

Degradation of hexachlorobenzene by electron beam irradiation

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Abstract

Hexachlorobenzene removal efficiencies in different solvents by electron beam irradiation were investigated. Several factors that might affect the removal efficiencies were further examined. At 10 kGy, HCB degradation value was 85.8% in the solvent of acetone:water mixture (20:80, v/v), while at the same dose, the reduction value of 42.6% was achieved in hexane solvent. In the solvent of acetone:water mixture (20:80, v/v), Na₂CO₃ as additive could enhance the degradation efficiency by 4.5%. However, Triton X-100, NaNO₃, NaNO₂ and H₂O₂ as additives reduced the degradation value by 20.0%, 6.3%, 85.7% and 20.5%, respectively. Furthermore, the increase of these additives would result in the decrease of the degradation efficiencies. The pH value of the solvent of acetone:water mixture (20:80, v/v) could affect HCB removal efficiency. At pH 11.8, reduction value of 90.2% was achieved at 10 kGy, while at the same dose, at pH 2.7 and 6.8, the reduction values were only 82.4% and 86.9%, respectively. At the same time, the degradation value of pentachlorobenzene was 94.7% at 10 kGy. In the presence or absence of additives, pH value of the solvent of acetone:water mixture (20:80, v/v) became lower with increasing dose after electron beam irradiation.

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1. Introduction

Hexachlorobenzene (HCB) is one of twelve typical persistent organic pollutants and widely distributed in the environment. HCB's average half-life from all the studies is about 9 years and HCB is therefore very persistent in the environment [1]. The aqueous solubility value of HCB at 25 °C is 0.0096 mg L⁻¹ [2]. HCB has a log octanol/water partition coefficient (log *K*_{ow}) of 6.18 [3]. Log *K*_{ow} for HCB in humic substances from Aldrich HA, Tohro ando soil, Bibai peat soil, Dando brown forest soil and Inogashira ando soil is 4.90, 4.89, 4.73, 4.13 and 4.11, separately [4]. The octanol/air and octanol/water partition coefficients are lower than for many other persistent organic pollutants, which indicate it is more likely to undergo environmental re-cycling than – for example – polychlorinated biphenyls [1]. People expose themselves to it by ambient air, polluted water, food

and the occupational environment. It is difficult to be degraded via less expensive technologies such as bioremediation due to low bioavailability. In many cases, incineration is the only feasible way for contaminant degradation. However, degradation of HCB requires very high combustion temperature and inadequate operating temperature often leads to incomplete contaminant combustion and the formation of by-products having similar or greater toxicity, such as chlorobenzofurans.

Up to now, a lot of researches have been carried out to remove HCB. With a short residence time of 2 s, the removal of HCB was achieved at 1000 °C under 21% of O₂ and at 900 °C with oxygen concentrations of 35% and 50% [5]; the thermal decomposition process was used to remove HCB in pyrolytic environments [6]. Two commercial V₂O₅ ± WO₃/TiO₂-based catalysts were used to catalyze the dechlorination of HCB [7]. Photosensitized dechlorination of HCB has also been carried out [8]. O₂⁻ could react with HCB to form C₆Cl₅OH [9]. HCB removed by solvated electrons was also studied [10]. The degradation of HCB was investigated in municipal sewage sludge by an anaerobic mixed culture [11]. Recently, dechlorination of HCB was achieved by

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a liquid potassium–sodium alloy [12]. Electron beam irradiation is considered to be an effective way to degrade organic compounds by chemical oxidation processes [13]. But decomposition of HCB by electron beam irradiation has not yet been studied.

Electron beam irradiation is considered as an effective way for degrading pollutants found in the environment [14]. In the irradiation process, no additives or a small quantity of them are needed and the possibility of secondary pollution decreases [15]. Electron beam irradiation could be used to destroy non-biodegradable contamination [15]. In the present study, experiments were carried out to investigate the feasibility of HCB degradation by electron beam irradiation.

2. Experimental

2.1. Chemicals and reagents

Standard HCB and pentachlorobenzene were obtained from Aldrich Ltd. Hexane was bought from Shanghai Experiment Reagent Co. Ltd. The other reagents were all analytical-grade.

2.2. Sample preparation

Different solutions containing HCB were prepared and different additives of different concentrations were added into the solvent of acetone:water mixture (20:80, v/v) to determine their effect on degradation. HCl and NaOH were put into the solvent of acetone:water mixture (20:80, v/v) to investigate the effect of pH on reduction efficiency of HCB. The solution with pentachlorobenzene was also prepared under similar condition.

2.3. Electron beam irradiation process

All irradiation experiments were conducted using electron accelerator, which belonged to Ningbo Superpower High-tech Co., Ltd., China and was shown in Fig. 1. The electron energy was 10 MeV and the power was 6 kW. The dose rate of 0.8 kGy s^{-1} was utilized. The experiments were carried out mainly at doses of 1–10 kGy. Samples (25 mL each) were placed in 50 mL airtight glass vessels, which were placed in radiation field to a specific distance from the source.

2.4. Analysis

Qualitative and quantitative analyses of HCB were performed by gas chromatogram–mass spectrum (GC/MS) (GC (HP6890)-

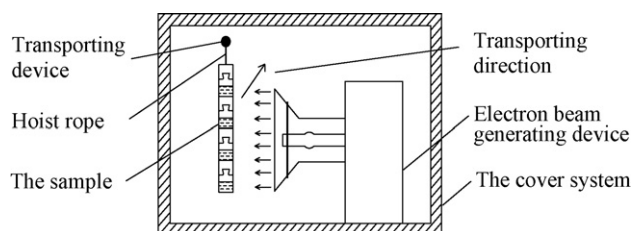


Fig. 1. Schematic diagram of experiment system.

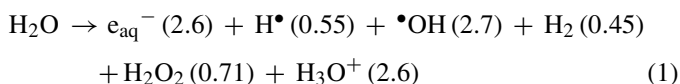
ECD) equipped with a $30 \text{ m} \times 0.25 \text{ mm}$ i.d. ($d_f = 0.25 \mu\text{m}$) Hp-5 silica capillary column. Helium carrier gas flow rate was 1.5 mL min^{-1} . The GC oven temperature was held at 60°C for 2 min, programmed to 220°C at $10^\circ\text{C min}^{-1}$. Injector and detector temperatures were 250 and 300°C , respectively. The pH value was measured by pH monitor (Shanghai Kangyi Instrument Co., Ltd., China, PHS-2C).

3. Results and discussion

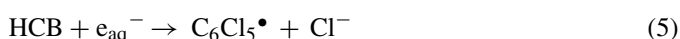
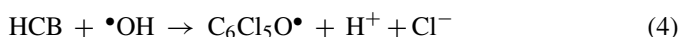
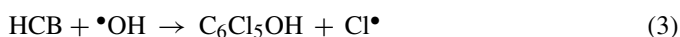
3.1. Electron beam radiation-induced reduction of HCB

The reaction between electron beam with hexane could create solvated electrons [16], hydrogen atoms H^\bullet and H_2 [17]. In hexane solvent, pentachlorobenzene is possibly the reaction product of free electrons, solvated electrons or geminate electrons with HCB and hexachlorocyclohexane is the possible reaction product of H^\bullet with HCB [15].

During electron beam irradiation, water radiolysis happened within a short time. Three reactive species, such as H^\bullet ; hydrated electrons e_{aq}^- ; and hydroxyl radicals $\bullet\text{OH}$, as well as less reactive species H_2O_2 , H_3O^+ and H_2 , which could be seen in Eq. (1) (the numbers in the brackets present the amount of the produced radicals ($100 \text{ eV energy}^{-1}$) [18], were formed:



The mechanism of radiation-induced degradation of HCB in aqueous solvent has been described previously. Both e_{aq}^- and $\bullet\text{OH}$, the most reducing among these species, reduced HCB by loss of the chlorine atoms and open ring reaction of benzene [19,20]:



The reaction products above could induce further loss of the chlorine atoms.

Fig. 2 shows the effect of different solvents on HCB degradation by electron beam irradiation. The results showed that the solvent could affect HCB degradation. The degradation efficiency in these two kinds of solvent increased with increase of dose. At the same dose, the degradation efficiency in the solvent of acetone:water mixture (20:80, v/v) was higher than that in hexane solvent. At the dose of 10 kGy, HCB degradation value in the solvent of acetone:water mixture (20:80, v/v) was 85.8%, while at the same dose, a reduction value of 42.6% was achieved in hexane solvent. Since the quantity of free radicals produced by irradiation was relatively small in organic solvent [16], the removal value in hexane solvent was lower than that in the solvent of acetone:water mixture (20:80, v/v) at the same dose.

Under different conditions, the amount of HCB reduced from per unit dose, i.e. specific reduction efficiency, was different.

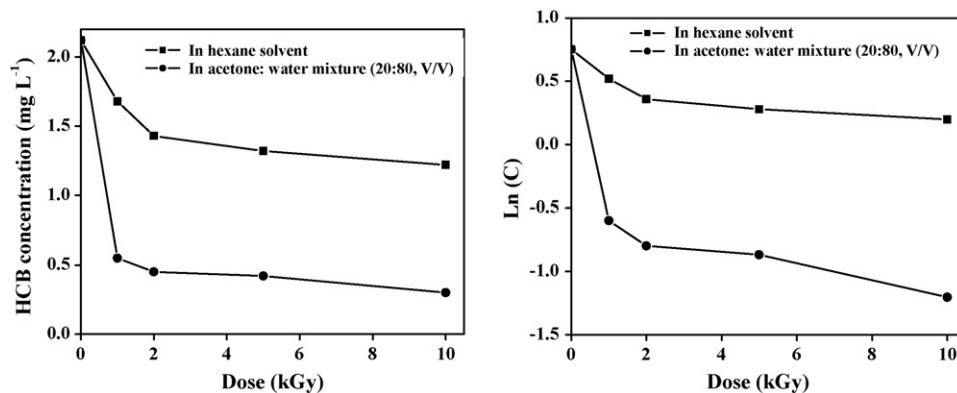


Fig. 2. Concentration changes of HCB in different solvents by electron beam irradiation.

Generally, G value could be used to express this parameter (Eq. (6)) [21]:

$$G = \frac{(\Delta R)(N_A)}{(D)(6.24 \times 10^{19})} \quad (6)$$

where ΔR is the amount of reduced HCB (mol L^{-1}), N_A the Avogadro constant, 6.02×10^{23} ($\text{molecules mol}^{-1}$), D the dose (10^{-2} kGy); 6.24×10^{19} the conversion constant from kGy to 100 eV L^{-1} ($100 \text{ eV L}^{-1} \text{ kGy}^{-1}$), and G is the specific reduction efficiency ($\text{molecules } (100 \text{ eV})^{-1}$).

According to Eq. (6), G values of HCB in the solvent of acetone:water mixture (20:80, v/v) were obtained, as shown in Table 1. The results showed that G values decreased with the enhancement of dose. Both of $\bullet\text{OH}$'s recombination probability and e_{aq}^- 's increase with increased dose. At the higher dose, the relative concentration of active radicals is lower [15]. So G values decreased with increased dose.

Figs. 3–5 show chromatogram of HCB, degradation products in hexane solvent and decomposition products in the solvent of acetone:water mixture (20:80, v/v), respectively. By MS, the degradation products were pentachlorobenzene (peak 1 in Fig. 4) and hexachlorocyclohexane (peak 3 in Fig. 4). It could be seen from Fig. 5 that the retention time of almost all degradation products was very short. As a result, HCB was decomposed into compounds of small molecules. According to the three chromatograms, hydrogenation, loss of the chlorine atoms and open ring reaction of benzene were realized on HCB.

3.2. Effect of different additives to the solvent of acetone:water mixture (20:80, v/v) on HCB degradation

Fig. 6 shows the effect of $10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{CO}_3$, 2.0% Triton X-100, 1.2% H_2O_2 on HCB decomposition by electron beam

Table 1
 G values of HCB in the solvent of acetone:water mixture (20:80, v/v)

Dose (kGy)	G ($\times 10^{-3}$ molecules (100 eV) $^{-1}$)
1	54.02
2	28.70
5	11.65
10	6.23

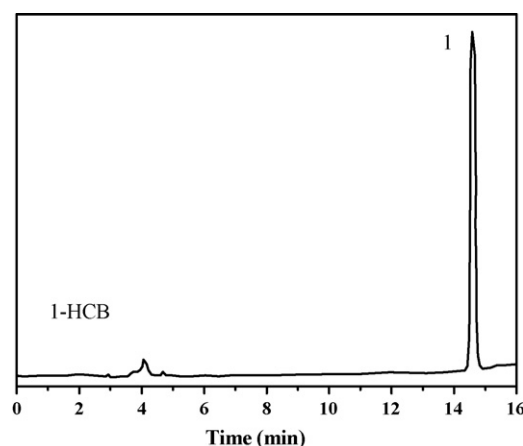


Fig. 3. Chromatogram of HCB.

irradiation. The results showed that the degradation efficiency in the presence or absence of additives improved with increasing dose. Since CO_3^{2-} could react with H_3O^+ , the inhibition of H_3O^+ on e_{aq}^- was reduced [16] and the concentration of e_{aq}^- produced by electron beam irradiation increased. In the present work, a certain amount of sodium carbonate was added into the samples (to obtain the concentration of 1.0 mmol L^{-1}) before irradiation. As shown in Fig. 6, at the same dose the reduction efficiency of HCB was some higher in the presence of

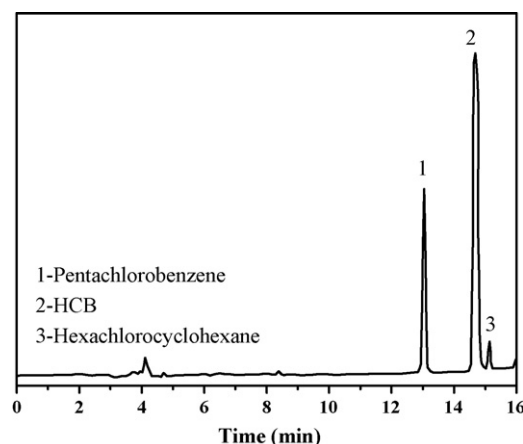


Fig. 4. Chromatogram of degradation products in hexane solvent.

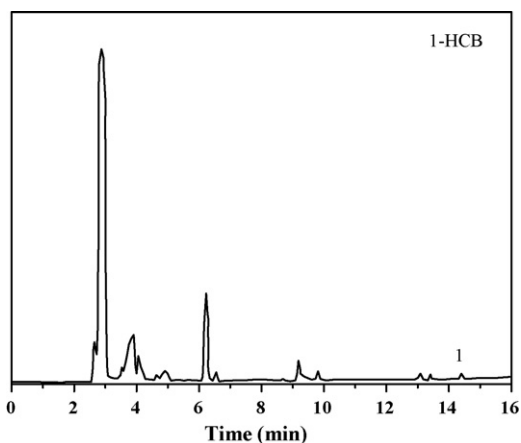


Fig. 5. Chromatogram of degradation products in the solvent of acetone:water mixture (20:80, v/v).

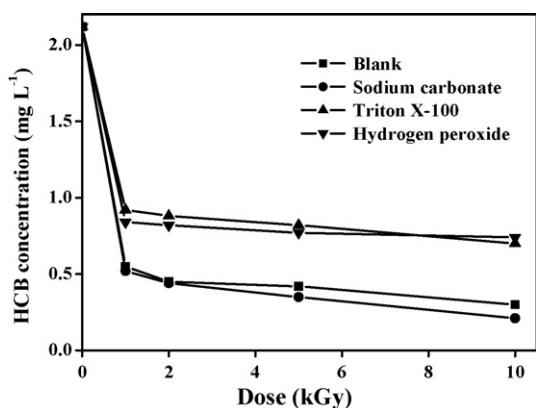


Fig. 6. Concentration changes of HCB in the solvent of acetone:water mixture (20:80, v/v) with adding different additives.

sodium carbonate than that in the absence of sodium carbonate. In the presence of Triton X-100, the decomposition value was lower than that in the absence of Triton X-100. Maybe it was resulted from the reaction between Triton X-100 and e_{aq}^- [22]. In the presence of H_2O_2 , the decomposition value was lower than that in the absence of H_2O_2 . Maybe this reason was that the hydroxyl radicals generated in Eq. (1) produced hydroperoxyl radicals (HO_2^\bullet) in the presence of a local excess of H_2O_2 [23,24]: $H_2O_2 + \bullet OH = HO_2^\bullet + H_2O$.

At 2 kGy and 10 kGy, Na_2CO_3 , $NaNO_3$, $NaNO_2$ and H_2O_2 of different concentrations were added to the solvent of acetone:water mixture (20:80, v/v). The removal values were shown in Table 2. The increase of these additives would result in the decrease of the degradation value. The addition of $NaNO_3$ and $NaNO_2$ resulted in reducing the removal value since e_{aq}^- was

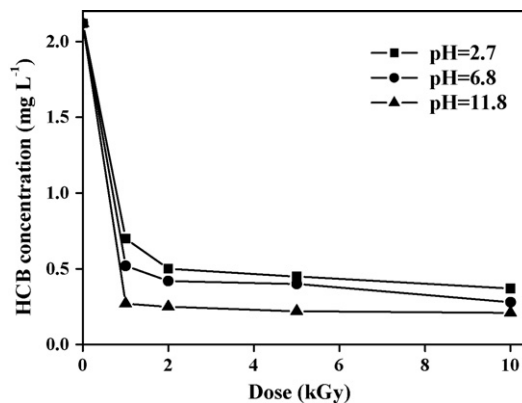


Fig. 7. Concentration changes of HCB by electron beam irradiation at different pH value.

quickly scavenged by them [25] and $\bullet OH$ was scavenged by $NaNO_2$ [26].

3.3. Effect of pH value on HCB degradation

Fig. 7 shows the effect of different pH value on HCB degradation by electron beam irradiation. The results showed that the pH value was an important factor that affected the reduction efficiency of HCB. Decomposition efficiency of HCB was enhanced in alkaline condition. At pH 11.8, a reduction of 90.2% was achieved at the dose of 10 kGy; while at the same dose, at pH 2.7 and 6.8, the degradation value of HCB was only 82.4% and 86.9%, respectively. The change of pH value resulted in concentration change of $[H^+]$ and $[OH^-]$. As we knew, $e_{aq}^- + H^+ \rightarrow H^\bullet$ (with rate constants of $2.3 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$). As a result, change of pH value could accelerate e_{aq}^- reacting with other matters.

3.4. Degradation of pentachlorobenzene

Since pentachlorobenzene was obtained in HCB degradation process by γ irradiation [27], degradation of pentachlorobenzene was also investigated in the present work. Fig. 8 shows the removal of pentachlorobenzene in the solvent of acetone:water mixture (20:80, v/v) and hexane solvent by electron beam irradiation. It could be seen from Fig. 8 that the degradation efficiency of pentachlorobenzene in these two kinds of solvent increased with increasing dose. At the same dose, the removal value was higher in the solvent of acetone:water mixture (20:80, v/v) than that in hexane solvent. At 10 kGy, the degradation efficiency in hexane solvent and in the solvent of acetone:water mixture (20:80, v/v) was 43.3% and 94.7%, respectively.

Table 2
The degradation efficiencies of HCB with adding different additives of different concentration

Dose (kGy)	Blank	Na_2CO_3 (mol L^{-1})		$NaNO_3$ (mol L^{-1})		$NaNO_2$ (mol L^{-1})		H_2O_2 (%)	
		10^{-3}	10^{-2}	10^{-3}	10^{-2}	10^{-3}	10^{-2}	1.2	3.0
2	80.0%	80.4%	87.6%	79.7%	73.7%	67.5%	0	62.3%	60.5%
10	86.9%	91.4%	89.2%	83.4%	77.1%	85.7%	0	66.1%	61.6%

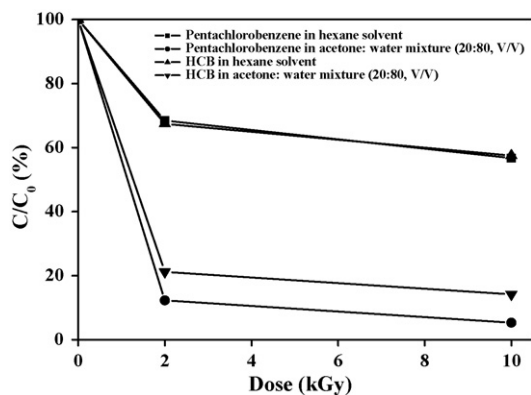


Fig. 8. Removal of pentachlorobenzene and HCB in different solvent by electron beam irradiation.

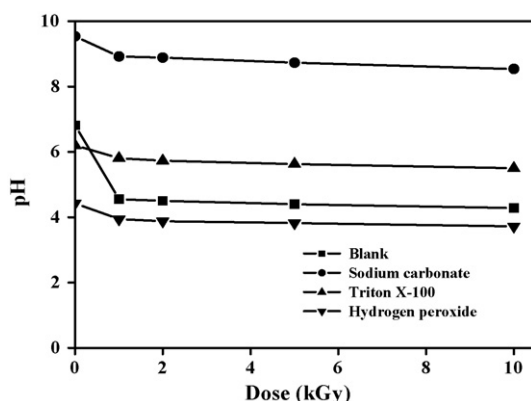


Fig. 9. Changes of pH value after electron beam irradiation.

3.5. Change of pH value

Fig. 9 shows the effect of electron beam irradiation and different additives on pH value. The results showed that the pH value decreased with increasing irradiation dose due to lots of H_3O^+ produced in the irradiation process (in Eq. (1)). In the solutions tested, $[\text{H}^+]$ was mainly from irradiation (Eq. (1)) and Eq. (4).

4. Conclusions

Electron beam irradiation could degrade HCB. At the dose of 10 kGy, HCB degradation value in the solvent of acetone:water mixture (20:80, v/v) was 85.8%, while at the same dose, a reduction of 42.6% was achieved in hexane solvent. HCB was removed possibly because of $\bullet\text{OH}$, solvated electrons, free electrons, geminate electrons or H^\bullet reacting with it.

In the solvent of acetone:water mixture (20:80, v/v), the addition of Na_2CO_3 could enhance the removal efficiency of HCB. However, Triton X-100, NaNO_3 , NaNO_2 and H_2O_2 as additives reduced the removal value. Furthermore, the increase of these additives will result in the decrease of the degradation value.

The pH value of the solvent of acetone:water mixture (20:80, v/v) could affect the reduction efficiency. Degradation value of HCB was enhanced in alkaline condition. Based on the experimental results above, electron beam irradiation was a promising method to decompose HCB.

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