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).

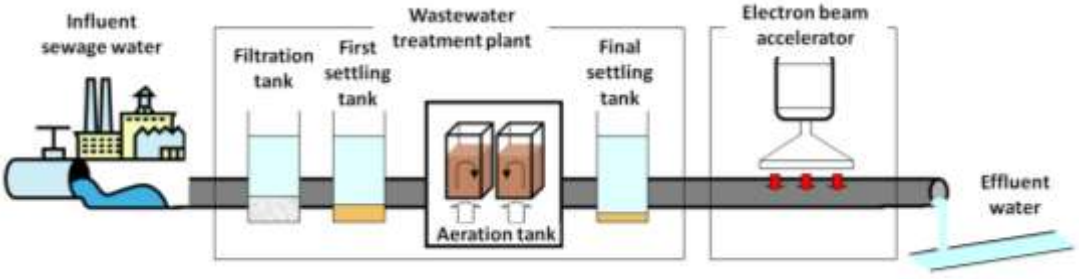

Fig. 1. Wastewater treatment in combination of activated sludge and ionizing radiation.

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.

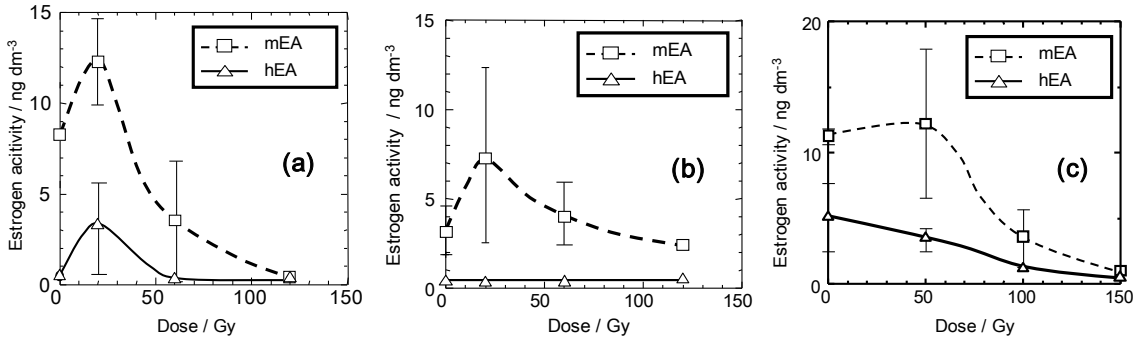

Fig. 2. Estrogen activities estimated using medaka estrogen receptor (mEA:□) *and human estrogen receptor* (hEA:Δ) *for real wastewaters by γ-ray irradiation. (a):Sample 1 (b):Sample 2 (c): Sample 3.*

4.2 Simulation of decrease in estrogen activity of real wastewater

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

$$\text{EDCs} + \text{OH} \xrightarrow{k_1} \text{Product 1a, Product 1b} \quad (1)$$

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

$$\text{Product 1a} + \text{OH} \xrightarrow{k_2} \text{Product 2 (Secondary product)} \quad (2)$$

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:

$$\text{OC} + \text{OH} \xrightarrow{k_3} \text{Unknown products} \quad (3)$$

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

$$-\frac{\mathrm{d}[\mathrm{EDCs}]}{\mathrm{d}D}=\frac{G_{\mathrm{OH}}}{100\cdot 1.6\times 10^{-19}\cdot N_{\mathrm{a}}}\frac{k_1[\mathrm{EDCs}]}{k_1[\mathrm{EDCs}]+k_2[\mathrm{Product1a}]+k_3[\mathrm{OC}]} \tag{4}$$

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 10^7~10^{10} $\mathrm{mol^{-1}}$ $\mathrm{dm^3\ s^{-1}}$, and the concentration of OC is about 10^7 times higher than that of EDCs and Product 1a. Equation (4) is lead into:

$$-\frac{\mathrm{d}[\mathrm{EDCs}]}{\mathrm{d}D}=\frac{G_{\mathrm{OH}}}{100\cdot 1.6\times 10^{-19}\cdot N_{\mathrm{a}}}\frac{k_1[\mathrm{EDCs}]}{k_3[\mathrm{OC}]} \tag{5}$$

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

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:

$$EA=CR_1[\mathrm{EDC_1}]+CR_2[\mathrm{EDC_2}]+\cdots+CR_{\mathrm{n}}[\mathrm{EDC_n}] \tag{7}$$

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:

$$EA=CR_1[\mathrm{EDC_1}]+CR_2[\mathrm{Product\ 1a}] \tag{8}$$

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:

$$\frac{\mathrm{d}[\mathrm{Product\ 1a}]}{\mathrm{d}D}=\frac{A}{[\mathrm{OC}]}[\mathrm{EDCs_1}]-\frac{A}{[\mathrm{OC}]}\frac{\mathrm{k_2}}{\mathrm{k_1}}[\mathrm{Product\ 1a}] \tag{9}$$

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} $\mathrm{mol^{-1}\ dm^3\ s^{-1}}$, 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 $\mathrm{Gy^{-1}}$ and 2.5×10^{-4} g / L $\mathrm{Gy^{-1}}$ obtained by the decomposition of NPs and E2 in the model wastewater.

Simulation results of $D_{1\mathrm{ng}}$ 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.

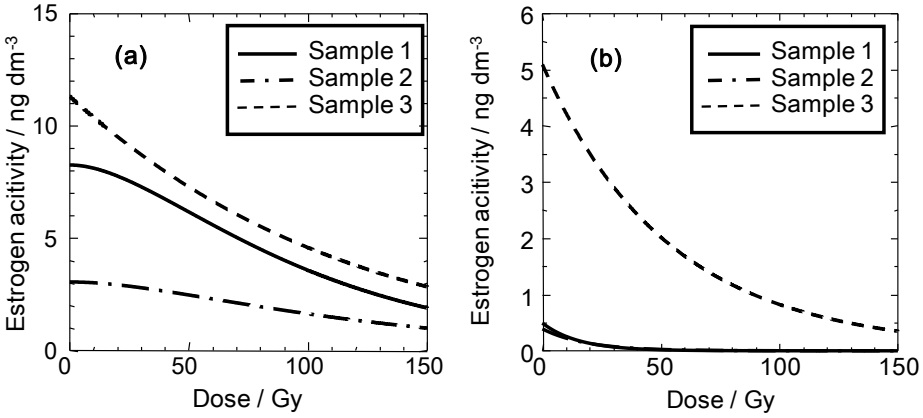

FIG. 3. Simulation of decrease in estrogen activity using medaka estrogen receptor (a) and human estrogen receptor (b).

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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