JASEM ISSN 1119-8362

Full-text Available Online at
www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage. December, 2007
Vol. 11(4) 143 - 146

Effect of gamma radiation on destruction of toxic polychlorinated biphenyls (PCBs) in hydraulic oils

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ABSTRACT: Polychlorinated biphenyls (PCBs) are synthetic organic chemicals and have been commercially used worldwide in many applications. PCBs have been used in oils because of their remarkable properties like flame resistance , thermal stability , dielectric constant , high break down voltage , low volatility etc . However , due to their adverse affects on human health and environment , the use of PCBs has now been banned . PCBs are today considered among widespread pollutants in the global system. Various remedial technologies have been developed in the world to detoxify PCBs. In the recent years, the radiation technology has emerged as an environment friendly technique for treatment of wide spread pollutants. The process involving gamma radiation is safe, reliable, energy efficient and environment- friendly. A study was undertaken to detoxify PCBs in hydraulic oils by gamma radiation using Cobalt 60 as radiation source. Analysis of PCBs in hydraulic oil before and after radiation was carried out by GC –MS instrument. The method used was found to be highly effective and destruction of PCBs was as high as 78.51 %. The degradation efficiency of PCBs destruction was found to be dependent on the applied radiation dose, source of hydraulic oil and also on the type of PCBs. @ JASEM

Polychlorinated Biphenyls (PCBs) are synthetic organic chemicals and were discovered hundred years ago. Their production and commercial use began in 1929. For several decades, PCBs were routinely used in the manufacture of a wide variety of products such as: oils,, paints, plastics, rubbers, adhesives, varnishes, etc., due to the attractive properties e.g., flame-resistance, better thermal stability, high dielectric constant, low thermal conductivity, high breakdown voltage, etc. (Schmelling *et al.,* 1998).

PCBs are hazardous compounds and persistent in eco-system (Arbon *et. al.,* 1994). Commercial productions of PCBs have been banned in 1977 in the world due to their adverse affects on human health. Presently, PCBs are considered among the most widespread pollutants in the global ecosystem (Ilu *et al* ., 1995). The major sources where toxic PCBs exist as a minor ingredient includes: oils, paints, rubbers, cables, electrical & electronic appliances, waste streams etc. All over the world various methods have been developed for detoxification or safe disposal of PCBs. At present, incineration at temperature above 1200°C appears to be the most widely used method for destruction and disposal of PCBs (Singh *et al*., 1985 and Zhang *et al.,* 1995). On heating or incineration they are converted into toxic "Dioxins" or escape as such into the environment and also this method is not cost-effective.

One of the most promising techniques which have been evolved over the last two decades is radiation technology as a safe means to decompose these stable PCBs (Mucka *et al.,* 2000). The radiation induced decomposition of PCBs has been investigated in a variety of organic solvents, mineral oil and iso-propanol (Cury *et al*., 1999). The radiolytic dechlorination process using gamma irradiation using Cobalt -60 source has been successfully done with alkaline solution of PCBs in iso-propanol as well as with drained capacitor containing absorbed PCBs and also in soil contaminant. Further, the radiolysis offers a number of advantages over conventional incineration process such as: minimization of gaseous and effluents, recovery of bulk solvents, oils etc for recycling and destruction at ambient temperature. It also has high destruction efficiency depending upon the nature of PCBs congeners. The process also allows the recycling of valuable products such as oils without much altering their properties The radiolytic degradation of PCBs in water/alcohol mixtures and in transformer oil has also been investigated. Various Cobalt 60 radiators and electron beam accelerator design both static and portable has been used for decontamination process. The process involving gamma radiation is safe, reliable, energy efficient and environment friendly.

In the current investigation, we have examined gamma radiation induced degradation of PCBs in hydraulic oils using Cobalt-60 as radiation source. A detail evaluation of PCBs before and after radiation has been carried out.

MATERIALS AND METHODS

Sampling: Samples of PCBs containing hydraulic oils used for the present study was collected from Ship Breaking Yard, Alang , Gujarat (India). The details of hydraulic oils used for the present study are presented in Table 1.

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Table 1 : Samples of Hydraulic Oil used

S/ No.	Items	Ship	Source
1	Hydraulic oil (Sample 1)	Tema	Plot No. V-2 Ship Breaking Yard, Alang, Gujarat (India)
2	Hydraulic oil (Sample 2)	Lambda	Plot No. 8 Ship Breaking Yard, Alang, Gujarat (India)
3	Hydraulic oil (Sample 3)	Chemical Exporter	Plot No. 24 Ship Breaking Yard, Alang, Gujarat (India)
4	Hydraulic oil (Sample 4)	MV Victory	Plot No. 34 Ship Breaking Yard, Alang, Gujarat (India)

Gamma radiation of hydraulic oil samples*:* Gamma radiation of hydraulic oil samples was conducted at Shriram Applied Radiation Centre, Delhi (India) using Cobalt 60 as radiation source. Experiments on gamma radiation treatment of hydraulic oil samples for studying the PCBs destructions was carried in an fabricated stainless steel sample vessel (310 mm x 150mmx 290 mm). Approx. 250 gm of hydraulic oil samples was taken in a dried sample vessel. The vessel was dried and deareted thoroughly by applying vacuum for 15 mts. This process of dearation was repeated twice. Further, the sample vessel containing hydraulic oil samples was then purged with nitrogen gas for 10 mts. The vessel was then sealed off from the air sources to maintain a nitrogen and were exposed to gamma radiation at varying doses viz. 150 kGy, 200 kGy & 250 kGy for studying the extent of destruction of PCBs.

Analysis of PCBs by GC-MS: Estimation of PCBs in hydraulic oil samples before and after radiation was determined using GC-MS instrument, Model: 200, Saturn, Varian. An accurately weighed hydraulic oil sample (~ 0.2 g) was taken in a volumetric flask and 100ml n-hexane (HPLC grade) was added and mixed thoroughly . 20ml of oil extracted sample in n-hexane was cleaned up by passing it through a florisil packed column (using florisil adsorbent 100 mesh) , height of florisil column 35mm, outer diameter 7-8mm, florisil activated at 130°C for 15 hrs). 10ml of extract in n-hexane from the florisil cleanup was then subjected to sulfuric acid cleanup to further eliminate interference that prevent accurate quantification of PCBs. 1-2ml of concentrated sulfuric acid was taken in a volumetric flask and 10ml extract in n-hexane from the florisil cleanup was added dropwise under constant stirring. The mixture was then transferred to a separating funnel and shaken for 10 mts. The mixture was then allowed to separate into two layers. The bottom layer was discarded and the upper n-hexane layer (extract) was transferred to a separating funnel. Washing of the n-hexane layer (extract) was carried out several times with distilled water until the water was neutral to pH and the n-hexane layer (extract) acid free. Drying of the n-hexane layer (extract) was carried out with anhydrous sodium sulfate (dried at 120°C and cooled in a desicator). It was further filtered through a Whatman filter paper No.42 and transferred to a standard volumetric flask. This extract was analyzed by GC-MS.

RESULTS AND DISCUSSION

The results of total PCBs content determined in hydraulic oil samples before and after radiation at different doses are presented in Table 2. The degradation of PCBs was found to occur for all the samples of hydraulic oil studied. The extent of PCBs destruction was found to be dependent on the applied radiation dose, source of hydraulic oil and also on the type of PCBs. The minimum and maximum extent of destruction of PCBs in exposed hydraulic oil samples were found to be 38.02 % of the ship Lambda (Sample 2) and 79.51% of the ship Tema (Sample 2).

Table 2*:* Total PCBs Content in Hydraulic Oil Samples Before and After Radiation

S/No.	Sample	Before radiation (at 0 kGy)	After radiation at 150 kGy		After radiation at 200 kGy		After radiation at 250 kGy	
		PCBs (ppm)	PCBs (ppm)	PCBs destruc-tion (%)	PCBs (ppm)	PCBs destruction (%)	PCBs (ppm)	PCBs destruc-tion (%)
1	Hydraulic oil (Sample 1)	238.17	110.05	53.79	109.91	53.85	51.10	78.51
2	Hydraulic oil (Sample 2)	388.83	240.99	38.02	150.30	61.34	143..44	63.11
3	Hydraulic oil (Sample 3)	278.40	119.02	57.24	117.21	57.89	110	60.48
4	Hydraulic oil (Sample 4)	234171.57	11436.8	50.64	9008.44	61.12	8503.55	63.30

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It can also be seen that with an increase in radiation dose, PCBs content decreases. By gamma radiation, the level of PCBs have been reduced from 238.17ppm initially to 51.10ppm in case of hydraulic oil of ship Tema (Sample 1), 388.83ppm to 143. 44 ppm in case of hydraulic oil ship Lambda (Sample 2) , 278.40ppm to 110ppm in case of hydraulic oil ship Chemical Exporter (Sample 3) and 23171.5ppm to 8503.55ppm in case of hydraulic oil ship MV Victory (Sample 4) .

The results of PCBs homolog content determined in hydraulic oil samples before and after radiation at different applied radiation doses are presented in Table 3. It shows, that on gamma radiation, the homologs of PCBs initially present in hydraulic oil samples i.e., (monochlorbiphenyl, dichlorbiphenyl, trichlorbiphenyl and tetrachlorobiphenyl) are either destroyed or are converted into lower homologs of PCBs effectively. Further, the content of lower homologs of PCBs in the hydraulic oil sample of ship (i.e., monochlorbiphenyl, dichlorobiphenyl, trichlorbiphenyl and tetrachlorbiphenyl) decreased with increasing dose of radiation.

Table. 3: Homologs of PCBs in Hydraulic Oil Samples Before and After Radiation

S/No.	Oil samples	PCBs Homolog	Before Radiation (0 kGy)	After Radiation		
				At 150 kGy	At 200 kGy	At 250 kGy
			PCBs (ppm)	PCBs (ppm)	PCBs (ppm)	PCBs (ppm)
1.	Hydraulic Oil (Sample 1)	Monochlorobiphenyl	19.16	Nil	Nil	Nil
		Dichlorobiphenyl	133.44	47.56	46.56	7.75
		Trichlorobiphenyl	44.30	26.31	27. 44	17.71
		Tetrachlorobiphenyl	41.27	36.18	35.91	25.59
		Total	**238.17**	**110.05**	**109.91**	**51.05**
2.	Hydraulic Oil (Sample 2)	Monochlorobiphenyl	65.79	23.65	13.52	13.02
		Dichlorobiphenyl	136.59	90.77	55.14	50.14
		Trichlorobiphenyl	133.22	94.76	60.15	59.16
		Tetrachlorobiphenyl	53.33	31. 81	21.30	21.12
		Total	**388.93**	**240.99**	**150.30**	**143.44**
3.	Hydraulic oil (Sample 3)	Monochlorobiphenyl	70.58	39.92	45.14	44.27
		Dichlorobiphenyl	71.93	45.02	43.40	39.23
		Trichlorobiphenyl	65.36	34.08	28.07	26.50
		Tetrachlorobiphenyl	70.53	Nil	Nil	Nil
		Total	**278.40**	**119.02**	**117.21**	**110**
4.	Hydraulic oil (Sample 4)	Monochlorobiphenyl	7174.83	7067.99	6360.20	6276.24
		Dichlorobiphenyl	5447.63	2408.35	1539.54	1327.31
		Trichlorobiphenyl	7001.48	1634.49	1108.70	1000
		Tetrachlorobiphenyl	3547.56	325.97	Nil	Nil
		Total	**23171.5**	**11436.8**	**9008.44**	**8503.55**

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Table 4: Homolog of PCBs Degradation on Gamma Irradiation (Applied dose 150-250 kGy)

PCBs Homolog	Homolog of PCBs Destruction (%)			
	Hydraulic oil (Sample 1)	Hydraulic oil (Sample 2)	Hydraulic oil (Sample 3)	Hydraulic oil (Sample 4)
Monochlorobiphenyl	100	64.05- 80.20	37.27-43.44	1.48-12.52
Dichlorobiphenyl	64.35-94.19	33.54- 63.29	37.41-45.46	30.39-5.63
Trichlorobiphenyl	40.60-60.92	28.86- 55.59	47.85-59.45	76.65-5.71
Tetrachlorobiphenyl	12.33-37.99	40.35- 60.39	100	90.81-100

The results of homologs of PCBs degradation found on gamma radiation are given in Table 4. It shows, that the radiolytic degradation in case of hydraulic oil of ship Tema (Sample 1) were found to be: 100 % of monochlorobiphenyl, 64.35- 94.19% of dichlorobiphenyl, 40.60-60.02% of trichlorobiphenyl and 12.33-37.99% for tetrachlorobiphenyl . Similarly, in case of hydraulic oil of ship Lambda (Sample 2) were: 64.05-80.20 % of monochlorobiphenyl, 33.54-63.29% drichlorobiphenyl, 28.86-55.59% trichlorobiphenyl and 40.35-60.39% of tetrachlorobiphenyl . Similarly in case of hydraulic oil of ship Chemical Exporter (Sample 3) were: 37.27 -43.44-% of monochlorobiphenyl, 37.41-45.46 % dichlorobipheny, 47.85 –54.5 % of trichlorobiphenyl and 100% of tetrachlorobiphenyl, and in case of hydraulic oil of ship MV Victory (Sample 4) were: 1.48- 12.52% of monochlorobiphenyl, 55.79-75.63% dichlorobiphenyl, 76.65 –85.71 % of trichlorobiphenyl and 90.81-100% of tetrachlorobiphenyl.

The degradation of PCBs has been experimentally investigated in hydraulic oil using Cobalt 60 as the gamma ray source. The maximum extents of PCBs destruction in the irradiated sample of hydraulic oil samples were found to be 78.51 % at 250kGy. Further, the results of these experiments suggest that the gamma radiation process using Cobalt 60 radiation source can be used as an alternative method for detoxification of PCBs in hydraulic oil effectively. The radiolysis process by gamma irradiation is technically feasible and can be safely used for treatment of containing hydraulic oils containing toxic PCBs compared to conventional high temperature incineration method.

Acknowledgements: The authors are thankful to Ministry of Environment and Forests, New Delhi (India) for providing financial support and also to the senior management of the Institute for their valuable technical guidance.

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