

Research Article

Two-Phase Dechlorination/Detoxification of Lindane (Hexachlorocyclohexane)

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Dechlorination of lindane was carried out in a two-phase reaction. In first phase Devarda's alloy and sodium borohydride were used in aqueous/ethanol reaction media. The reaction duration and temperature were optimized. In first phase higher dechlorination (78%) was achieved at 80°C with 40-minute reaction time and the products were chlorobenzene, dichlorobenzene, and chlorocyclohexane. In second phase, Ca(OH)₂ and sulfur were added in reaction media. The reactions conditions like temperature and reaction time were optimized. After 30 minutes, dechlorination was enhanced from 78% to 94% and the final products were benzene, phenol, catechol, benzenethiol, cyclohexane, cyclohexanol, and cyclohexanethiol. The results suggested that dechlorination of lindane in first and second phase was carried out through hydrodechlorination and substitution reactions, respectively. The developed method was applied for lindane containing real wastewater and higher dechlorination (91%) was achieved under optimized reaction conditions.

1. Introduction

Hexachlorocyclohexane (HCH) (also called lindane), the effective component of technical insecticide HCH, had been widely used in agriculture in the mixture of technical HCH or in pure lindane throughout the world since the 1940s. It is estimated that around 10 million tons technical HCH were used between 1947 and 1997 [1]. In 2009, the use of lindane was completely banned by Stockholm Convention on Persistent Organic Pollutants [2] due to its proven adverse effect on human and other animals health and the serious environmental problems. But lindane has been used in Pakistan and is currently being used for seed treatment in Canada and the United States [3]. In addition, there are tons of HCH produced over the past and are still stored in containers waiting for being disposed of [4]. Pakistan mainly is an insecticide consumer country; the OCPs (organochlorine pesticides) were previously extensively used in the cotton production and other agricultural activities and the use of pesticide has increased by 11 to 69% in the last 20 years [5]. On the other hand at least three thousand metric tons of obsolete and expired pesticides have been stored under

extreme hazardous conditions in more than thousand sites. Locally banned or severely restricted pesticides are easily available and are continuously illegally imported in Pakistan [6–8]. It is desirable to develop remediation technologies to clean up soil, water, and waste sites contaminated by lindane and to help speed up disposal of HCH products.

Few methods like incineration, photochemical dechlorination, and catalytic dechlorination have been studied. The photochemical method needs a radiation source with strict experimental conditions, and deactivation of catalyst in catalytic dechlorination also makes this particular method unfavorable. The incineration method is expensive and produces undesirable polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans as byproducts [9, 10]. In our previous studies we used fly ash, activated carbon, and reducing media to achieve hydrodechlorination. Dechlorination of chlorobenzene compounds was achieved by applying alkaline solutions and sulfur in aqueous/organic solvent [11–14]. We applied Devarda's alloy and NaBH₄ for dechlorination of DDT and TCP. Dechlorination of PCDFs and PCDFs was achieved by applying calcium polysulfide [15]. In continuation of our previous work we developed a

convenient and practicable method for dechlorination of lindane. According to our previous observations dechlorination of monochlorinated compounds always makes a problem as the compounds are very persistent to dechlorinate [11–14]. In this study reaction we carried out dechlorination in two phases; in first phase dechlorination was achieved through hydrodechlorination while in second phase substitution reactions were carried out to enhance dechlorination. This practice not only increased dechlorination (%) but also reduced the reaction time. The effects of temperature and application of hydrodechlorination and substitution reactions in simultaneous and consequent mode were investigated.

2. Experimental

Devarda's alloy powder (45% Al, 50% Cu, and 5% Zn; BDH, England), sodium borohydride, chlorinated aromatic compounds, and organic solvents were received from Merck Company. Calcium hydroxide and sulfur were received as industrial chemical material (>99%). Stock solution of lindane was prepared in pure ethanol (HPLC grade).

The experiments were carried out in a glass reactor equipped with an agitator (90–1000 rpm) and a digitally temperature controlled hot plate (250°C Max.).

The reaction mixture was extracted twice with hexane, with a total final volume of 20–30 mL. Combined organic layers were washed, dried on MgSO_4 , and then concentrated by evaporation to 5 mL volume. Reaction products were analyzed using a gas chromatograph (HP 5890; Hewlett Packard series II) equipped with DB-5 m column (30 m \times 0.25 mm \times 1 μm) and a quadrupole mass spectrometer (JEOL). Ionization was performed under 70 eV electron impact conditions (300 μA , 400 V) where the initial temperature of the column was 35°C, raised at 15°C/min to 150°C and then at 3°C/min to 280°C.

The series of experiments were conducted by changing the concentration of reactants, temperature, and heating duration to optimize the efficiency of the method. In first phase, the solution of 2.85 g lindane (10 mmol) was treated with a mixture of Devarda's alloy and sodium borohydride in water at 40–110°C with agitation (250 rpm) for different durations. The experimental conditions were optimized to achieve the highest dechlorination as shown in Figure 1.

In second phase, the reaction was continued by adding $\text{Ca}(\text{OH})_2$ and sulfur with heating at different temperature from 70 to 110°C and the reaction conditions were optimized to achieve the highest dechlorination (Figure 1). In this paper, results with optimized chemical conditions will be mentioned and discussed.

Experimental yields (amount of products obtained in experiments) are presented in tables in which the contents of chlorocompounds substrates and dechlorinated products were expressed in wt%, and the extent of dechlorination was expressed as the percent of chlorine lost by dechlorination in comparison with the original chlorine content in the substrates by the following formula:

$$\text{Dechlorination (\%)} = \left[\frac{(C_s - C_p)}{C_s} \right] \times 100, \quad (1)$$

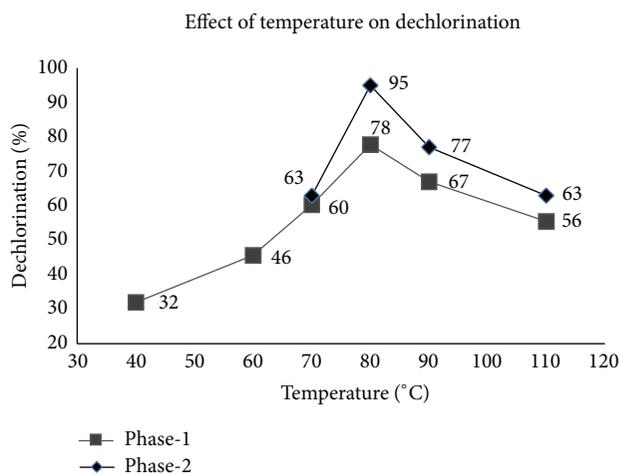


FIGURE 1: Effect of temperature on two-phase dechlorination of lindane.

where C_s and C_p denote the chlorine contents (wt%) in substrate and products, respectively.

3. Results and Discussion

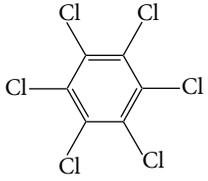
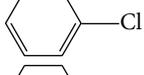
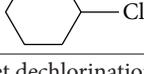
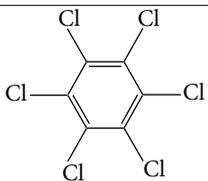
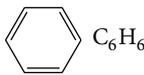
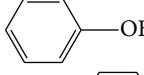
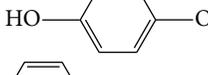
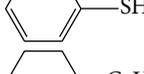
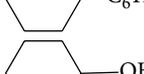
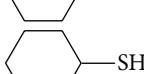
In first phase, a higher dechlorination of lindane (78%) was achieved at 80°C with 0.5 g Devarda's alloy and 0.7 g sodium borohydride with agitation for 40 minutes (after 40 minutes dechlorination was constant) and dechlorination products were chlorobenzene (major) and dichlorobenzene (minor) whereas chlorocyclohexane was also found in traces, as shown in Table 1.

However, in second phase the dechlorination of lindane was enhanced from 78% to 95% with 3 g $\text{Ca}(\text{OH})_2$ and 5 g sulfur by extending heating for further 30-minute reaction time (after 30 minutes dechlorination was constant). Analytical data suggested that the dechlorination products were benzene, phenol, and catechol in major fraction whereas the thiophenol, cyclohexane, cyclohexanol, and cyclohexanethiol were found in minor fraction (Table 1). The formation of benzene derivatives and HCl in reaction media suggested the hydrodechlorination process through elimination of HCl among two vicinal carbon atoms with the formation of double bond.

The resultant products revealed that dechlorination of lindane in first phase was preceded through reduction/hydrogenation reactions. Devarda's alloy along with sodium borohydride generated strong reducing media with plenty of free protons. The formation of chlorobenzene (major), dichlorobenzene, and chlorocyclohexane (minor) suggested a reduction process. Despite strong reducing media, the existence of chlorobenzene in reaction media suggests the stability of this compound. The removal of chloride atom from chlorobenzene to produce benzene is always a difficult task because of the C–Cl bond which is persistent in nature as suggested by other researchers [16–18].

In second phase the removal of chloride atom from C_nH_nCl compounds was achieved through substitution reactions. The provision of media with ample of hydroxyl and

TABLE 1: Dechlorination of lindane.

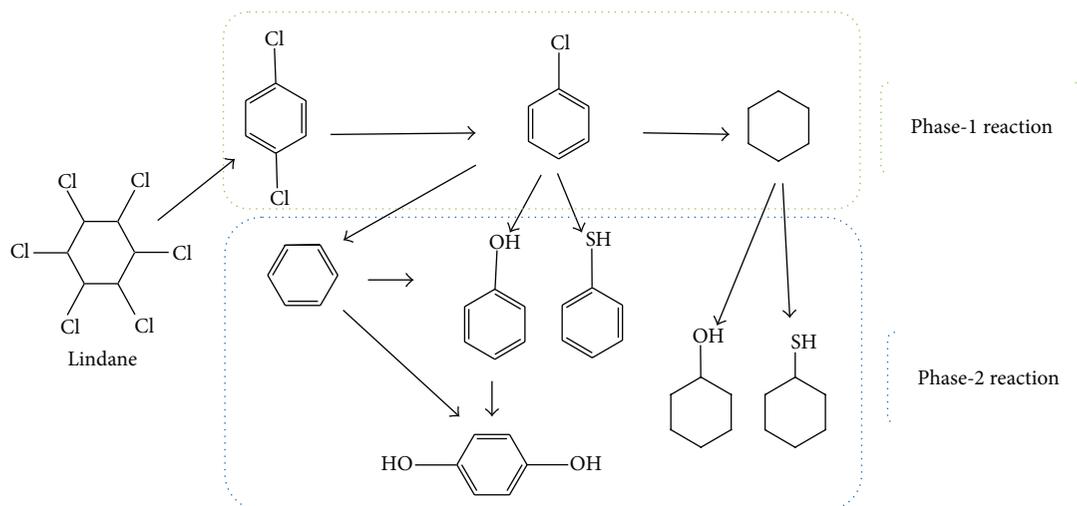
	Organic species	Yield (%) at temperature					
		40°C	60°C	70°C	80°C	90°C	110°C
Phase-1	 C_6Cl_6	52	38	22	5	16	25
	 $C_6H_4Cl_2$	48	36	28	8	18	42
	 C_6H_5Cl	—	26	43	62	48	27
	 $C_6H_{11}Cl$	—	—	07	25	18	06
Net dechlorination (Phase-1)		32%	46%	60%	78%	67%	56%
Phase-2	 C_6Cl_6			10	2	7	11
	 C_6H_6			26	32	32	28
	 $C_6H_5(OH)$			24	18	20	25
	 $C_6H_4(OH)_2$			5	4		2
	 $C_6H_5(SH)$			6	8	6	2
	 C_6H_{14}			6	5	4	14
	 $C_6H_{13}(OH)$			18	26	22	12
	 $C_6H_{13}(SH)$			5	4	9	6
Net dechlorination (Phase-2)			8%	17%	10%	7%	
Overall dechlorination = 78% + 17% = 95%							

(Phase-1): lindane (2.85 g), Devarda's alloy (0.5 g), sodium borohydride (0.7 g) in water, heating time 40 minutes; (Phase-2): reaction mixture of Phase-1, $Ca(OH)_2$ (3 g), sulfur (5 g), heating for 30 minutes.

thiol ions facilitated the substitution reaction and converted the organic chloride into the organic thiol/ol compounds. The formation of phenol, catechol, cyclohexanol, cyclohexanethiol, and benzenethiol advocated a substitution reaction where the chloride ion was substituted by the hydroxyl and thiol ions. The formation of the catechol was an interesting phenomenon which can be explained as follows: the phenol undergoes further hydroxylation by the hydroxyl ions in the reaction mixture. The removal of chloride from chlorobenzene was not feasible through reduction process but it was

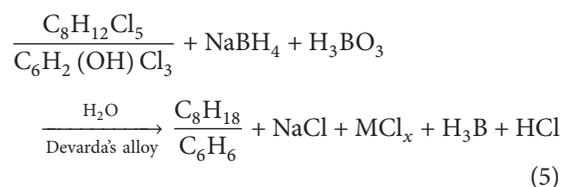
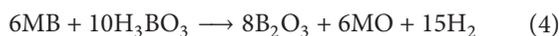
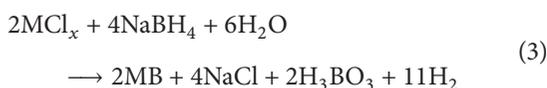
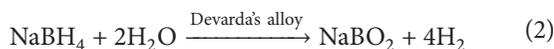
achieved through substitution reaction, whereas the formation of catechol advocated that hydrodechlorination process occurred in first phase prior to that of second phase.

Based on the results a mechanism was postulated that $NaBH_4$ in presence of Devarda's alloy and water decomposes to produce $NaBO_2$ and hydrogen (2) which eventually facilitate the removal of chloride from the substrate. The free chloride in the media reacts with oxidized metals to produce the metal chlorides which further trigger the decomposition of $NaBH_4$ to produce plenty of hydrogen along with H_3BO_3

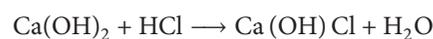
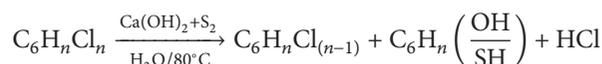
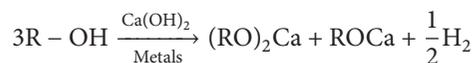
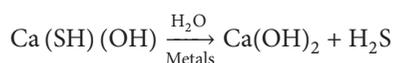
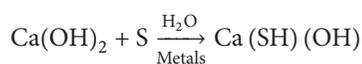


SCHEME 1: Two-phase reaction schematic diagram for dechlorination of lindane.

and MB (“M” presents Cu, Al, and Zn) (3). The MB further reacts with NaBH_4 to produce more hydrogen atoms in the reaction media (4) to produce a chain process for decomposition of NaBH_4 to liberate the hydrogen in the reaction media. However, on the other hand metals contents of Devarda’s alloy provide the free electrons in reaction mixture and thus collectively create a strong reducing media. The metals required in reaction media were provided by Devarda’s alloy:



In second phase calcium hydroxide and sulfur were reacted to produce calcium polysulfide. The calcium polysulfide, in presence of water, decomposed to provide a mixture of $\text{Ca}(\text{SH})_2$, $\text{Ca}(\text{OH})_2$, and $\text{Ca}(\text{SH})(\text{OH})$. In presence of water, $\text{Ca}(\text{SH})(\text{OH})$ further produced $\text{Ca}(\text{OH})_2$ and H_2S . In the reaction mixture, the H_2S acted as strong species to weaken the C–Cl bond. The presence of free OH^- and SH^- ions substituted the Cl^- present on the ring:



(6)

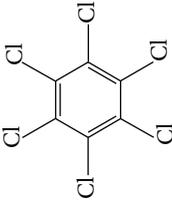
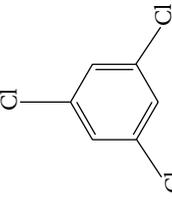
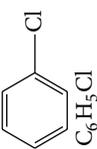
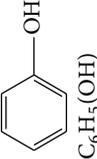
The reactants and the resultant products have been shown in schematic diagram as shown in Scheme 1.

The dechlorination yield (%) was substantially affected by the change in temperature as shown in Figure 1. After achieving highest dechlorination, temperature did not affect dechlorination as it became almost constant. The dechlorination (%) was decreased by the increase in temperature ($>80^\circ\text{C}$). This temperature dependent phenomenon led us to assume the reaction media to remain in reaction vessel in liquid phase. The reaction was carried out in water with ethanol that was used to prepare the lindane solution. Experiments showed that dechlorination (%) was not affected by changing the fraction of organic solvent. This phenomenon supported the proposed mechanism describing the provision of hydrogen by the sodium borohydride.

4. Simultaneous Application of Phase-1 and Phase-2

To check the importance of two-phase procedure, experiments were performed in one phase by applying reduction and substitution media simultaneously. Experiments were performed by treating the lindane with Devarda’s alloy, sodium borohydride, $\text{Ca}(\text{OH})_2$, and sulfur in aqueous/ethanol reaction media, simultaneously. Interesting results were achieved, as shown in Table 2. The presence of chlorophenol and chlorobenzene in trace quantities suggested that the dechlorination (%) was decreased by applying both media simultaneously. It might be due to the reason that free proton (H^+) in reaction media

TABLE 2: Dechlorination of lindane by simultaneous additions of reactants at 80°C for 2-hour heating.

Organic species							
% Age yield	4	10	8	58	12	6	4
Net dechlorination = 75%							

(C₆Cl₆)

C₆H₄Cl₂

C₆H₃Cl₃

C₆H₅Cl

C₆H₁₁Cl

C₆H₅(OH)

C₆H₆

reacted/combined with OH^- and SH^- ions through hydrogen bonding to produce the H-OH and H-SH compounds and suppress their concentration or availability to substitute the chlorides from benzene.

5. Application of Developed Method

5.1. Dechlorination of Lindane Present in Industrial Wastewater. The developed method was applied for industrial wastewater treatment. The lindane containing industrial and agriculture sector effluent sample (3L) was collected from Gujranwala city, Punjab, Pakistan. The physical appearance was dark yellowish color with pH 7.51; EC 1.55 mS/cm; TDS 963 $\text{mg}\cdot\text{dm}^{-3}$; nitrates 57 ppm and the dissolved salt contents salinity was 0.1 $\text{ng}\cdot\text{dm}^{-3}$. The sample was preserved and filtered as described in earlier studies [11–14]. The filtered sample was analysed on GC-ECD for lindane using internal standard technique as described by Zinovyev et al. [19]. To cover the detection limit of lindane the sample was spiked with the 5 ppm lindane standard and then analyzed. Results showed that total $7.4 \pm 0.01 \text{ mg}\cdot\text{dm}^{-3}$ of lindane was found showing actual $2.4 \pm 0.04 \text{ mg}\cdot\text{dm}^{-3}$ of lindane was present in industrial wastewater. The spiked solution (50 mL) was then treated with optimized reaction parameters. The results suggested about $91 \pm 0.1\%$ removal of lindane from industrial wastewater.

6. Conclusion

A significant dechlorination of lindane was achieved by applying two-phase reaction procedure under mild conditions. In first phase dechlorination (78%) was achieved by reduction process by applying Devarda's alloy and NaBH_4 . In second phase dechlorination was further enhanced, from 78% to 95%, through substitution reactions by adding $\text{Ca}(\text{OH})_2$ and sulfur. In both phases reactions were most feasible at 80°C in aqueous/ethanol media. It is concluded that the consecutive application of reducing and substitution media produced different and better results as compared to their simultaneous application. The developed method was applied on lindane containing real wastewater and higher dechlorination was obtained under optimized reaction conditions.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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