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2.7 Electron Beam Treatment of Industrial Wastewater

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1. Electron Beam Treatment of Wastewater

The treatment of municipal and industrial wastewater becomes a more important subject in the field of environment engineering. The treatment of the industrial wastewater containing refractory pollutant with electron beam is actively studied in EB TECH Co. Electron beam treatment of wastewater often 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). Sometimes such reactions are accompanied by the other processes, and the synergistic effect upon the use of combined methods such as electron beam treatment with ozonation, electron beam and adsorption and others improves the effect of electron beam treatment of the wastewater purification. In the laboratory of EB-TECH Co., many industrial wastewater including leachate from landfill area, wastewater from papermill, dyeing complex, petrochemical processes are under investigation with e-beam irradiation.

TABLE I. Wastewater under investigation at EB-TECH Co.

Wastewater (from)	Purpose of investigation	Results
Dyeing company Impurities	Removal of color and organic Improve removal efficiencies	Pilot plant operates and shows
Papermill Increase re-use rate	Decrease COD, color Commercial plant designed	Reduction in impurities
Petrochemical co. after processing	Removal of organic residues	Removal of TCE, PCE, PVA, HEC and other substances
Leachate from landfill area	Removal of organic impurities Improvement of Bio-treatment	Bio-treatment efficiency improved
Heavy metals	Decrease in the content of heavy metal ions in water	Removal of Cd, Cr^{+6}, Hg up to 98 % (95 % in Pb)
Municipal sewage plant	Decrease in organic contents and microorganisms for re-use	Good for uses in industries and irrigation

2. Pilot Scale Test of Wastewater from Papermill

For the study of treating dyeing wastewater combined with conventional facilities, an electron beam pilot plant for treating 1,000 m^3/day of wastewater from 80,000 m^3/day of total dyeing wastewater has constructed and operated in Taegu Dyeing Industrial Complex. [1,2] A commercial plant for re-circulation of wastewater from Papermill Company is also designed for Pan Asia Paper Co. Cheongwon Mill, and after the successful installation, up to 80 % of wastewater could be re-used in paper producing process. [3] The method for the removal of heavy metals from wastewater and other technologies [4,5] are developed with the joint works with Institute of Physical Chemistry (IPC) of Russian Academy of Sciences.

A commercial plant for re-circulation of wastewater with electron beam from Papermill Company is also under planning in Pan Asia Paper Co. Cheongwon Mill and EB TECH Co. Cheongwon Mill is located from 120 km south of Seoul, and consumes 18,000 m^3 of water per day. The major products of this company are papers for newsprint (450 t/day) and are mainly made of recycled paper (91 %) and pulps. For the economical point of view, it is preferable to recycle the treated water to production lines, but now used only 20 - 30 % at total water since the amount of organic impurities after treatment are high and some of them are accumulated during re-circulation.

Purification of wastewater is now performed by 2-stages of chemical and biological treatment facilities. The existing facility for purification of wastewater under consideration consists of the following main stages:

1) Primary chemical coagulation + flocculation;
2) Biological treatment by activated sludge with subsequent sedimentation and filtration through sand filter
3) Secondary chemical coagulation (with the addition of hypochlorite);

The COD value after the first stage gives rise to decrease in COD value to around 150 ppm. The COD value after the third stage is 45 - 90 ppm. The COD value of finally purified wastewater should be less than 25 ppm.

In order to develop the most efficient method for re-circulation of wastewater, the experiments were conducted with samples in various stages of treatment. In the experiments, electron accelerator of 1 MeV, 40 kW with the dose rate of 40 kGy/s is used. In order to carry out the experiments, the laboratory unit schematically shown in Fig. 1 was constructed for irradiation under flow conditions. The initial water is placed in storage vessel, which serves as saturator-equalizer. Air or ozone-air mixture with controlled flow rate up to 40 l/min was fed to the vessel. Wastewater from the vessel is moved with controlled consumption by pump to multi-jet nozzle. Diameter of each jet 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 (it corresponded to the rate of wastewater in the industrial plant under design). The wastewater injected directed in parallel each other in horizontal plane; their flight length was equal to ~1.5 m (at the initial rate 3 m/s). The wastewater injected along horizontal part of their flight was treated by electron beam. Then irradiated wastewater was collected into the special container.

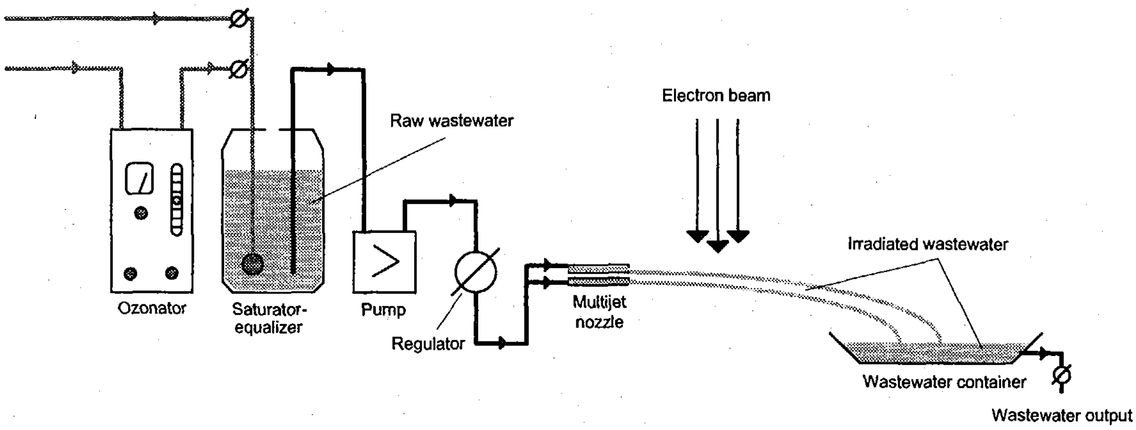

Fig. 1. Laboratory unit used in electron beam treatment experiments.

In order to develop the most efficient combined electron beam method for purification of the wastewater, the experiments were conducted initially with 4 various samples: initial raw wastewater, wastewater after primary coagulation, wastewater after biological treatment and filtration, and finally-purified wastewater. It is shown that the decrease in absorbance is the most for first and third samples. Because of it the relative changes in COD, BOD_5, TOC and absorbance at 235 nm were measured for raw wastewater and wastewater after the second stage of purification as a result of electron beam treatment at various doses and subsequent coagulation + flocculation. The $Al_2(SO_4)_3$ solution was used as a coagulant. Sometimes the $Al_2(SO_4)_3$ + $Fe_2(SO_4)_3$ solution served as a coagulant; in this case the better results were obtained. This effect is the most at doses < 3 kGy. Note that a small increase in BOD_5 value was observed in initial raw wastewater at doses < 1 kGy.

It was found that the positive influence of electron beam treatment is highest for wastewater after second stage of purification. The data obtained allowed to conclude that the most advantageous part of existing technological line for using electron beam treatment is after first coagulation + flocculation and biological treatment. Because of it the treatment of such a partially purified wastewater was studied in detail and under various conditions. The values of COD_{Cr}, COD_{Mn}, TOC and color were measured. The results obtained are shown in Fig. 2. In the figures, the following abbreviations were used: LFS - the treatment by $Fe_2(SO_4)_3$ coagulant and then by polyacrylamide, LAS - the treatment by $Al_2(SO_4)_3$ coagulant and then by polyacrylamide flocculant, LFAS - the treatment by mixed $Fe_2(SO_4)_3$ + $Al_2(SO_4)_3$ (mole ratio 1:1) coagulant and then by polyacryl amide flocculant, Electron beam treatment at maximum dose rate 40 kGy/s, dose 1.3 kGy and rate of water flow 3 m/s. In each figure, solid black line shows the mean value of the respective parameter for the initial wastewater (after primary coagulation + flocculation treatment and biological purification).

The decrease in the initial value of the parameter after any treatment is shown by vertical line. The sequence of treatments is given along vertical line. The vertical line is ended by an arrow, which indicates the achieved value of the parameter as a result of the treatment. The best result is irradiation of water after biological treatment combined with coagulation and filtration. Irradiation in this stage, the additional removal of impurities is up to 80 % in TOC (Total Organic Carbon) values.

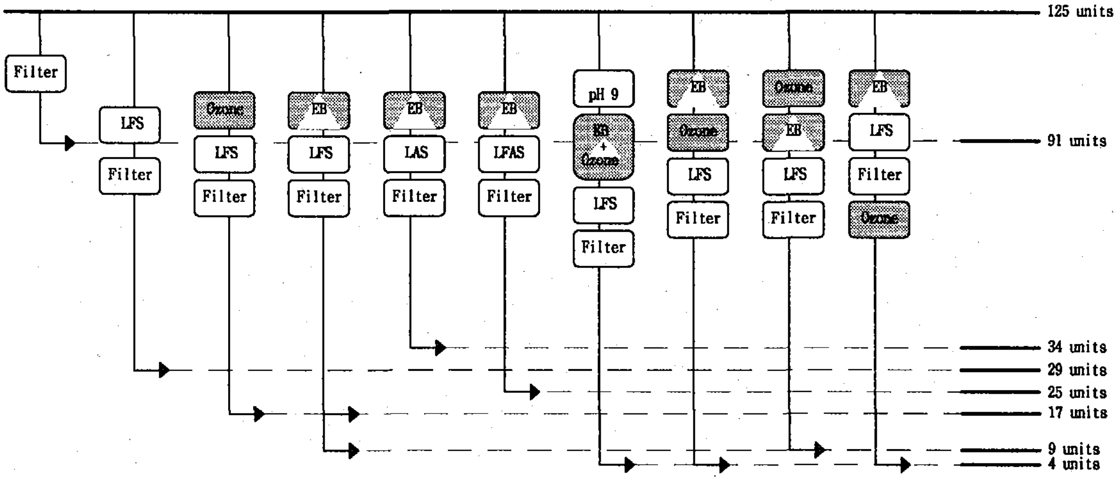

Fig. 2. Color index of wastewater after various treatments

3. Commercial Plant Construction

On the base of data obtained by EB-TECH Co. and IPC the suitable doses in this case are determined as around 1 kGy for the flow rate of 15,000 m^3 wastewater per day (since the 3,000 m^3 of wastewater is returned to initial stage with sludge). Therefore, three accelerators with the total power of 300 kW and treatment system are designed for,

- Decreasing the operation cost of wastewater treatment facility
- Improving the removal efficiency of organic impurities below 25 in COD
- Increasing the re-circulation rate up to 80 %

Expected construction period includes 11 months in civil and installation works and 3 months for trial operation. After the successful installation of electron beam treatment facilities, up to 80 % of wastewater could be re-used in paper producing process (Fig. 3).

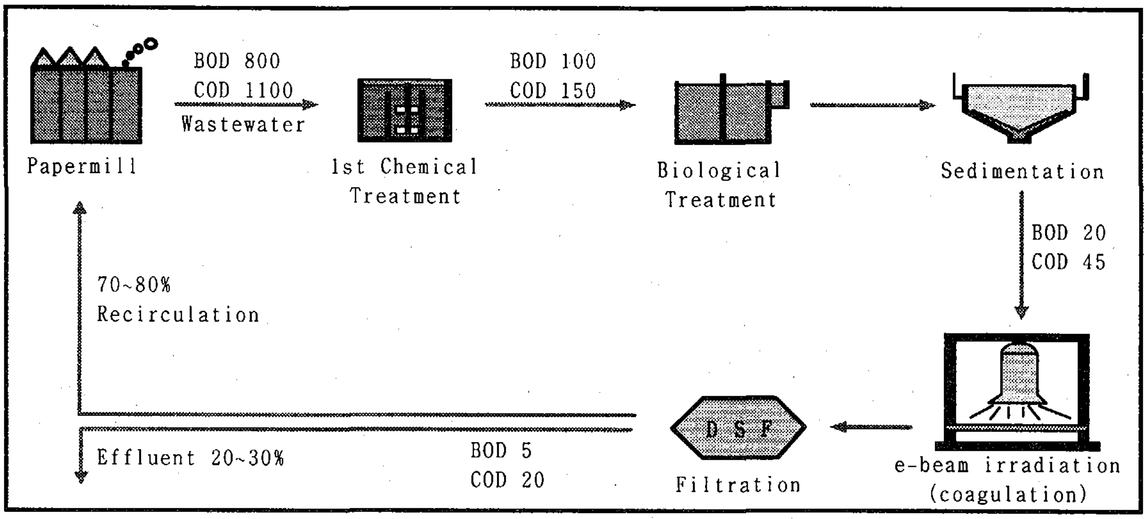

Fig. 3. Process flow of e-beam facility for wastewater from papermill.

4. Pilot plant operation and Commercial plant construction of Dyeing Wastewater

Taegu Dyeing Industrial Complex (TDIC) in Korea is composed of more than hundred factories occupying the area of 600,000 m^2 with 13,000 employees in total. The production of TDIC requires high consumption of water (90,000 m^3/day), steam, and electric power, being characterized by large amount of highly colored industrial wastewater.

Purification of the wastewater is performed by conventional methods – mixed Chemical-Biological treatment (Fig. 4), and treats up to 80,000 m^3 of wastewater per day, extracting thereby up to 730 m^3 of sludge. Rather high cost of purification results from high contamination of water with various dyes and ultra-dispersed solids.

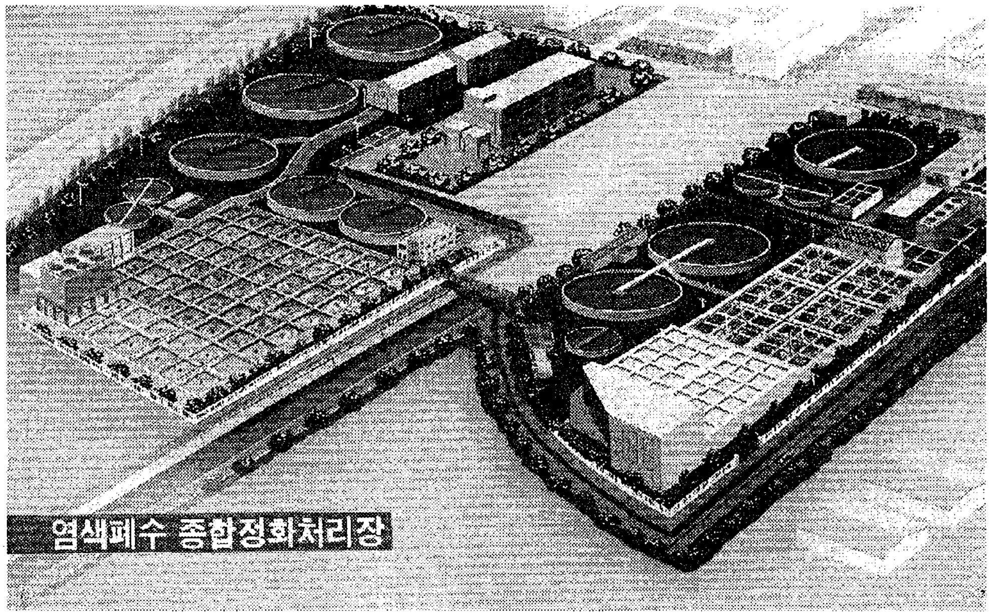

Fig. 4 Existing Wastewater Treatment Facility in TDIC

5. Lab-scale Feasibility Study with E-beam

Because of increase in productivity of factories and increased assortment of dyes and other chemicals, substantial necessity appears in re-equipment of purification facilities by application of efficient methods of wastewater treatment. The existing purification system is close to its limit ability in treatment of incoming wastewater.

The studies have been carried out regarding the possibility of electron beam application for purification of wastewater. The experiments on irradiation of model dye solutions and real wastewater samples (from various stages of current treatment process) have been performed. The results of laboratory investigations of representative sets of samples showed the application of electron beam treatment of wastewater to be perspective for its purification (Fig. 5). The most significant improvements result in decolorizing and destructive oxidation of organic impurities in wastewater. Installation of the radiation treatment on the stage of chemical treatment or immediately before biological treatment may results in appreciable reduction of chemical reagent consumption, in reduction of the treatment time, and in increase in flow rate limit of existing facilities by 30 - 40 %.

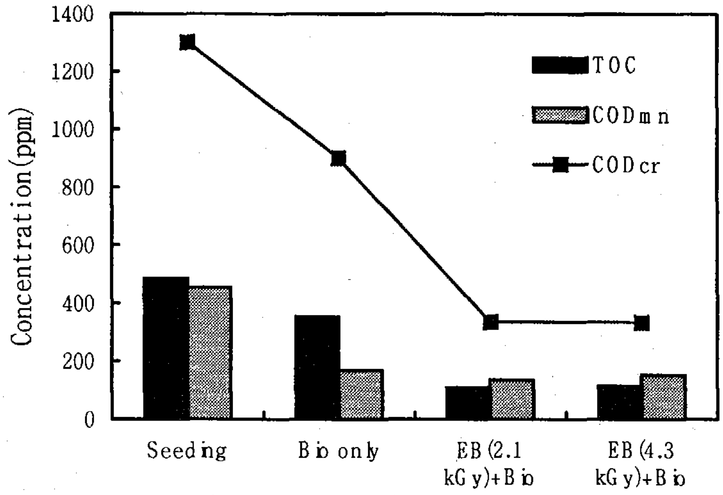

Fig.5. Results of feasibility test

6. Construction and Operation of Pilot Plant

Being convinced with the feasibility test results, a pilot plant for a large-scale test (flow rate of 1,000 m^3 per day) of wastewater has constructed and is now under operation with the electron accelerator of 1 MeV, 40 kW (Fig. 6). The size of extraction window is 1500 mm wide and Titanium foil is used for window material. The accelerator was installed in Feb. 1998 and the technical lines are finished in May. For the uniform irradiation of water, nozzle type injector with the width of 1500 mm was introduced. The wastewater is injected under the e-beam irradiation area through the injector to obtain the adequate penetration depth. The speed of injection could be varied upon the dose and dose rate. Once the wastewater has passed under the irradiation area, then directly moved into the biological treatment system. The Tower Style Biological treatment facility (TSB) that could treat up to 1,000 m^3 per day has also installed in October 1998. TSB is composed of equalizer, neutralizer, and 6 steps of contact aeration media. Each aeration basins are filled with floating or fixed bio-media to increase the contact area and removal efficiency.

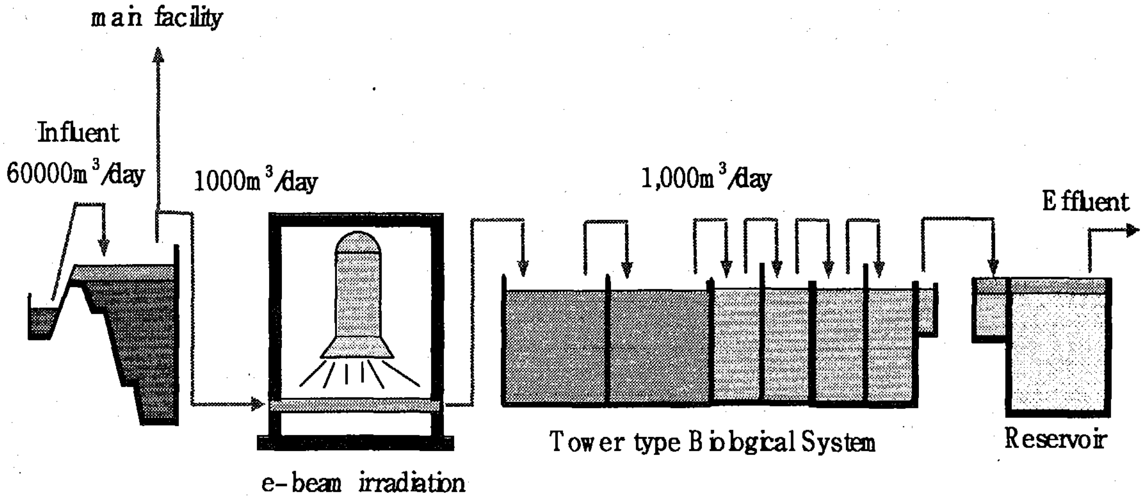

Fig. 6 Schematic Drawing of Pilot Plant

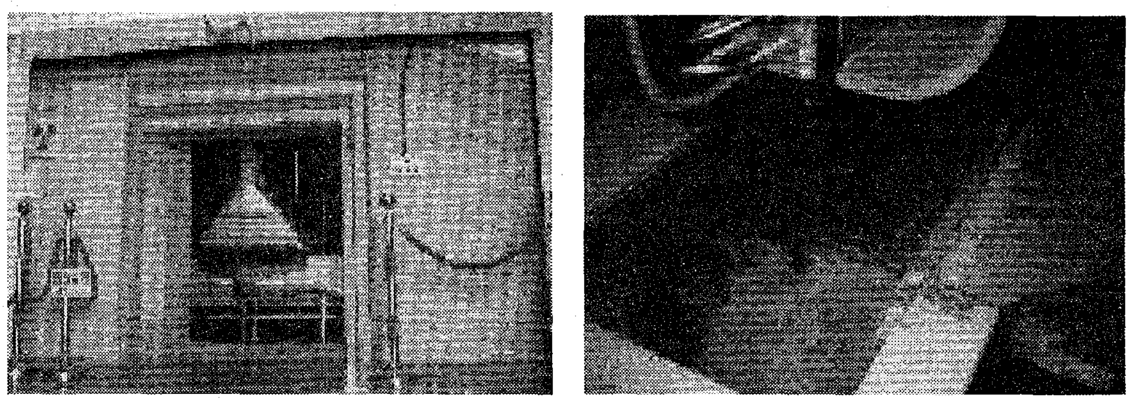

Fig. 7. Electron Accelerator and Wastewater under Injection

7. Operation results of Pilot Plant

Pilot plant inlet flow is a mixture of two flows: raw wastewater from dyeing process and wastewater from polyester fiber production enriched with Terephthalic acid (TPA) and Ethylene glycol (EG); relative flow rate of the latter being 6 - 8 % of total inlet flow rate. Concentration of terephthalic acid in a pilot plant influent is about $2 \cdot 10^{-2}$ mol/l that is much higher than total concentration of all other dissolved pollutants. This concentration corresponds to electron fraction of TPA about 0.2 % that makes direct action of radiation on TPA (or other pollutant) be negligible when treating the wastewater by electron beam. On the other hand, this concentration is high enough to prevent recombination of radical products of water radiolysis in the bulk of solution, taking into account high rate constants of reactions of both reducing (hydrated electrons, hydrogen atoms) and oxidizing (hydroxyl radicals) particles with terephthalate anion:

$$e^-_{aq} + 1,4\text{-}C_6H_4(COO^-)_2 \longrightarrow R^1 \qquad k = 7.3\times10^9\ l\ mol^{-1}\ s^{-1}$$
$$H + 1,4\text{-}C_6H_4(COO^-)_2 \longrightarrow R^2 \qquad k \cong 1\times10^9\ l\ mol^{-1}\ s^{-1}$$
$$OH + 1,4\text{-}C_6H_4(COO^-)_2 \longrightarrow R^3 \qquad k = 3.3\times10^9\ l\ mol^{-1}\ s^{-1}$$

Besides, because of high relative concentration of TPA comparing to other polluting compounds, competition between listed reactions and reactions of radical products from water with other compounds appears to be much in favor of the former ones. It follows from above mentioned that the main (if not the only) result of electron-beam treatment of pilot plant influent would be radiolytical transformations of TPA which can improve its removal by biological treatment. Radiolytical transformations of other initially present compounds, if those take place at all, can proceed via radical or molecular products from TPA. Fig. 8 shows that TPA enriched wastewater can be efficiently purified by biological treatment. However, preliminary electron-beam treatment improves the process, resulting in more significant decreasing TOC, COD_{Cr}, and BOD_5.

As concerns changes in TOC, COD_{Cr}, and BOD_5 during biological treatment, from the data presented in Fig. 8 it follows that preliminary electron-beam treatment make it possible to reduce bio-treatment time twice at the same degree of removal. Coincident results were obtained in a separate set of experiments on the same pilot plant but with reduced wastewater flow rate (~130 l/day). In this case inlet flow was divided into two flows: the first one passed only biological treatment while the second one passed electron-beam treatment, then biological treatment with reduced hydraulic retention time (HRT). Averaged for one month's period decrease in TOC values amounted 72 %, for the first flow (48 h HRT biotreatment), and 78 %, for the second flow (1 kGy electron-beam treatment followed by 24 h HRT biotreatment).

Usually, increase in biodegradability after radiation treatment of aqueous-organic systems is due to radiolytical conversions of some non-biodegradable compounds. It was observed for the cases of radiation-induced elimination of sulfuric group from isobuthylnaphtalene sulfonates or chlorine from various chlorinated organic compounds. In present pilot plant experiments the improvement of biological treatment of wastewater after preliminary electron-beam treatment was found to be caused by radiolytical transformations of biodegradable compound. Electron-beam treatment of wastewater should not appreciably affect total biodegradability of pollutants if the main pollutant is biodegradable, but can improve biodegradation process at initial stages. In other words, irradiation at comparatively low doses (several Grays) for this case does not change total amount of biodegradable substance characterized by BOD_5 but convert part of it into easier digestible form. This is confirmed, also, by the data presented in Fig. 11 where one can see that decrease in TOC, COD_{Cr}, and BOD_5 during biological treatment is close to linear one for non-irradiated wastewater, while for electron beam treated wastewater the decrease is faster at the beginning of biological treatment and decelerates during the process. [1]

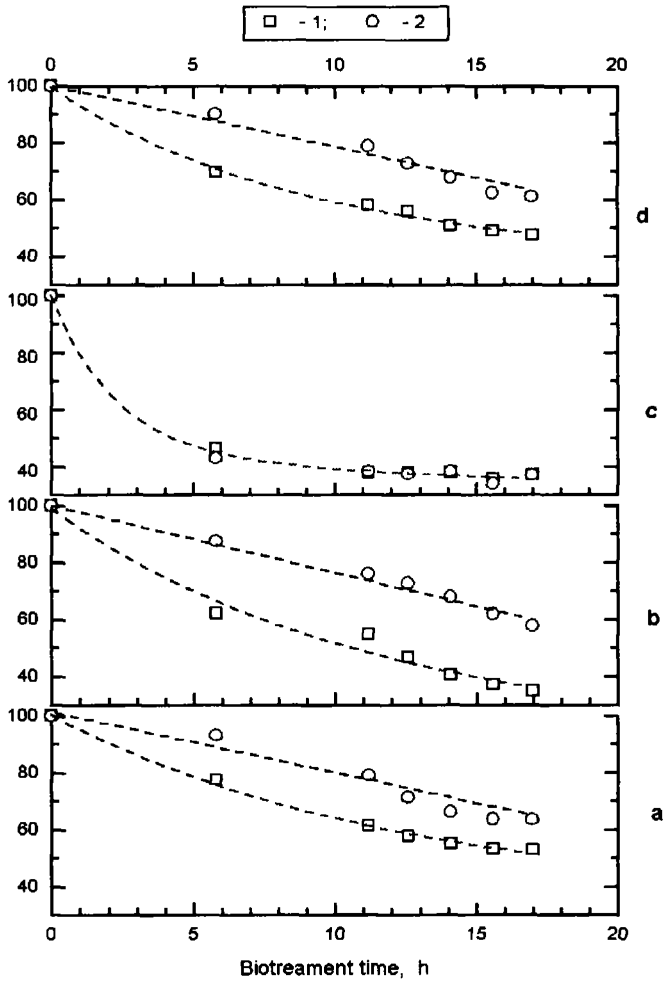

Fig.8 Effect of irradiation and biological treatment on wastewater parameters:
a-TOC; b-COD_{Cr}; c-COD_{Mn}; d-BOD
1- without EB treatment;
2- after EB treatment (dose 2 kGy).

-. Plan for Commercial Plant Construction

On the economical evaluation of electron beam treatment facilities, Commercial plant for Dyeing wastewater is under consideration in TDIC and SHI for,

- Decreasing the amount of chemical reagent up to 50 %
- Improving the removal efficiency of harmful organic impurities by 30 %
- Decreasing the retention time in Bio-treatment facility

The characteristics of commercial plant are with the maximum flow rate of 10,000 m^3/day using one 1 MeV, 400 kW accelerator, and combined with existing Bio-treatment facility in TDIC. Expected construction schedule is shown in below,

Month	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Remarks
Basic Design of Plant	—	—	—															IPC
Detail Design of Plant				—	—	—												
Shield Room Construction				—	—	—	—	—	—	—								
Accelerator Installation											—	—	—	—				BINP
Piping and Equipment										—	—	—	—	—	—			
Trial Operation																—	—	DYETEC

8. Summary

-. For industrial wastewater with low impurity levels such as contaminated ground water, cleaning water and etc., purification only with electron beam is possible, but it should be managed carefully with reducing required irradiation doses as low as possible. Also for industrial wastewater with high impurity levels such as dyeing wastewater, leachate and etc., purification only with electron beam requires high amount of doses and far beyond economies.

-. Electron beam treatment combined with conventional purification methods such as coagulation, biological treatment, etc. is suitable for reduction of non-biodegradable impurities in wastewater and will extend the application area of electron beam.

-. A pilot plant with electron beam for treating 1,000 m^3/day of wastewater from dyeing industries has constructed and operated continuously since Oct 1998. Electron beam irradiation instead of chemical treatment shows much improvement in removing impurities and increases the efficiency of biological treatment. Actual plant is under consideration based upon the experimental results.

References

1. B.HAN, et al., "Combined electron-beam and biological treatment of dyeing complex wastewater. Pilot plant experiments", Radiat. Phys. Chem., Vol. 64, pp. 53-59, 2002

2. A.K.PIKAEV, et. al., "Combined electron beam and coagulation method of purification of water from dyes", Mendeleev Communication, June 1997 pp. 176-178
3. B.HAN et. al "Application of Electron Beam to Wastewater from Papermill", XIIth IMRP, 2001, Avignon, France
4. A.V.PONOMAREV, et. al. "Combined electron-beam and adsorption purification of water from Mercury and Chromium using materials of vegetable origin as sorbents", Radiat. Phys. Chem., Vol.49, No.4, pp. 473-476, 1997
5. A.K.PIKAEV, et. al. "Removal of heavy metals from water by electron beam treatment in the presence of an hydroxyl radical scavenger", Mendeleev Communication, Jan., 1997, pp.52-53