Bull Environ Contam Toxicol (2008) 81:7–11
DOI 10.1007/s00128-008-9435-4

Degradation of Naturally Contaminated Polycyclic Aromatic Hydrocarbons in Municipal Sewage Sludge by Electron Beam Irradiation

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Received: 3 September 2007 / Accepted: 14 April 2008 / Published online: 20 May 2008

Abstract This study was to evaluate the degradation efficiency of naturally contaminated polycyclic aromatic hydrocarbons in sewage sludge by using electron beam irradiation as a function of the absorbed dose. Degradation efficiency of PAHs was near to 90% at the absorbed doses 5 kGy. The degradation of PAHs was "first order" reaction rates with respect to absorbed dose. The electron beam irradiation was found effective in means of removing PAHs in domestic wastewater.

Keywords Polycyclic aromatic hydrocarbons · PAHs · Electron beam irradiation

Global attention to the increasing of hazardous pollutants reaching the ecosystem has led to a need for the development of new alternative technologies devoted to the degradation of persistent organic pollutants (POPs). The ability of ionizing radiation to convert non-biodegradable substances to more readily degradable ones and its capacity to eliminate microorganisms and several organic pollutants can aid in the treatment of sewage and sludge in the near future (Sampa et al. 1995; Kurucz et al. 1995; Weihua et al. 2002; Al-Bachir et al. 2003; cited in Borrely et al. 1998). According to Martin et al. (2005), the electron beam process uses the Coulomb interaction of the accelerated electrons with atoms or molecules of gases, liquids, or solids. Irradiation by the electron beam of water produces radicals such as e_{aq}^{-}, OH^{*}, H^{*}, H_2^{*}, $H_2O_2^{*}$, OH_{aq}^{-*}, H_2O^{*}, and O_2^{-*}. The fact that the interaction by the radicals is effective on a wide range of pollutants is one of the advantages of electron beam irradiation.

The degradation of POPs and disinfection of pathogenic microorganisms by radiation technology has been widely reported. High-energy electron beam irradiation is among the advanced oxidation processes (AOPs), which can degrade chlorinated compounds, benzene, and other organic compounds. High-energy electron irradiation of waters of varying quality effectively removes hazardous organic chemicals from solutions. This process is considered as an innovative technology that could be utilized within water treatment processes (Weihua et al. 2002). Sampa et al. (1995) described the potential use of an electron beam accelerator for disinfection of domestic wastewater, chemical degradation of dyes, phenols, oils, and greases in industrial wastewater, and reduction of trihalomethane concentrations in drinking water. A high-energy electron beam can degrade 2-, 3-, 4-nitrophenol and 2, 4-dinitrophenol solutions (Weihua et al. 2002). In a recent paper, Kim et al. (2007) claimed that electron beam irradiation can transform refractory organic compounds into easily biodegradable products, thus improving the efficiency and reducing the cost of a further biological treatment step.

The polycyclic aromatic hydrocarbons (PAHs), a class of environmental pollutants that are mainly derived from the incomplete combustion of fossil fuels, enter ground waters and surface waters through leaching processes. While their solubility is generally quite low and usually decreases with increasing molecular weight, thus making their presence in the water cycle an acute and chronic risk to human health and environmental quality (Psillakis et al.

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2004). Degradation of PAHs under ultrasonic and ultraviolet (UV) irradiation has been investigated in numerous experiments. For example, dissolved organic matter inhibition of sonochemical degradation of aqueous PAHs (Taylor et al. 1999); aqueous sonolytic decomposition of PAHs in the presence of additional dissolved species (Laughrey et al. 2001); degradation of PAHs by ultrasonic irradiation (Park et al. 2000); degradation of PAHs by UV/H_2O_2 in perfluorinated surfactant solution (An and Carraway 2002); pyrene photochemical oxidation in aqueous and surfactant solution (Sigman et al. 1998); oxidation of PAHs in water using UV radiation (Beltran et al. 1996).

Electron beam irradiation can effectively destroy toxic organic chemicals. However, relatively few studies have reported the degradation and transformation of PAH compounds by using electron beam irradiation. The scope of this study was to evaluate the degradation efficiency of naturally contaminated PAHs in sewage sludge by using electron beam irradiation as a function of the absorbed dose.

Materials and Methods

The liquid municipal sewage sludge used in this study was collected from Jeonju Waste Water Treatment Plant located in Jeonju-si, Jeollabuk-do, Republic of Korea (North latitude: 35°49′, East longitude: 127°09′). Jeonju Waste Water Treatment Plant is an activated sludge-extended aeration plant that contains a mechanical screen, grit removal tanks, primary sedimentation tanks, extended aeration tanks, final sedimentation tanks, and a chlorination tank (capacity: 403,000 m^3/day) (Chung et al. 2007). The liquid municipal sewage sludge was 23.1 ± 5.9% dry matter, with an organic matter content of 432.5 ± 91.2 g/kg, T–N of 31.1 ± 0.9 g/kg, and T–P of 33.8 ± 1.3 g/kg. All measurements, except dry matter, were evaluated on a dry-weight basis.

Electron beam radiation was performed using an EB-TECH Co. (ELV-4, 1.0 MeV, 40 kW) at the Advanced Radiation Technology Institute, which is located in Jeongeup-si, Jeollabuk-do, Republic of Korea. Using a conveyor at 6.7 m/min, the maximum 10 mm thickness of the sludge layer was irradiated by an electron beam 2 cm wide and scanned a 120 cm length. The liquid municipal sewage sludge was placed in Petri dishes to obtain different volumes, and irradiation was performed with absorbed doses from 1 to 5 kGy.

All of the samples were stored in foil-wrapped vials at 4°C until extraction. More details concerning the materials, analytical procedure, extraction, separation, cleanup, and analysis of PAHs in the samples were previously provided by Cho et al. (2003) and U.S. Environmental Protection Agency (1992); they are briefly mentioned here. The 16 individual PAH compounds used in this study were naphthalene [NAP], acenaphthylene [ACE], acenaphthene [ACT], fluorene [FLN], phenanthrene [PHE], anthracene [ANT], fluoranthene [FLU], pyrene [PYR], benzo(a)anthracene [B(a)A], chrysene [CHR], benzo(b)fluoranthene [B(b)F], benzo(k)fluoranthene [B(k)F], benzo(a)pyrene [B(a)P], dibenzo(a, h)anthracene [DB(ah)A], indeno(1,2,3-cd)pyrene [I(cd)P], and benzo(g, h, i)perylene [B(ghi)P]. Authentic PAH standards and surrogate compounds were purchased from Supelco (Bellefonte, PA, USA).

Concentrations of 16 individual PAHs were determined by gas chromatograph-mass spectrometry (GC–MS) on a device that was also equipped with a mass selective detector (electronic impact mode: 70 eV) as described in the previous paper (Cho et al. 2003; Chung et al. 2007). The detection limits of this method for 16 individual PAHs ranged from 0.33 to 3.21 ng/g. The mean recoveries (%) for surrogates in the samples were 88.1–99.2% (average: 94.4%). The average recoveries of the 16 individual PAHs varied from 53.2% (naphthalene) to 98.4% (benzo(g, h, i)perylene) (average: 89.4%).

Results and Discussion

The reaction mechanisms involved in the degradation of the PAHs using electron beam irradiation are rather complicated, and were not investigated in these experiments (Weihua et al. 2002). Furthermore, in this study, only the degradation rates of 16 individual PAHs were examined. The liquid municipal sewage sludge samples were then irradiated in the presence of air at 1, 3, and 5 kGy electron beam doses. Degradation rates of naturally contaminated PAHs in liquid municipal sewage sludge at various electron beam doses are shown in Table 1. In the liquid municipal sewage sludge, the FLU was at the highest concentration (320.3 ± 72.0 ng/g, n = 3, mean ± SD), and DB(ah)A was detected at the lowest concentration (5.1 ± 4.2 ng/g). The Σ PAH (as the sum of the 16 congeners listed in Table 1) concentration was 1,885.1 ± 35.1 ng/g. The two dominant PAHs in liquid municipal sewage sludge were identified as fluoranthene and phenanthrene. Indeed, phenanthrene in three-ring PAHs, fluoranthene in four-ring PAHs, and benzo(a)pyrene in five-ring PAHs also generate a relatively high contribution, as compared with the rest of the PAHs. The predominance of high molecular-weight PAHs (five- to six-ring) is observed far less frequently. The low molecular-weight PAHs (two- to four-ring) were found to comprise approximately 80% of the Σ PAH concentration.

The consequences on the degradation of PAHs by electron beam irradiation are explored for each case as naphthalene (two-ring), phenanthrene (three-ring), benzo(a)anthracene

Table 1 Degradation of individual PAHs in liquid municipal sewage sludge at various electron beam irradiation doses (ng/g dry wt)

Compounds	Untreated				Electron beam irradiation dose (kGy)											
					1				3				5			
	Mean	SD	Minimum	Maximum	Mean	SD	Minimum	Maximum	Mean	SD	Minimum	Maximum	Mean	SD	Minimum	Maximum
NAP	300.8	36.7	259.6	330.2	108.1	13.0	96.5	122.2	39.6	2.8	36.9	42.5	16.0	2.7	13.9	19.0
ACE	26.3	8.6	21.2	36.2	9.2	1.2	8.1	10.5	6.3	0.5	5.9	6.8	2.5	0.9	1.5	3.1
ACT	85.2	22.4	59.4	99.8	16.9	3.7	12.6	19.6	6.4	2.5	4.2	9.1	2.0	1.2	1.1	3.3
FLN	130.3	6.2	124.1	136.5	31.0	2.0	29.5	33.3	9.3	5.1	5.9	15.2	0.8	0.5	0.3	1.2
PHE	275.4	23.2	260.7	302.2	111.6	47.6	69.4	163.2	7.2	6.9	2.6	15.2	2.0	0.3	1.6	2.2
ANT	65.4	22.3	41.4	85.4	32.8	2.9	29.6	35.4	6.1	3.2	3.4	9.6	2.2	1.1	1.2	3.4
FLU	320.3	72.0	263.3	401.2	93.0	24.3	65.5	111.5	24.9	9.8	16.9	35.8	6.7	1.5	5.5	8.4
PYR	200.9	13.3	187.9	214.5	76.3	8.2	69.1	85.2	37.2	13.6	23.9	51.1	17.8	5.9	12.5	24.1
B(a)A	52.6	16.4	36.5	69.2	27.5	4.7	22.1	30.5	14.9	2.3	12.2	16.3	9.4	2.2	6.9	11.1
CHR	73.3	12.8	59.8	85.2	72.0	2.0	69.9	73.9	65.1	1.3	63.6	66.2	47.6	7.0	39.5	52.2
B(b)F	53.4	6.4	47.6	60.2	43.7	5.7	39.0	50.1	31.5	2.1	29.2	33.3	16.7	1.2	15.6	18.0
B(k)F	77.8	12.6	63.3	85.2	42.9	7.0	36.1	50.1	16.6	3.9	13.8	21.1	12.9	3.2	9.9	16.3
B(a)P	109.5	14.9	96.9	125.9	71.9	8.7	62.1	78.5	27.0	2.7	25.1	30.1	9.4	3.2	5.9	12.1
DB(ah)A	5.1	4.2	1.9	9.9	2.6	0.5	2.2	3.2	1.3	0.3	1.0	1.6	1.0	0.2	0.9	1.2
I(cd)P	32.3	18.6	15.3	52.1	18.7	4.3	13.9	22.2	5.2	2.1	2.7	6.5	2.5	1.4	1.1	3.9
B(ghi)P	76.6	8.3	69.8	85.9	63.7	6.5	59.6	71.2	43.0	3.0	39.6	45.2	19.4	6.4	12.1	23.9

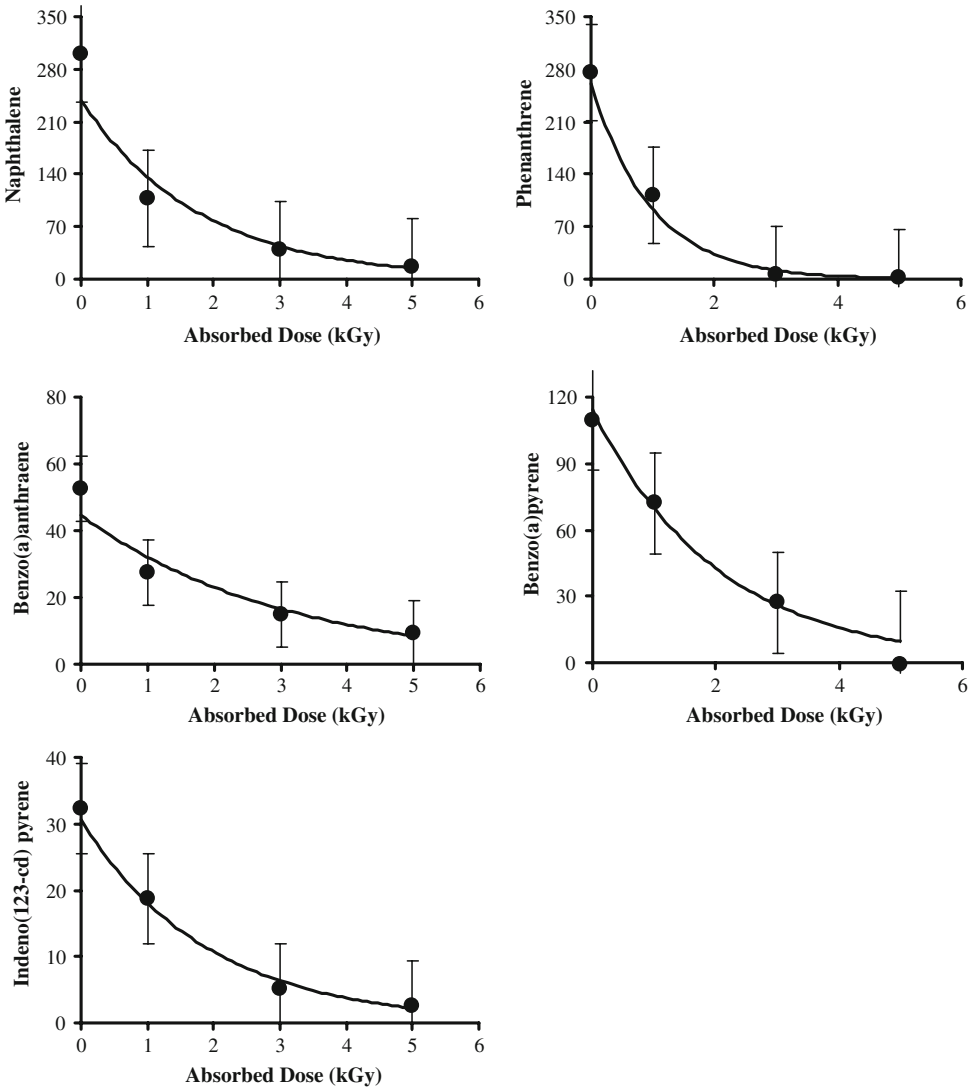

Fig. 1 Degradation of naphthalene, phenanthrene, benzo(a)anthracene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene in liquid municipal sewage sludge at various electron beam doses. The lines show the fittings for the first-order reaction rates

(four-ring), benzo(a)pyrene (five-ring), and indeno(1,2,3-cd)pyrene (six-ring). The degradation rates of individual PAHs were 64.07% of 1 kGy, 86.83% of 3 kGy, and 94.67% of 5 kGy for NAP; 59.48% of 1 kGy, 97.37% of 3 kGy, and 99.29% of 5 kGy for PHE; 47.72% of 1 kGy, 71.67% of 3 kGy, and 82.13% of 5 kGy for B(a)A; 34.29% of 1 kGy, 75.30% of 3 kGy, and 91.44% of 5 kGy for B(a)P; and 48.40% of 1 kGy, 75.18% of 3 kGy, and 79.75% of 5 kGy for I(cd)P, respectively (Table 1). Unusually, in the case of the chrysene [CHR], the degradation rate was lowest, at 1.73% of 1 kGy, 11.15% of 3 kGy, and 35.03% of 5 kGy. Table 1 shows that a dose of 5 kGy may remove approximately 95% of two- to three-ring PAHs, 90% of four-ring PAHs (except for CHR), 80% of five-ring PAHs (except for B(b)F), and 75–92% of six-ring PAHs. The results showed a degradation efficiency close to 90% at an absorbed dose of 5 kGy. The research results demonstrated the electron beam irradiation technology to be an effective means of removing toxic POPs in liquid municipal sewage sludge.

According to Gerasimov (2007), the OH radicals play a dominant initiating role in the destruction of PAH molecules, forming unstable OH– adducts (Atkinson 2000). The interaction of OH with aromatic molecules is characterized by the reaction rate constant, k_{OH}, as a non-monotonic function of temperature (Atkinson 1986). At low temperature ($T < 80°C$), the interaction of the OH radical with the aromatic molecule A_i, containing i aromatic rings, can be represented as the reaction sequence of the OH radical addition to A_i, the formation of a bi-cyclic radical, and the subsequent decomposition of the aromatic ring in the interaction of the bi-cyclic radical with molecular oxygen and nitrogen oxide (Atkinson 2000). The conversion of aromatic molecules occurs in the direction of the decrease in the number of aromatic rings. The rate of this process is almost wholly independent of temperature, and is governed by the rate of the first step with a rate constant of k_{OH}, which depends on the type of compound. The availability of air is also a determining factor.

The degradation of individual PAHs was "first-order" with respect to absorbed dose (Fig. 1). The degradation rates were higher for low molecular-weight PAHs (two- to four-ring) than for high molecular-weight PAHs (five- to six-ring), except in the case of chrysene. The results of this study were similar to those reported by Gerasimov (2007). There remains the possibility that sewage sludge could be recycled as a soil conditioner after the careful elimination of pathogenic microorganisms and the control of organic compounds and heavy metals. Sewage sludge contains macronutrients such as nitrogen and phosphorus, which are essential to plant and animal growth, as well as micronutrients such as zinc, iron, and copper. In this sense, the ability of radiation to reduce biological contamination can be appropriate for decontamination of both sewage and sewage sludge (Borrely et al. 1998).

References

Al-Bachir M, Al-Adawi MA, Shamma M (2003) Synergetic effect of gamma irradiation and moisture content on decontamination of sewage sludge. Bioresour Technol 90:139–143. doi:10.1016/S0960-8524(03)00124-X

An YJ, Carraway ER (2002) PAH degradation by UV/H_2O_2 in perfluorinated surfactant solutions. Water Res 36:309–314. doi:10.1016/S0043-1354(01)00206-8

Atkinson R (1986) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. Chem Rev 86:69–201. doi:10.1021/cr00071a004

Atkinson R (2000) Atmospheric chemistry of VOCs and NOx. Atmos Environ 34:2063–2101. doi:10.1016/S1352-2310(99)00460-4

Beltran FJ, Ovejero G, Rivas J (1996) Oxidation of polynuclear aromatic hydrocarbons in water: UV radiation combined with hydrogen peroxide. Ind Eng Chem Res 36:883–890. doi:10.1021/ie9503631

Borrely SI, Cruz AC, Del Mastro NL, Sampa MHO, Somessari ES (1998) Radiation processing of sewage and sludge: a review. Prog Nucl Energy 33:3–21. doi:10.1016/S0149-1970(97)87287-3

Cho JY, Han KW, Kim JH, Son JK, Yoon KS (2003) Distribution and sources of PAHs in Saemangeum reclaimed tidal lands of central Korea. Bull Environ Contam Toxicol 71:182–188. doi:10.1007/s00128-003-0147-5

Chung NJ, Cho JY, Park SW, Park BJ, Hwang SA, Park TI (2007) Polycyclic aromatic hydrocarbons (PAHs) in soils and crops after irrigation of wastewater discharged from domestic sewage treatment plants. Bull Environ Contam Toxicol (in press)

Gerasimov A (2007) Modelling study of electron-beam polycyclic and nitro-polycyclic aromatic hydrocarbons treatment. Radiat Phys Chem 76:27–36. doi:10.1016/j.radphyschem.2005.12.042

Kim TH, Lee JK, Lee MJ (2007) Biodegradability enhancement of textile wastewater by electron beam irradiation. Radiat Phys Chem 76:1037–1041. doi:10.1016/j.radphyschem.2006.10.001

Kurucz CN, Waite TD, Cooper WJ, Nickelsen MG (1995) Empirical models for estimating the destruction of toxic organic compounds utilizing electron beam irradiation at full scale. Radiat Phys Chem 45:805–816. doi:10.1016/0969-806X(94)00104-R

Laughrey Z, Bear E, Jones R, Tarr MA (2001) Aqueous sonolytic decomposition of polycyclic aromatic hydrocarbons in the presence of additional dissolved species. Ultrason Sonochem 8:353–357. doi:10.1016/S1350-4177(00)00080-8

Martin DI, Margaritescu I, Cirstea E, Togoe I, Ighigeanu D, Nemtanu MR, Oproiu C, Iacob N (2005) Application of accelerated electron beam and microwave irradiation to biological waste treatment. Vacuum 77:501–506. doi:10.1016/j.vacuum.2004.09.019

Park JK, Hong SW, Chang WS (2000) Degradation of polycyclic aromatic hydrocarbons by ultrasonic irradiation. Environ Technol 21:1317–1323

Psillakis E, Goula G, Kalogerakis N, Mantzavinos D (2004) Degradation of polycyclic aromatic hydrocarbons in aqueous solutions by ultrasonic irradiation. J Hazard Mater 108:95–102. doi:10.1016/j.jhazmat.2004.01.004

Sampa MHO, Borrely SI, Silva BL, Vieira JM, Rela PR, Calvo WAP, Nieto RC, Duarte CL, Perez HEB, Somessari ES, Lugao AB (1995) The use of electron beam acceleration for the treatment of drinking water and wastewater in Brazil. Radiat Phys Chem 46:1143–1146. doi:10.1016/0969-806X(95)00345-X

Sigman ME, Schuler PF, Ghosh MM, Dabestani RT (1998) Mechanism of pyrene photochemical oxidation in aqueous and surfactant solution. Environ Sci Technol 32:3980–3985. doi:10.1021/es9804767

Taylor E, Cook BB, Tarr MA (1999) Dissolved organic matter inhibition of sonochemical degradation of aqueous polycyclic aromatic hydrocarbons. Ultrason Sonochem 6:175–183. doi:10.1016/S1350-4177(99)00015-2

U.S. Environmental Protection Agency (1992) Test methods for evaluating solid waste, update II. Method 3540. Washington, DC, EPA report SW-846

Weihua S, Zheng Z, Rami A-S, Tao Z, Desheng H (2002) Degradation and detoxification of aqueous nitrophenol solutions by electron beam irradiation. Radiat Phys Chem 65:559–563. doi:10.1016/S0969-806X(02)00365-1