Removal of EDCs from Industrial Sludge by Electron Beam

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Abstract - Endocrine disrupting chemicals (EDCs) and potential EDCs are mostly man-made, found in various materials such as pesticides, additives or contaminants in food, and personal care products. The high energy ionizing radiation has the ability to remove the EDCs with a very high degree of reliability and in a clean and efficient manner. The ionizing radiation interacts with EDCs both directly and indirectly. Direct interaction takes place with EDCs and the structure of EDCs is destroyed or changed. During indirect interaction, radiolysis products of water result in the formation of highly reactive intermediates which then react with the target molecules, culminating in structural changes. To confirm the radiation reduction of EDCs in industrial sludge, a pilot scale experiment up to 50 kGy of electron beam (EB) was conducted with samples from the textile dyeing industries. The experimental result showed the over 90% of reduction of Nonylphenol (NP) and Di(2-ethylhexyl) phthalate (DEHP) at around 10 kGy of absorbed doses.

Key words : EDCs, Industrial sludge, Electron beam, Radiation

INTRODUCTION

Endocrine disruptors are chemicals that may interfere with the human body's endocrine system and produce adverse developmental, reproductive, neurological, and immune effects in both humans and wildlife. A wide range of substances, both natural and man-made, are thought to cause endocrine disruption, including pharmaceuticals, dioxin and dioxin-like compounds, polychlorinated biphenyls, DDT and other pesticides, and plasticizers such as bisphenol A (BPA) (Schäfer *et al*. 2012). These chemicals are found in many of the everyday products we use, including some plastic bottles and containers, liners of metal food cans, detergents, flame retardants, food, toys, cosmetics, and pesticides. Although limited scientific information is available on the potential adverse human health effects, concern arises because endocrine disrupting chemicals present in the environment at very low levels have been shown to have adverse effects in wildlife species as well as in laboratory animals. The difficulty of assessing public health effects is increased by the fact that people are typically exposed to multiple endocrine disruptors simultaneously.

Conventional processes of coagulation, filtration and adsorptions were introduced regarding their removal potential of endocrine disrupters, however, such technologies may be significant risks in water recycling where contaminants accumulate to comparably high quantities and may be release during treatment. This requires further investigations to understand how easily those contaminants are released and where they accumulate in the water cycle (Colborn *et al*. 1993).

Chemicals(Table 1) that are known endocrine disruptors include diethylstilbestrol (the synthetic estrogen DES), dioxin and dioxin-like compounds, polychlorinated biphenyls (PCBs), DDT, and some other pesticides. BPA is a chemical produced in large quantities for use primarily in the produc-

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Table 1. List of known and suspected endocrine disrupting chemicals

Known EDCs	Suspected EDCs
Persistent Organohalogens dioxins/furans, PCBs, PBBs, octachlorostyrene hexachlorobenzene, pentachlorophenol	2,4-dichlorophenol, Diethylhexyl adipate, Benzophenone, N-butyl benzene
Pesticides 2,4,5-T, 2,4-D, alachlor, aldicarb, amitrole, atrazine, benomyl, beta-HCH, carbaryl, chlordane, cypermethrin, DBCP, DDT, DDT metabolites, dicofol, dieldrin, endosulfan, esfenvalerate, ethylparathion, fenvalerate, lindane, heptachlor, h-epoxide, kelthane, kepone, malathion, mancozeb, maneb, methomyl, methoxychlor, metribuzin, mirex, nitrofen, oxychlordane, metiram, permethrin, synthetic pyrethriods, toxaphene, transnonachlor, tributyltin	
Phthalates DEHP (Di-ethylhexyl phthalate), DHP (Di-hexyl phthalate) BBP (Butyl benzyl phthalate), DprP (Di-propyl phthalate) DBP (Di-n-butyl phthalate), DCHP (Dicyclohexyl phthalate) DPP (Di-n-pentyl phthalate), DEP (Diethyl phthalate)	
Benzo(a)pyrene	
Heavy metals : mercury, lead, cadmium	
Penta-to Nonyl Phenols	
Bisphenol A	
Styrene dimers and trimers	

tion of polycarbonate plastics and epoxy resins. DEHP is a high production volume chemical used in the manufacture of a wide variety of consumer food packaging, some children's products, and some polyvinyl chloride (PVC) medical devices. Phytoestrogens are naturally occurring substances in plants that have hormone-like activity. Examples of phytoestrogens are genistein and daidzein, which can be found in soy-derived products.

The sludge resulting from municipal or industrial wastewater treatment is usually in the form of a liquid or semi-solid liquid that typically contains 0.25～12% solids by weight, depending on the operations and processes used. Table 2 shows sludge treatment plant by radiation. Of the components removed in wastewater treatment, sludge is by far the greatest in volume, and the problems associated with its processing and disposal are complex because:

- It is composed of the substances responsible for the offensive character of untreated wastewater;
- The portion of sludge produced from biological treatment and requiring disposal is composed of the organic matter contained in the wastewater, but in a form that can decompose and become offensive;
- Only a small portion of the sludge is solid matter.

In addition to those, the industrial sludge contains the EDCs, and they may impact a broad range of health effects. When absorbed in the body, an endocrine disruptor can decrease or increase normal hormone levels, mimic the body's natural hormones, or alter the natural production of hormones.

The previous works are mainly to disinfect the microorganisms since the sludge generated by a sewage plant contains a high concentration of pathogens, which limits the reuse of this waste - a rich source of plant nutrients, the disposal of sewage sludge in its original form is an economic loss to society (Breer 1993; Pikaev *et al*. 1994; Lafitte-Trouque *et al*. 2002). However, the industrial sludge is used to send to incineration plant or to the sanitary landfilling area, but causing the secondary problems by the release of EDCs into the environment. Thus, it is necessary to enhance the treatment process to ensure the removal of the EDCs with a high degree of reliability.

A number of processes were investigated regarding their

Table 2. Sludge treatment plant by radiation (Gamma ray or electron beam)

Facilities	Irradiation source	Irradiated material	Operation	Remarks
Munich, Germany (1973 ~ 1984)	Gamma-ray (^{60}Co) 0.57 Mci	Liquid Sewage sludge, 145 m^3 day^{-1}	2 ~ 3 kGy,	Commercial
New Maxico, USA (1978)	Gamma-ray (^{137}Cs) 0.9 MCi	Sewage sludge cake 22 ~ 90 t day^{-1}	10 kGy	Pilot Plant
Vadodara, India (1989)	Gamma-ray (^{60}Co) 0.5 Mci	Liquid Sewage sludge, 110 m^3 day^{-1} (4%SS)	3 ~ 5 kGy	Commercial
Tucuman, Argentina (1998)	Gamma-ray (^{60}Co) 0.7 Mci	Liquid Sewage sludge, 180 m^3 day^{-1} (8 ~ 10%SS)	3 kGy	
Weldel, Germany (1980)	Electron beam 50 kW (1.0 MeV, 50 mA)	Liquid Sewage sludge 500 m^3 day^{-1}	4 kGy	
Verginia Key Florida, USA (1984)	Electron beam (ICT type) (75 kW/1.5 MeV/50 mA)	Liquid Sewage sludge, 645 m^3 hr^{-1}, 4%ss	4 kGy 10 mm-thick	Pilot plant
Takasaki, Japan (1991)	Electron beam (Cockcroft-walton) (15 kW/2 MeV/15 kW)	Sewage sludge cake 300 kg h^{-1}	5 kGy 1 ~ 10 mm thick	Pilot scale
Sao paulo, Brazil (1993)	Electron beam 25 kW (1.5 MeV, 25 mA)	Liquid Sewage sludge 3 m^3 hr^{-1}	3 kGy	Pilot Plant
Warsaw, Poland (1994)	Electron beam (LAE13/9) (10 MeV, 15 kW)	Sewage sludge cake, 70 t day^{-1}	5 ~ 7 kGy 2 ~ 3 cm thick	Design
Daejeon, Korea (2005)	Electron beam 40 kW (1.0 MeV, 40 mA)	Dewatered Sludge	1~3 kGy 6 mm thick	Pilot scale

removal potential of endocrine disrupters. Those processes are ferric chloride coagulation, powdered activated carbon, magnetic ion exchange combined with microfiltration or ultrafiltration, as well as nanofiltration and reverse osmosis.

Key findings were a negligible removal (< 10%) of estrone with ferric chloride coagulation and very high removal (> 90%) with powdered activated carbon. Magnetic ion exchange varied from 40 to 70% removal depending on solution chemistry and dissociation of the hormone. Nanofiltration showed an initial retention of 70 ~ 95%, but for most membranes this retention dropped significantly after an initial filtration period. For some reverse osmosis membranes retention was similar to nanofiltration, but others showed a very high and stable retention of the compounds. Microfiltration also showed near complete retention initially followed by a drop to 0% as expected. The presence of matrix compounds from water and wastewaters affected retention for some membranes. These results, while initially surprising, showed a common theme, which is the adsorption of polar contaminants on materials used in treatment. This includes ion exchange resins, membranes and many other materials that come in contact with the trace contaminants. Implications of those findings are that there may be a significant risk in water recycling where contaminants accumulate to comparably high quantities and may be release during treatment.

MATERIALS AND METHODS

1. Experimental system

To confirm the use of EB as to reduce the EDCs in industrial sludge, pilot scale experiments were conducted in EB Tech Co., Ltd. with samples from the Textile Dyeing Complex in Daegu City which has the capacity of 800 m^3 day^{-1} equipped with the conventional belt press and filter press system (Han *et al*. 2002; Han *et al*. 2005). The experimental scheme is shown in Fig. 1, and typical data of the sludge is in Table 3, 4, and 5. EDCs materials are contained in the sludge, they are used a dye in a dyeing process and an additive in a manufacturing process of polyester. Most of EDCs substance are introduced into the wastewater treatment through the washing process in dyeing process. EDCs material is mostly a non-biodegradable organic substances, that is contained within a large amount of sludge after the wastewater treatment.

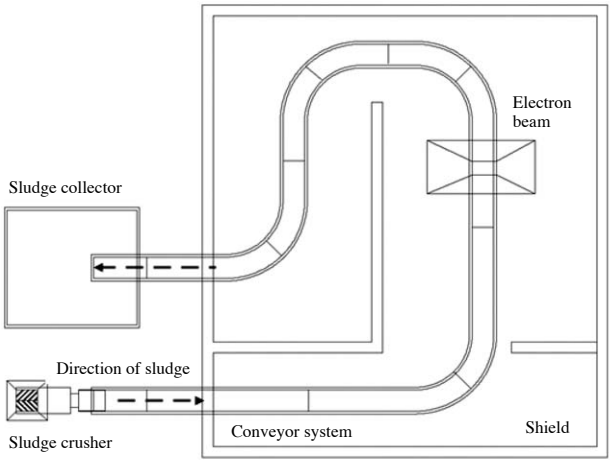

Fig. 1. Pilot scale industrial sludge treatment system at continuous operation mode.

Table 3. Major compounds in sludge cakes of textile dyeing complex

Items	Unit	Result	Method
Carbon (fixed)	%	1.2	ASTM D 5142-04
Ash	%	27.8	ASTM D 5142-04
Water	%	77.3	KS E 3804 : 1996
Volatile matter	%	71.0	ASTM D 5142-04

Table 4. Element analysis in sludge cakes of textile dyeing complex

Items	Unit	Result	Method
C	%	50.9	Element Analyzer
H	%	7.5	Element Analyzer
N	%	5.4	Element Analyzer
O	%	8.2	Element Analyzer
S	%	1.0	Element Analyzer
Cl	mg kg^{-1}	240	EN 14582 : 2007 (IC)
Ash	%	27.6	KS M 0009 : 2005

In this experiment, electron accelerator of 2.5 MeV, 100 kW with the dose rate of 40 kGy s^{-1} is used with the laboratory unit, schematically shown in Fig. 1 was constructed for irradiation under continuous treatment conditions. The initial samples (sludge cakes) are placed in crusher, which produces crushed granular sludge. The crushed sludge is delivered to cart tray by hopper. Thickness of sludge is controlled from 2 to 10 mm; where to consider the range of 2.5 MeV electrons in sludge. The rate of sludge moving under the beam is controlled within the range of 5 ~ 10 m min^{-1}. The sludge moved under the beam window is treated by EB, and then irradiated sludge is collected into the special container. The experiments were conducted with the doses up to 50 kGy at atmospheric temperature (20 ~ 25°C).

Table 5. Inorganic compounds in sludge cakes of textile dyeing complex

Items	Unit	Result	Method
SiO_2	%	0.7	KS L 3128 : 2004
Al_2O_3	%	0.6	KS L 3128 : 2004
Fe_2O_3	%	20.3	KS L 3128 : 2004
CaO	%	0.57	KS L 3128 : 2004
MgO	%	0.16	KS L 3128 : 2004
K_2O	%	0.07	KS L 3128 : 2004
Na_2O	%	0.50	KS L 3128 : 2004
TiO_2	%	1.50	KS L 3128 : 2004
P_2O_5	%	1.27	KS L 3128 : 2004

2. Analysis of EDCs

The analysis of EDCs requires precision and accuracy since the contents of EDCs are relatively small amounts in the sludge. Thus, to achieve the sensitivity, accuracy, precision, selectivity or specificity, and linearity, we also conducted the blank test, control test, standard addition test etc. Two different extraction methods were used in this experiment. The first method is to extract the EDCs by SPE (Solid phase extraction) method from the absorbed sludge by sonicated in water solution. DCM (Dichloromethane), n-Hexane, ethanol, acetone are used as for the solvent of sludge. After the turvovap, the concentrated samples were analyzed by LC-MS/MS (Agilent; Liquid chromatography triple Quadropole 6400). Second method is to use solute extractor from the frozen samples. The sludge samples are rapidly freezing with freezer (EYELA, FUD-2100), and then extracted by solute extractor (Dionex; ASE-200), after concentrating (Turbovap), the extracted solute were analyzed by LC-MS/MS (Agilent; Liquid chromatography triple Quadropole 6400) without any additional purification process (Kim *et al*. 2005; Zhang *et al*. 2007).

RESULTS AND DISCUSSION

1. EDCs in industrial sludge

The initial EDCs concentration of industrial sludge from Daegu Textile Dyeing Complex was analyzed with two different extraction methods (SPE and ASE-200). The data with ASE-200 showed slightly high amount of Nonylphenols and

Table 6. EDCs in sludge cakes of textile dyeing complex

Materials	SPE	ASE-200
Nonylphenols (mg kg^{-1})	0.982	1.245
phthalate (mg kg^{-1})	1.374	2.013
Bisphenol-A	N.D	0.017

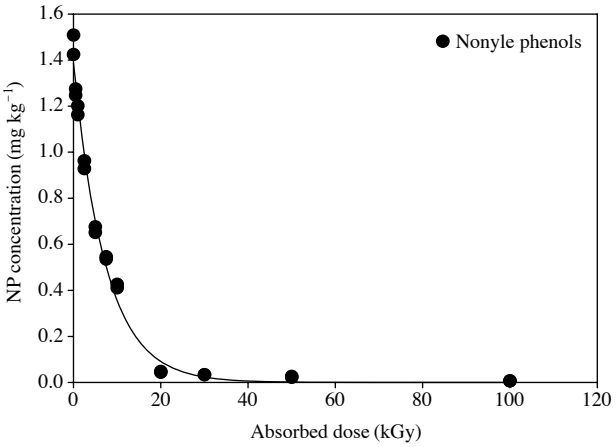

Fig. 2. Decrease of Nonylphenol in sludge cake from textile dyeing complex.

phthalate, where as Bisphenol-A is not detected or detected as low amount which can be negligible in this experiments. The detailed data is shown in Table 6.

2. Degradation of EDCs from industrial sludge by electron beam irradiation

The initial concentration Nonylphenol in raw sludge was 1.5 mg kg^{-1} and it was confirmed at duplicate analysis. The experimental result of Nonylphenol is shown Fig. 2. The concentration of Nonylphenol decrease with absorbed doses, and showed the 90% of removal at 15 kGy and 95% removal at 20 kGy.

The experimental data of DEHP showed the similar trend with Nonylphenol. The initial concentration Nonylphenol in raw sludge was 0.7 mg kg^{-1} and it was also confirmed at duplicate analysis. The experimental result of DEHP is shown Fig. 3. The concentration of DEHP decrease with absorbed doses, and showed the 95% of removal at 20 kGy.

To find the optimum thickness of sludge, the experiments with different sludge thickness from 2 mm to 10 mm has been conducted. The initial concentration of Nonylphenol has increased by intentional addition of Nonylphenol for measurement in model sludge. The experimental result is

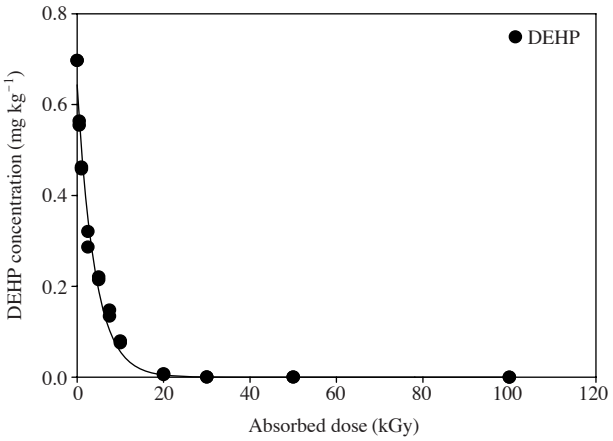

Fig. 3. Decrease of DEHP in sludge cake from textile dyeing complex.

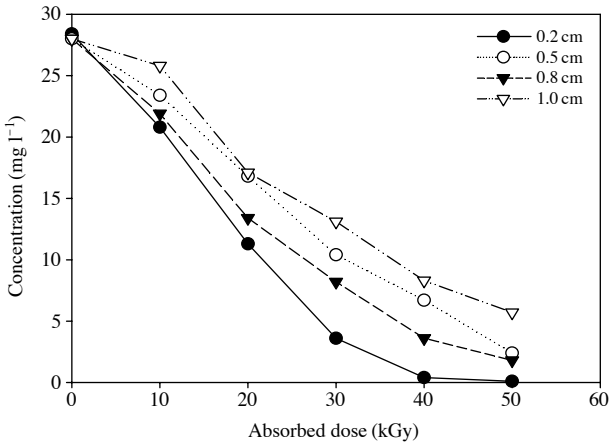

Fig. 4. Decrease of Nonyl phenol on the thickness of sludge cakes.

shown Fig. 4. The removal efficiencies of Nonylphenol decrease with the sludge thickness, and the data will be used for estimation of treatment cost.

CONCLUSIONS

Experimental system to irradiate the industrial sludge with electron beam has been set up and showed continuous treatment of sludge with cart carriage on conveyor. Analytical methods used to detect the EDCs (NP, DEHP, BPA etc.) were based on LC-MS/MS. The industrial sludge from the textile dyeing process showed contamination with NP (1.5 mg kg^{-1}) and DEHP (0.7 mg kg^{-1}), and BPA has not been detected. To remove the NP (95%) and DEHP (95%), the

required absorbed dose is 20 kGy, and it is higher than the required doses reported by others who made the experiments with the EDCs in aqueous system.

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