Electron Beam Treatment Plant for Textile Dyeing Wastewater

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Abstract. A pilot plant for treating 1,000m^3 of textile dyeing wastewater per day with electron beam has constructed and operated continuously in Daegu, Korea since 1998. This plant is combined with biological treatment system and it shows the reduction of chemical reagent consumption, and also the reduction in retention time with the increase in removal efficiencies of COD_{Cr} and BOD_5 up to 30~40%. Increase in biodegradability after radiation treatment of aqueous-organic systems is due to radiolytical conversions of non-biodegradable compounds. On the basis of data obtained from pilot plant operation, construction of actual industrial scale plant has started in 2003, and will be finished by 2005. This plant is located on the area of existing wastewater treatment facility (Daegu Dyeing Industrial Complex) and to have treatment capacity 10,000m^3 of wastewater per day using one 1MeV, 400kW accelerator, and combined with existing bio- treatment facility. The overall construction cost and the operation cost in the radiation processing, when compared to other conventional and advanced oxidation techniques, are more cost-effective and convenient for wastewater treatment. This project is supported by the International Atomic Energy Agency (IAEA) and Korean Government.

1. Introduction

Purification of wastewater by electron beam 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 [1]. Sometimes such reactions are accompanied by the other processes, and the synergistic effect upon the use of combined methods such as e-beam with bio-treatment, adsorption and others improves the effect of electron beam treatment of the wastewater. In the process of e-beam 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 pollutant contents 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. [2]

The complex wastewater from textile dyeing companies in Daegu Dyeing Industrial Center (DYECEN) was investigated in this research. DYECEN includes about hundred factories occupying the area of 600,000m^2 with 13,000 employees in total. A majority of the factories has equipment used for dip dyeing, printing, and yarn dyeing. The production requires high consumption of water (90,000m^3/day), steam, and electric power, being characterized by large amount of highly coloured industrial wastewater. Purification of the wastewater is performed by chemical and biological treatment). Current facility treats up to 80,000m^3 of wastewater per day, extracting thereby up to 500m^3 of sludge. Rather high cost of purification results from high contamination of water with various dyes and ultra-dispersed solids.

Characteristics of DYECEN wastewater undergo both short-term and long-term variations, the former being equal to 10-13 % while the latter amounting up to 20 % of mean value. Overall characteristics, 5 day's biological oxygen demand (BOD_5), chemical oxygen demand by permanganate method (COD_{Mn}), suspended solid (S/S) are presented in TABLE I. [3]

TABLE I: TYPICAL CHRACTERISTICS OF WASTEWATER IN DYECEN

Parameter	pH	BOD_5(mg/l)	COD_{Mn}(mg/l)	S/S (mg/l)	Colour units
Raw wastewater	12	2,000	900	100	1,000
Chemical treated	6.8~7.5	1,700	450	50	500
After 1st Bio-treat	7.0~8.0	1,300	250	50	400
After 2nd Bio-treat	7.0~8.0	50	80	50	250

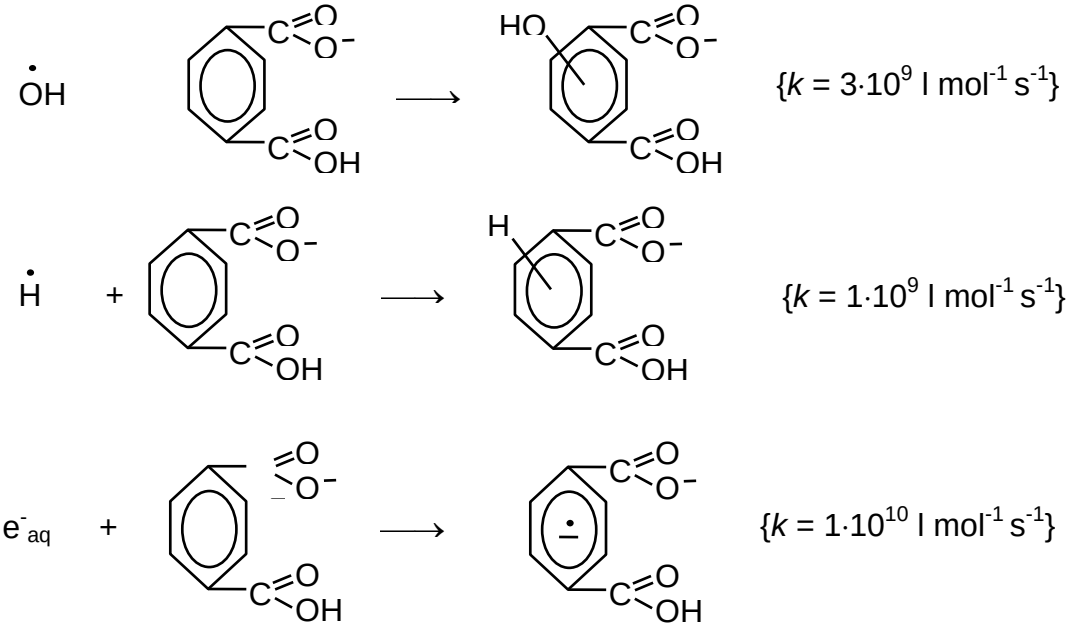
Because of increase in productivity of factories and increased assortment of dyes and other chemicals, substantial necessity appears in re-equipment of purification facilities by application of efficient methods of wastewater treatment. The existing purification system is close to its limit ability in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

2. Radiation Induced Decomposition of Soluble Components in Wastewater

Chemical composition of the wastewater in this plant is not constant. Chemical analysis showed that terephtalic acid (TPA) in dissociated or semi-dissociated form, ethylene glycol (EG), organic dyes, surfactants and other organic compounds exists in the wastewater. TPA and EG are the major components of the wastewater pollutants. Organic dyes and surfactants, even at comparatively low concentration, determine such objectionable properties of the wastewater as colour and foaming, so concentration of these compounds should be substantially reduced. Inorganic compounds are presented mainly by sulphate anion and sodium cation (result of pH adjustment) and small amounts of chlorides and carbonates.

2.1. Decomposition of Major Pollutants

Major components of wastewater, TPA and EG, efficiently react with radical products of water radiolysis. In the case of TPA, at the first stage, all radicals attack on the benzene ring, in the case of EG - abstraction of H atom by H and OH radicals (rate constants from [4]):



Further transformation of TPA radicals is (in reactions with other radicals donating H-atoms) changing benzene ring into cyclodiene structure, formation of phenols and decyclization.

Ethylene glycol radicals formed in reactions (as shown in below) are known [1] to take part in reactions of combination and disproportion, as well as in monomolecular reaction of dehydration, giving rise to formation of tetra-oxy-butane, glyoxal, and acetic aldehyde:

$$\dot{H} + HOCH_2{-}CH_2OH \longrightarrow H_2 + HOCH_2{-}\dot{C}HOH \quad \{k = 1.4\cdot10^7\ l\ mol^{-1}\ s^{-1}\}$$

$$\dot{O}H + HOCH_2{-}CH_2OH \longrightarrow H_2O + HOCH_2{-}\dot{C}HOH \quad \{k = 1.4\cdot10^7\ l\ mol^{-1}\ s^{-1}\}$$

$$2\ OHCH_2{-}\dot{C}HOH \longrightarrow HOCH_2{-}(CHOH)_2{-}CH_2OH$$

$$2\ OHCH_2{-}\dot{C}HOH \longrightarrow HOCH_2{-}CH_2OH + HOCH_2{-}CHO$$

$$OHCH_2{-}\dot{C}HOH \longrightarrow H_2O + CH_2{-}CHO \xrightarrow[(H)]{} CH_3{-}CHO$$

In the presence of oxygen fast reaction of its addition to the radicals proceeds:

$$O_2 + OHCH_2{-}\dot{C}HOH \longrightarrow OHCH_2{-}\underset{\displaystyle O{-}O\,\bullet}{\underset{|}{C}}HOH\ ,$$

resulted in organic molecules oxidation and decarboxylation. Processes of oxidation and decarboxylation (like in the case of TPA solutions radiolysis) proceed, as well, in reactions of peroxide radicals and hydrogen peroxide with organic radicals.

2.2. Decomposition of Organic Dyes

Organic dyes in aqueous solutions are easily decomposed upon irradiation. It is due to effective destruction of chromogenic groups and related system of conjugated double-bonds (that cause intensive light absorption in visible range) by radical products of water radiolysis. Usually, on the first stage of radiolysis, in reactions of dye molecule with e^-_{aq} and H-atom, the semi-reduced form of dye is formed, while in reaction with OH-radical semi-oxidized form is formed. Reactions between two semi-reduced or two semi-oxidized forms lead to degradation of dye.

Figures 1 illustrate the results of electron-beam treatment of aqueous solution of organic dye: acid red dye AB LDN. It shows that almost complete decolouration is observed at absorbed dose less than 7-9 kGy. Presence of dissolved oxygen increases decolouration rate. Together with decolouration of dyes, total degradation of organic molecules into carbon dioxide and water takes place. It follows from presented in the figures data on changes in COD_{Cr} and TOC values of dye solutions upon electron-beam treatment, where substantial decrease in both COD_{Cr} and TOC is observed in absorbed dose range of several kilograys.

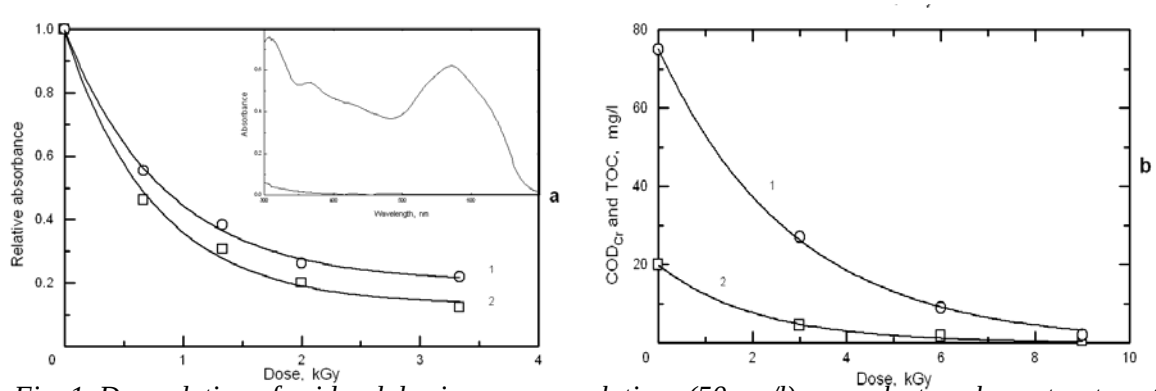


Fig. 1. Degradation of acid red dye in aqueous solutions (50 mg/l) upon electron-beam treatment: ***a*** *- decrease in relative absorbance at 570 nm with dose in de-aerated (1) and aerated (2) solutions;* ***b*** *- decrease in COD_{Cr} (1) and TOC (2) with dose in aerated solutions.*
Insert in ***a*** *- optical absorption spectra of the dye solution before and after irradiation at 9 kGy.*

2.3. Synthetic Surfactants

Synthetic surfactants, like other organic compounds in aqueous solutions, are decomposed in reactions with primary radicals from water followed by reactions of organic radicals, oxidation and decarboxylation. [2, 5] Usually, there is no necessity to decompose all the substance, since concentration of surfactant in wastewater, comparing to other organic compounds, is relatively low and surfactant is not extremely toxic itself. Elimination or transformation of functional group is sufficient for deactivation of the surfactant or reducing its surface activity. It makes also the molecule biodegradable and does not require high absorption dose. Radiation induces degradation of other organic compounds presented in the wastewater, like saturated hydrocarbons, phenols, derivatives of cellulose, etc., proceeds approximately in the same way as that of described above.

2.4. Total Changes in Wastewater Characteristics under EB Treatment

The main changes in textile dyeing wastewater resulting from electron-beam treatment concern transformations of TPA and EG molecules as major components of soluble pollutants. Mean yield of complete degradation of the compounds is equal to about 0.6 μmol/J. It means that less than 10 % (mass) of organic substance will be completely decomposed into water and carbon dioxide at initial concentration near 1500 mg/l and absorbed dose up to 3 kGy. Numerous experiments on electron-beam treatment of DYCEN wastewater showed, indeed, that no significant decrease was observed for parameters characterizing total content of organic compounds, such as TOC, COD, and BOD, after irradiation at several kGy absorption doses. The most notable effect of just irradiation, as it is seen in Fig.1, was decrease in colour of the wastewater as a result of dyes molecules decomposition.

High yields of decarboxylation demonstrate, however, that major part of organic molecules initially contained in solution, from 50 to 90 %, undergo structural transformations. These transformations have an effect on efficiency of the further wastewater treatment processes, like chemical coagulation, settling, and, mainly, bio-treatment (see Fig. 2).

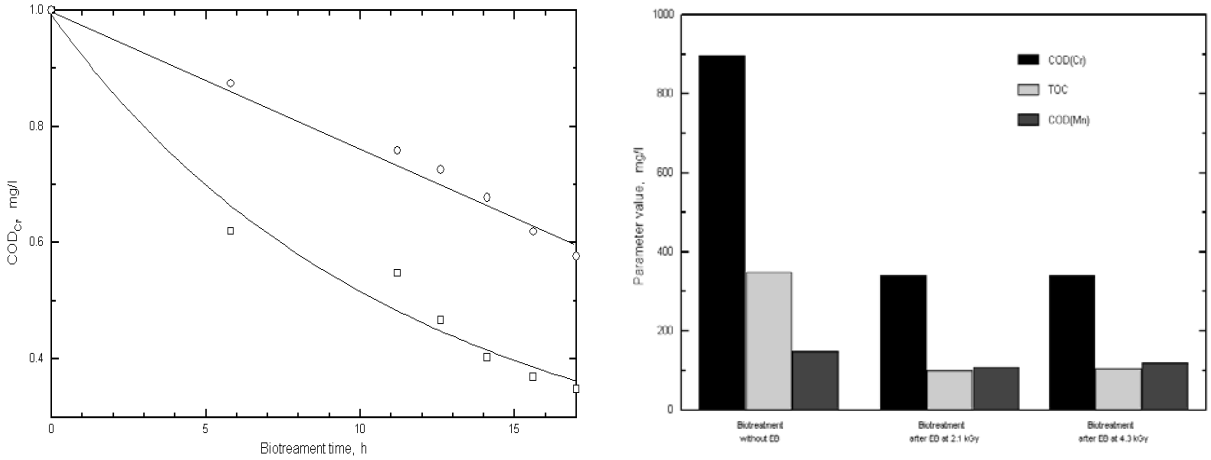


Fig. 2. Effect of electron-beam treatment on biological treatment of DYCEN wastewater:
***a** - kinetics of biotreatment of irradiated (1) and unirradiated (2) wastewater;*
***b** - absorbed dose effect on combined electron-beam/biological treatment.*

From results of laboratory and pilot plant experiments it follows that optimum absorbed dose while electron-beam treating DYCEN wastewater, that provides appreciable improvement of subsequent biological treatment, is the dose 2 kGy. At this dose additional decrease in TOC, COD, and BOD after biological treatment of irradiated wastewater, comparing to unirradiated one, may achieve 30-60 %, and hydraulic retention time of bio-treatment may be reduced by factor of two at the same bio-treatment efficiency.

3. Construction of Industrial Scale Plant

On the experiences from the pilot scale electron beam treatment facility, the industrial scale plant for treating textile dyeing wastewater is under construction 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

According to the data obtained in experiments with DYCEN wastewater [6], the optimum absorbed dose for electron-beam treatment was chosen to be near 2 kGy. For those purpose 400 kW electron accelerators with three separate irradiators was proposed as a source of ionizing radiation. The plant is located on the area of existing wastewater treatment facility in DYCEN and to have treatment capacity 10,000 cubic meters of wastewater a day using one 1MeV, 400kW accelerator, and combined with existing bio- treatment facility.

The process of wastewater treatment consists of the following steps [7]:

- collecting the inflow wastewater in primary (stock) basin;
- pumping the wastewater from primary basin to reactor;
- irradiating the wastewater inside reactor, cooling air being also irradiated;
- collecting irradiated wastewater in secondary basin;
- bubbling irradiated air (containing ozone) through the wastewater in a basin;
- pumping the wastewater from secondary basin to outlet line

Total technological scheme and instrumental diagram of the plant is presented in FIG. 3.

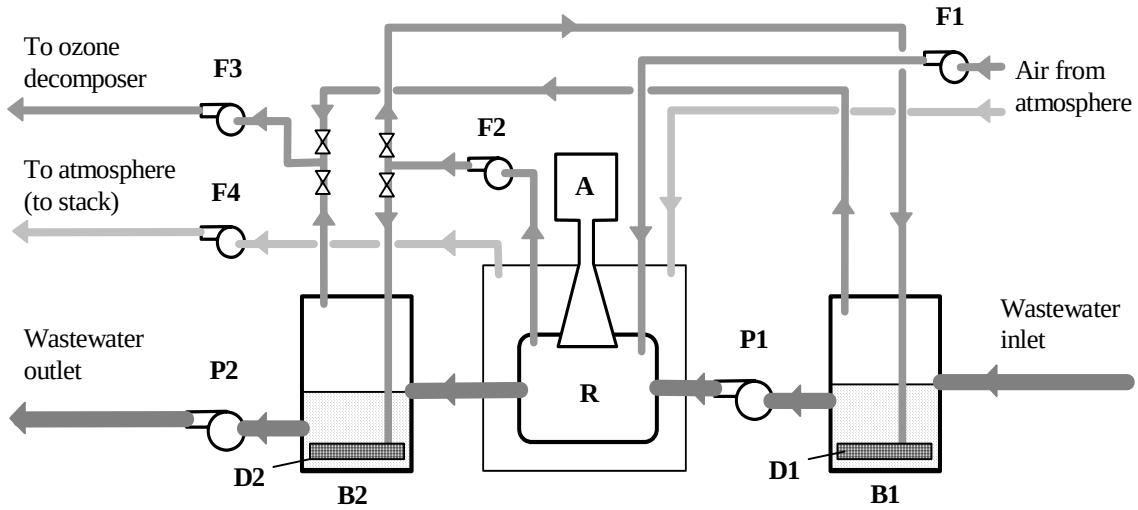


FIG 3. PNID and technological Scheme of Industrial Plant
***F1-F4** – Air fans, **P1-P2** – Water pumps, **D1** and **D2** – Diffusers,*
***A** – Accelerator, **R** – Reactor, **B1** and **B2** – Primary and secondary basins.*

4. CONCLUSIONS

1. A pilot plant for treating 1,000m^3 of textile dyeing wastewater per day with electron beam has constructed and operated continuously since October 1998. This plant is combined with biological treatment system and it shows the reduction of chemical reagent consumption, and also the reduction in retention time with the increase in removal efficiencies of COD_{Cr} and BOD_5 up to 30~40%.
2. Increase in biodegradability after radiation treatment of aqueous-organic systems is due to radiolytical conversions of non-biodegradable compounds. In present experiments the improvement of biological treatment of wastewater after preliminary electron-beam treatment was found to be caused by radiolytical transformations of biodegradable compound.
3. On the basis of data obtained from pilot plant operation, construction of actual industrial scale plant has started in 2003, and will be finished by July 2005. This plant is located on the area of existing wastewater treatment facility in DYCEN and to have treatment capacity 10,000m^3 of wastewater per day using one 1MeV, 400kW accelerator, and combined with existing bio- treatment facility.

Acknowledgment

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