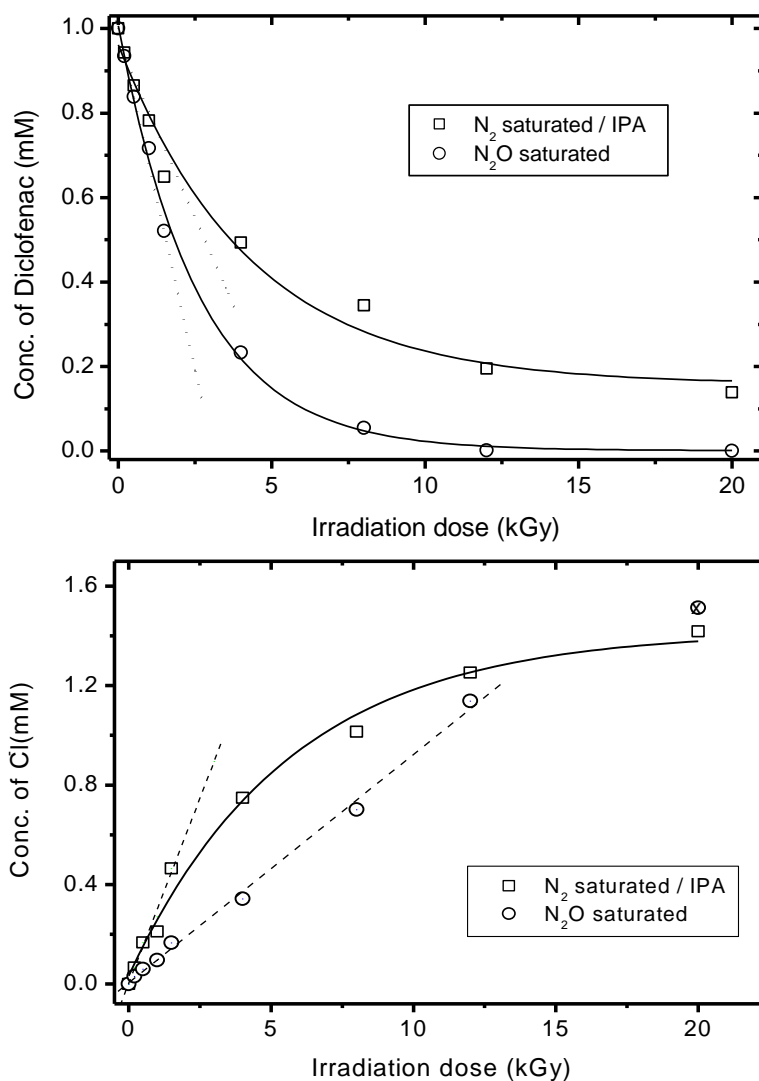
Fig. 2. Degradation curve of diclofenac at pH 7.0. Fast N₂O purging, medium air saturated, slowest N₂ purge and added isopropyl alcohol.

Degradation mechanism. Analyses by LC-MS at various doses revealed diclofenac decomposition products at N₂O saturated (•OH oxidation) or 0.1 M isopropanol N₂ saturated (solvated electron reduction) solutions. Our structural assignments of the breakdown products of diclofenac during γ-irradiation were based on the analysis of the Total Ion Chromatogram (TIC) and the corresponding mass spectra with consideration of isotopic abundance. The masses of the different products were determined from the peaks corresponding to the protonated molecule, [M+H] $^{+}$. For the purpose of this paper, we will refer to the products by molecular weight (MW).

The major degradation products produced in the steady-state γ irradiation of diclofenac in N₂O saturated solutions are summarized in Figure 3. Three separate products with MW of 311 were observed, corresponding to the addition of 16 mass units to the parent peak. This is

consistent with hydroxylation of the aromatic ring. The addition of the electrophilic hydroxyl radical to the aromatic ring forms a resonance-stabilized carbon-centered radical with subsequent addition of oxygen and elimination of a hydroperoxyl radical, yielding the phenolic products. Generally the specificity of electrophilic aromatic substitution is governed by the nature of the substituents, which may account for our observation of three different products with the same m/z ratio. Since the amino group is a strong electron donating group and acts as ortho-para directors, three main products are proposed in the Figure 3.

With further hydroxyl radical oxidation, multi di-hydroxylation products (MW 327) were formed, which verifies the assumption of hydroxyl substitution on the rings, since the hydroxyl group increases the electron density and the hydroxyl radical electrophilic adductions are favorable. It is proposed that the product with MW 309 is the result of further oxidation with the primary phenolic degradation product (a) to form quinine imine product, which is also observed in photo-Fenton degradation products (Pérez-Estrada et al. 2005). One minor product was observed with the MW 275, corresponding to the loss of HCl from the primary phenolic product (b). This suggests that the phenol group attacks the chlorine substituted carbon with subsequent cyclization to form a six-membered ring. The compound with a MW 177 could be formed, following hydroxyl radical ipso-adduction to the primary product MW 311 (c). Another mono-aromatic product of MW 151was observed and isotope mass peak indicates there no chloric group present in this product. Therefore, the structure has also been proposed in Figure 3. It is suggested from hydroxyl radical ipso-adduction to the DCA ring. The associated product MW 162 is not detected under our experimental conditions, it may due to the low response for the positive ionization.
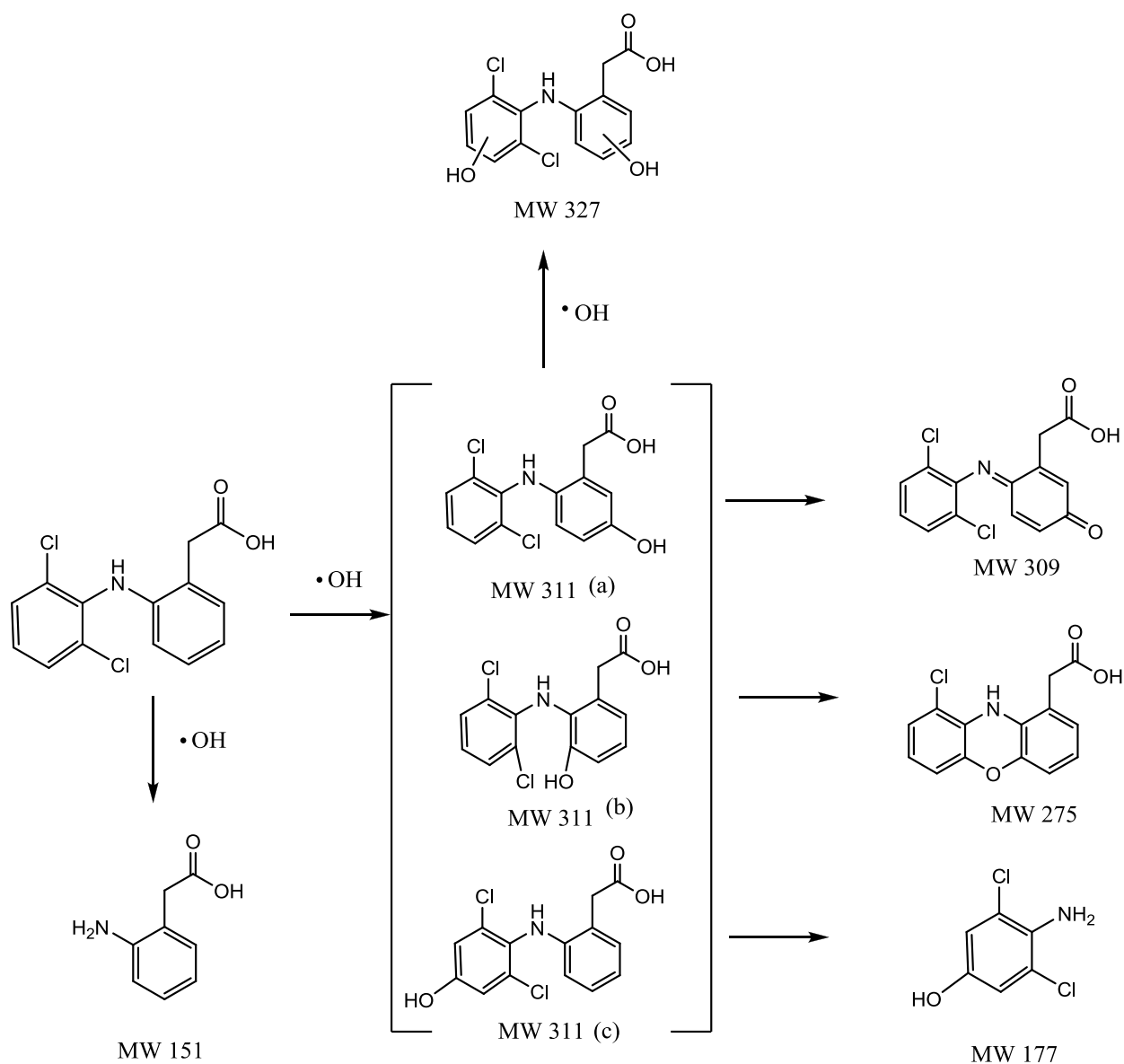
Fig. 3. Proposed oxidative (•OH) degradation mechanism for diclofenac.

Diclofenac solution (with 0.1 M isopropanol) and N_2 saturated were used to study the solvated electron degradation mechanism. Dechlorination is the major degradation pathway, which is in agreement with chloride ion release. As carbon centered radical was the major intermediates after dechlorination, which either further abstract H atom from H_2O forming the product of MW 261, or with intra-molecular reaction forming the product of MW 259, as illustrated in Figure 4.
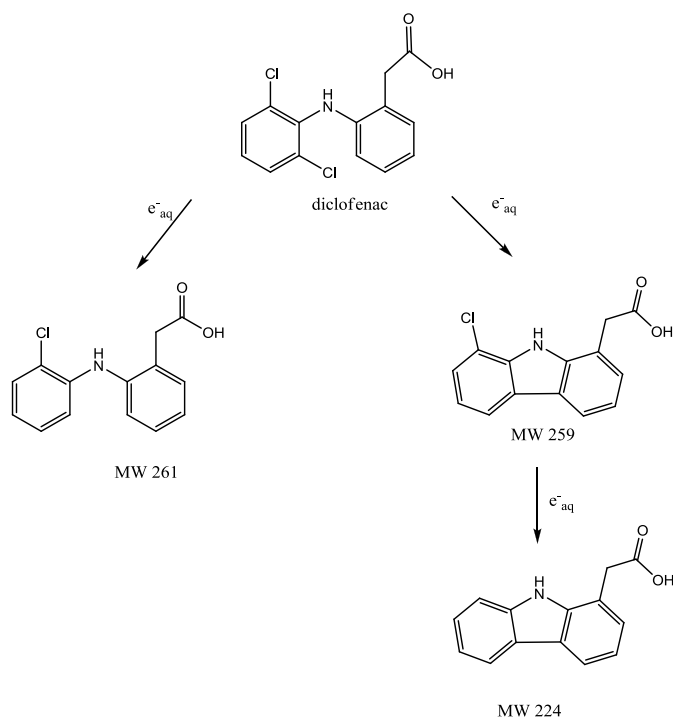
Fig. 4. Proposed reductive (e⁻aq) degradation mechanism for diclofenac.

Toxicity assessments. While our results demonstrate that •OH radical and e^-_{aq} effectively degrade diclofenac, it is critical to establish the biological activity of the resulting treated solution or the individual breakdown products. In general, •OH radical and e^-_{aq} lead to a complex mixture of products with low overall yields. As it is a daunting task to identify the individual reaction byproducts and assess their individual biological activities, we chose to use the *Vibrio fischeri* luminescent bacteria assay to assess the biological activity of the treated solutions at various doses. A calibration curve for the bacteria inhibition as a function of the concentration of diclofenac was used to evaluate the toxicity at increasing dose. With •OH radical oxidation in initial 4 kGy, 75 % of diclofenac had been destroyed. However, the biological activity of the treated samples was constant, implying that toxic breakdown products are formed to a significant extent. With further oxidation, the toxic products were eliminated and the toxicities of treated solution decrease slowly. While 100 % of diclofenac has been removed at 12 kGy, residence toxicity has been remained at 40 % inhibition.

Conclusion

The oxidative and reductive free radical reactions of diclofenac have been determined and their respective degradation mechanisms proposed. Not surprisingly the mechanisms are considerably different and result in different reaction by-products. The residual toxicity, as measured by the change in bioluminescence of V. fischeri showed that the by-products of the reductive processes were less toxic than those obtained by oxidative destruction of diclofenac. The reaction efficiency of both oxidation and reduction processes was approximately 60 % which confirms that diclofenac is relatively resistant to free AOP treatment.

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E-BEAM BASED IONIZING RADIATION TECHNOLOGY FOR MUNICIPAL BIOSOLID TREATMENT

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Abstract

Ionizing radiation technology, specifically electron beam irradiation, presents an effective and economically viable alternative to traditional wastewater treatment methods.

1. Background

Principles of Electron Beam Radiation

Stopping Power and LET: Electrons traveling through matter lose their energy by exciting and ionizing atoms within the material. The average linear rate of energy loss of these electrons in a particular medium is referred to as "stopping power" and generally has units of MeV per cm. This quantity is also often referred to as the linear energy transfer (LET) of the particle with units generally expressed as keV per μm (Turner, 1995). Stopping power and LET are closely related to the dose imparted to the material by the electrons traveling through that material.

Range and Penetration: The distance that a charged particle travels before coming to rest is known as the "range" of the particle (Turner, 1995). The range of electrons in sludge and effluent water is of particular interest when designing the parameters for sludge treatment by ionizing radiation. Cleland, Lisanti, and Galloway utilized the one-dimensional ITS TIGER Monte Carlo code to calculate electron range values in water (Cleland, Lisanti, and Galloway, 2004). They compared their calculated results with the electron energy versus range equation given in ICRU Report 35 (ICRU, 1984a). This energy versus range equation is given in (0.1) below.

$$E_P = 0.22 + 1.98 R_P + 0.0025 (R_P)^2, \text{ (0.1)}$$

where,
E_P = electron energy in MeV and
R_P = practical range in g/cm^2.

Cleland, Lisanti, and Galloway calculated the range of 10-MeV electrons in water to be 4.922 cm (Cleland, Lisanti, and Galloway, 2004), which corresponded to an electron energy of 10.025 from the ICRU equation (ICRU, 1984a). This resulted in a less than 1% difference between the two methods. Therefore, the range for 10-MeV electrons penetration in water can be considered to be 5 cm.

Absorbed Dose

Absorbed dose is the primary quantity used in the field of dosimetry. It is defined as the energy absorbed per unit mass from any kind of ionizing radiation in any target. The SI unit

of absorbed dose is the gray (Gy). One Gy represents one joule of energy deposited per kilogram of material.

2. Objective

The goal is to develop an electron beam irradiation design that can be effectively used to irradiate municipal wastewater effluent and sludge or slurry. The irradiation process should inactivate pathogens and possibly destroy undesirable compounds commonly found in wastewater materials. The goal of the proposed treatment process is material that can be land-applied, resulting in a cost-effective and environmentally-sustainable end use for the material (Zhou and Mavinic, 2003). The United States Environmental Protection Agency (USEPA) released the technical standards for the use and disposal of biosolids and introduced the criteria for Class-A biosolids in 1993 (USEPA, 2007). To be classified as Class-A material, biosolids must be essentially be pathogen-free and must meet specific metal concentration and vector attraction reduction requirements (Bastian, 1997). Upon meeting these requirements, the material can be land-applied without restrictions (Zhou and Mavinic, 2003).

Standards for pathogen-load reduction in biosolids intended for Class A applications are as follows (USEPA, 2007). Either the density of fecal coliform in the sewage sludge shall be less than 1000 Most Probable Number per gram (MPN/g) of total solids (dry weight basis) or the density of *Salmonella* sp. Bacteria shall be less than three MPN per four grams of total solids (dry weight basis). The density of enteric viruses shall be less than one Plaque-Forming Unit per four grams of total solids (dry weight basis). The density of viable helminth ova density shall be less than one per four grams of total solids (dry weight basis).

3. Current Technologies

Co-60 Technology: The first sewage sludge irradiation plant was the Geiselbullach Treatment Plant, a pilot-scale Co-60 irradiation plant near Munich, Germany (Lessel, 1997). This plant was established in 1973, and it provided great momentum for the prospect of using ionizing radiation for environmental applications (McKeown et al. 1998; Graino and Magnavacca 1998). Almost 30 years later, a full-scale commercial plant has yet to be constructed, but many researchers have reviewed the value of ionizing radiation in the treatment of sludge materials. Co-60 was also used as the source for a municipal wastewater treatment plant build by the Isotope Division of the Bhabha Atomic Research Center in collaboration with M.S. University of Baroda, Bujarat Water Supply and Sewerage Board, and Municipal Corporation of Baroda, India (Shah et al., 2001). The Co-60 source for this facility had a maximum activity of 500,000 Ci,, and the treatment capacity was 110 m^3/day (Shah et al., 2001). The plant was commissioned in 1992 and has been in daily operation since that time implementing a target dose of 2 kGy (Shah et al., 2001; Gautam et al., 2005). Sandia National Laboratories in Albuquerque, NM, USA, developed a pilot and demonstration plant to treat dewatered and compost sludge in 1979 (Lessel, 1997). The Sandia plant employed a Cs-137 source with a maximum activity of 1,000,000 Ci. The capacity of the plant was 8 dry tons (about 50% solids) per day with a target dose of 10 kGy. The plant ceased operation due to unknown reasons. Graino and Magnavacca (1998) explored a Co-60 facility design for sludge irradiation in Argentina. The irradiation plant in their design was intended for anaerobically-digested sludges with solids concentrations of 8-10% (Graino and Magnavacca 1998). The irradiation treatment process incorporated an irradiation tank with a recirculation system used to irradiate batches of 6.0 m^3 in 30-minute intervals. The Graino and Magnavacca research examined physicochemical changes induced by ionizing radiation such as diminishing viscosity, decrease in filtration specific resistance, and change in sedimentation velocity.

They also explored chemical effects such as decomposition and evidence of a protection effect.

Electron Beam Technology: Electron beam technology has not been widely employed in sewage sludge treatment on a commercial scale(Wang and Wang, 2007). An electron accelerator was built to treat sewage sludge as a demonstration project at the Deer Island Wastewater Treatment Plant in Boston in 1976 (Lessel, 1997). The project was designed and supervised by Massachusetts Institute of Technology, and the plant capacity was reported to be 400 m^3/day (Lessel, 1997). The study was performed in a laboratory, and the researchers decommissioned the project, never scaling it up, in 1984. Another electron beam accelerator was built at a wastewater treatment plant in Virginia Key, Miami, Florida, during 1981-1983 (Lessel, 1997). The accelerator employed at this facility operated at 75 kW utilizing a 50 mA current of 1.5 MeV electrons (Lessel, 1997). The daily capacity was 645 m^3 with a target dose of 4 kGy (Lessel, 1997).

McKeown et al. (1998) explored the viability of the IMPELA accelerator family for sludge irradiation. IMPELA is a family of electron linear accelerators first developed in 1988 at the Chalk River Nuclear Laboratories in Ontario, Canada (Lawrence et al. 1988). The McKeown team of researchers considered the use of these accelerators for a detoxification process in which a dose of 800 kGy would be necessary to render tetrachlorodibenzo-*p*-dioxin (TCDD) inactive. While this target dose is much greater than the intended target dose for this sludge irradiation project, the economic and logistical considerations involved in the McKeown study were quite constructive for developing the methodology of this study.

There are other reports of the application of electron-beam accelerator technology in small-scale plants in Germany, Australia, and Japan (Lessel, 1997), but these facilities were only operated for 2-4 years. No full-scale plant employing accelerators for sewage sludge processing has arisen (Wang and Wang, 2007).

4. Economic Analysis

Economic viability of a wastewater treatment plant is analyzed by first determining the throughput rate of the treatment process. Monte Carlo simulations were employed in a study at Texas A&M University to determine the E-Beam irradiation of municipal biosolids (Lazarine, 2007). Based on these simulations, the lowest dose rate across all materials for all voxel units in was determined to be 5.2 kGy/s By using the lowest dose-rate values for each material and a target dose of 15 kGy, it was determined using these simulations that each voxel of material should be exposed to the electron beam for 2.88 seconds. Throughput rates were calculated for two proprietary E-Beam configurations and specifications (Configuration A and Configuration B). The two linear accelerator configurations varied by their orientation, operating power and operating current. Using the samples obtained from a candidate aerobic digester and an anaerobic digester, (i.e., mass concentrations of 4.3% for aerobic and 2.6% for the anaerobic digester) the mass flow rate of material under the beam window using Configuration A was determined to be 1.5 kg of dry aerobic sludge in 2.88 seconds and 1.05 kg of dry anaerobic digester sludge in 2.88 seconds. These values result in throughput rates of 11,250 dry tons of aerobic sludge per year and 7,875 dry tons of anaerobic digester sludge per year. These calculations assume 20 hours of operation per day for 300 days per year. The throughput capacities for the two linear accelerator configurations are shown in Table 6 in units of dry tons/year and m^3/day. The Configuration B has about 50 times higher throughput than Configuration A.

E-Beam Configuration	Capacity (m³/day)		Capacity (dry tons/year)	
	Aerobic digester	Anaerobic Digester	Aerobic Digester	Anaerobic Digester
Configuration A	38.78	28.63	11,250	7,875
Configuration B	1927	1332	562,600	393,750

To calculate the capital cost per dry ton, it was assumed that a facility would cost on the order of $15 million at the very high end. The amortization of this value over 10 years at 7% interest with a 20% ($3 million) down payment would result in monthly payments of $139,330. Using Configuration A and the throughput rates calculated above, the capital cost for aerobic sludge processing will be $258 per dry ton and $5.16 per dry ton with Configuration B. The capital cost for anaerobic digester sludge processing will be $369 per dry ton with Configuration A, and $7.37 with Configuration B (Table 2).

TABLE 2. CAPITAL COSTS FOR E-BEAM PROCESSING OF AEROBICALLY AND ANAEROBICALLY DIGESTED MUNICIPAL BIOSOLIDS USING TWO DIFFERENT LINEAR ACCELERATOR (LINAC) CONFIGURATIONS

E-Beam Configuration	Capital Costs ($ dry ton)	
	Aerobically digested biosolids	Anaerobically digested biosolids
Configuration A	$ 258	$ 369
Configuration B	$ 5.16	$ 7.37

To evaluate the operating cost per dry ton, factors such as labor, electricity, preventive maintenance costs, etc., need to be considered. Table 3 represents a hypothetical operating cost scenario at a very high end. These figures are on purpose estimated on the high side. At $0.10/kW-h, the yearly electricity cost for the two E-Beam beam configurations was estimated to be $21,600.   Electricity for the facility itself can be expected to cost approximately $30,000 per year thus, totaling approximately $ 51,600. An average salary of $50,000 per year per employee for 20 employees is estimated to be $1 million per year. In addition, $150,000 has been budgeted for administrative costs and $100,000 has been budgeted for miscellaneous expenses. These expenses result in a total yearly operating cost of $1.502 million.

TABLE 3. HYPOTHETICAL E-BEAM FACILITY OPERATING COSTS FOR TREATING MUNICIPAL BIOSOLIDS

Cost Category	Cost per Year
Electricity	$ 51,600
Maintenance	$ 200,000
Labor costs (20 employees @ $50K/year)	$ 1,000,000
Administrative costs	$ 150,000
Miscellaneous costs	$ 100,000
Total operating Costs	**$ 1,501,600**

Operating costs have been determined for the Configuration A and Configuration B accelerator specifications. Based on the facility operating costs and the given biosolid throughput rates under the two LINAC configurations, the operating costs on a dry ton basis is shown in Table 4. As seen in Table 4, the aerobic and anaerobic sludge would cost approximately $232/dry ton and $ 378/dry ton respectively using Configuration A. Using

Configuration B, the operating costs for aerobic and anaerobic sludges would be $ 4.75 and $ 6.79 respectively.

TABLE 4. ESTIMATED OPERATING COSTS FOR TWO E-BEAM CONFIGURATIONS FOR TREATING AEROBICALLY AND ANAEROBICALLY DIGESTED MUNICIPAL BIOSOLIDS.

E-Beam Configuration	Operating Costs ($ dry ton)	
	Aerobically digested biosolids	Anaerobically digested biosolids
Configuration A	$ 232	$ 378
Configuration B	$ 4.75	$ 6.79

These estimated values compare favorably with the IMPELA concept studied by McKeown et al (1998). The IMPELA study calculated the capital cost for an $8 million facility at $444 per dry ton and the operating cost at $378/dry ton. They estimated an imparted dose of 800 kGy (McKeown et al., 1998). The IMPELA system can be expected to cost approximately $8.33 in capital costs per dry ton and $7.08 in operating costs per dry ton to achieve a 15 kGy target dose as shown in the Texas A&M University studies.

An economic viability study for the E-Beam based irradiation of municipal biosolids would be incomplete without a comparison with other traditional wastewater treatment methodologies. Table 5 gives an approximate cost per dry ton for incineration, thermophilic aerobic digestion, co-composting, thermophilic anaerobic digestion, thermophilic alkaline treatment, and heat drying.

TABLE 7 COST OF CONVENTIONAL WASTEWATER TREATMENT TECHNOLOGIES

Municipal Biosolid Treatment Method	Estimated Costs ($ dry ton)
Incineration	$ 250
Thermophilic aerobic digestion	$ 180
Co-composting	$ 150
Thermophilic Anaerobic digestion	$ 110
Thermophilic Alkaline treatment	$ 85
Heat drying	$ 85
E-Beam treatment (Configuration B) aerobic digester biosolids	$ 4.75
E-Beam treatment (Configuration B) anaerobic digester biosolids	$ 6.79

It is evident that a Configuration B based E-Beam system is much less expensive than any conventional methods used today. While the cost estimates for processing with the E-Beam under Configuration A may not appear to be competitive with these methods directly, it is important to remember that the methods in Table 5 are often used in series or tandem. The McKeown et al. (1998) study also showed that 100-mA linear accelerators can be effectively employed for treating municipal biosolids, supporting the claim that electron beam irradiation is far more cost effective than conventional wastewater treatment methods. There could be significant cost savings if E-Beam treatment is applied upstream of the treatment process thereby reducing digester holding times and additional treatments. Further studies are, however, needed to explore the various cost-effective options of incorporating E-Beam treatment into the wastewater industry.

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