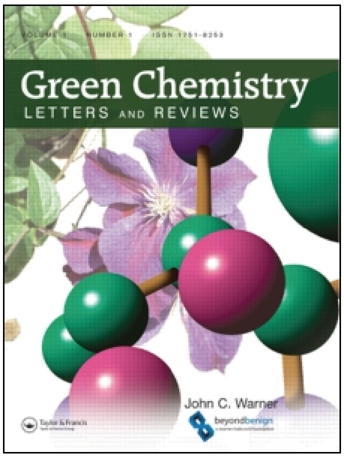

Green Chemistry Letters and Reviews

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t748292817

Enhanced dechlorination of chlorobenzene compounds on fly ash: effects of metals, solvents, and temperature

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To cite this Article Ghaffar, Abdul and Tabata, Masaaki(2010) 'Enhanced dechlorination of chlorobenzene compounds on fly ash: effects of metals, solvents, and temperature', Green Chemistry Letters and Reviews, 3: 3, 179 — 190

To link to this Article: DOI: 10.1080/17518251003660139

URL: http://dx.doi.org/10.1080/17518251003660139

Green Chemistry Letters and Reviews
Vol. 3, No. 3, September 2010, 179–190

RESEARCH REVIEW

Enhanced dechlorination of chlorobenzene compounds on fly ash: effects of metals, solvents, and temperature

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(Received 16 November 2008; final version received 25 January 2010)

Dechlorination of di-chlorobenzene and tri-chlorobenzene on fly ash was optimized. Solutions of sulfur with alkaline solutions of potassium hydroxide, sodium hydroxide, and calcium hydroxide were applied for dechlorination of chlorobenzene compounds. Higher dechlorination (%) on surface of fly ash was achieved in sulfur and calcium hydroxide mixture, which further was enhanced with the addition of sodium hydroxide. Higher dechlorination (%) was obtained at 90°C, where metals in general, and copper and lead, in particular, enhance the catalytic potential of fly ash for dechlorination by hydrodechlorination and substitution reactions. But at high temperatures (120–170°C), dechlorination process was adversely affected by these metals. Moreover, the fly ash particles provided the surface to accomplish reduction and substitution reactions by adsorbing the chlorinated aromatic compound, hydrogen, hydroxyl, and thiol ions. The effects of water, organic solvents, and temperature were studied and reactions conditions were optimized to get maximum dechlorination.

Keywords: fly ash; hydrodechlorination; temperature; aqueous/organic solvents; metals

Introduction

Chlorinated organic compounds are widely used in chemical and electronic industries. Disposal of chlorinated organic wastes in a way that minimizes the environmental hazards has become an urgent issue. Conventional incineration of these wastes produces harmful compounds, such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), unless the operating temperature is strictly controlled (*1*). Many methods for the dechlorination of chlorobenzene compounds have been consequently developed. For example, the techniques of decomposition by combustion with or without oxygen gas at high temperatures (*2,3*), vitrification (*4*), oxidative treatment using supercritical water (*5,6*), and dehalogenation by hydroxide using KOH in 1,3-dimethyl-2-imidazolidinone (DMI) with heating (*7,8*), seemed to present some success for detoxification. However, these methods, which involve high temperature and/or high pressure conditions, have some disadvantages in recovering the vaporized dioxins and poly-chlorinated biphenils (PCBs), in driving up operating costs, and in incurring the high risk of de novo synthesis of dioxins. On the other hand, a few methods using mild conditions, such as an alkali metal like metallic sodium in oil (*9*), bioremediation methods (*10*), and mechano-chemical systems by energy emissions from collision between metallic small balls (*11*) were proposed. However, these methods also present some unfavorable aspects concerning the use of dangerous reducing reagents, such as metallic sodium, low decomposition rates, and less efficiency.

Dechlorination is an effective alternative procedure for decomposing chlorinated organic wastes under relatively mild conditions without the formation of the toxic by-products (*12,13*). Catalytic dechlorination with noble-metal and transition-metal catalysts is an especially simple and efficient method. Molecular hydrogen is often used as a hydrogen source in the catalytic dechlorination. Hydrogen-transferring reactions using hydrogen donors, such as alcohols and formats also have been studied extensively (*14*).

In recent years, catalytic dechlorination methods have been developed including transfer hydrogenation by means of hydrogen donors, such as metal hydrides (*15*), formic acid and its salts, and alcohols (*16,17*). The practical application of catalysts to the dechlorination of organic halides is always accompanied by the problem of deactivation of the catalyst (*18*). Many researchers used fly ash to dechlorinate or detoxify the polychlorinated aromatic compounds and suggested that both chlorination and dechlorination reactions are catalyzed by

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ISSN 1751-8253 print/ISSN 1751-7192 online

DOI: 10.1080/17518251003660139
http://www.informaworld.com

municipal waste incinerator (MWI) fly ash at elevated temperatures and proceed simultaneously on the fly ash surface (*19–23*). Hagenmaier et al. demonstrated that, under oxygen deficient conditions, the destruction of PCDD, PCDF, and other chlorinated aromatics is a general property of fly ash (*24,25*). The authors have proved that dechlorination/hydrogenation of PCDD/PCDF and other chlorinated aromatic compounds on fly ash are catalyzed under certain conditions (*26*). This catalytic property of fly ash is being applied for low temperature decontamination of fly ash during industrial scale operations (*27,28*).

In our previous studies, dechlorination of chlorinated aromatic compounds and substituted chlorinated aromatic compounds was achieved on surface of fly ash by using sulfur and sodium hydroxide solution (*29,30*). It was observed that presence of sulfur, alkali solution, organic, and aqueous media was important to dechlorinate the chlorinated compounds (*31*). In present studies, research was focused to enhance the dechlorination (%) of di-chlorobenzene and tri-chlorobenzene compounds by using various alkali solutions under mild conditions.

Results

The analyzed metals concentration (mg/kg) in fly ash was as: Al 3700, As (2.8), Ba (105), Cd (39.5), Co (11), Cr (53.5), Cu (452), Fe (6340), Mn (453), Pb (1200), Sn (4.95), Sr (157), and Zn (3730).

Maximum dechlorination of di-chlorobenzene (0.25 mol/dm^3) was achieved at 90°C in water/isopropanol mixture. Dechorination (%) was higher in calcium hydroxide as compared to sodium hydroxide and potassium hydroxide, where the sulfur contents were the same in these solutions (Tables 1–3). The dechlorination (%) with calcium hydroxide was further increased by the addition of sodium hydroxide (Table 4). At lower temperature (60–90°C), chlorobenzene, 2-chlorophenol, and chlorobenzene thiol were produced, whereas at higher temperature (120–170°C), 1,3,5-tri-chlorobenzene was produced.

At 90°C, dechlorination of tri-chlorobenzene (0.25 mol/dm^3) was higher in calcium hydroxide as

Table 1. Dechlorination of di-chlorobenzene (fly ash, 4 g; potassium hydroxide, 2 g; sulfur, 4 g; and heating for 13 hours).

	Yields (%)					
Temperature (°C)	$C_6H_4Cl_2$	C_6H_5Cl	$C_6H_4(OH)Cl$	$C_6H_4(SH)Cl$	$C_6H_3Cl_3$	Dechlorination
Water/methanol solvent (15/5 ml)						
60	78	20	2			11
70	76	14	10			12
80	65	15	10	10		22
90	35	45	10	10		32
120	38	34	5	5	18	13
150	52	30			18	6
170	50	30			20	5
Water/ethanol solvent (15/5 ml)						
60	70	25	5			15
70	65	25	10			17
80	48	35	12	5		26
90	37	45	10	8		31
120	38	37	4	5	16	15
150	44	40			16	12
170	45	33			22	5
Water/isopropanol solvent (15/5 ml)						
60	60	30	10			20
70	52	33	10	5		24
80	35	45	10	10		32
90	28	52	10	10		36
120	25	55		5	15	22
150	32	50			18	16
170	35	40			25	7

Table 2. Dechlorination of di-chlorobenzene (0.25 M; fly ash, 4 g; sodium hydroxide, 2 g; sulfur, 4 g; and heating for 13 hours).

	Yields (%)				
Temperature (°C)	$C_6H_4Cl_2$	C_6H_5Cl	$C_6H_4(OH)Cl$	$C_6H_3Cl_3$	Dechlorination
Water/methanol solvent (15/5 ml)					
60	80	18	2		10
70	70	25	5		15
80	54	38	8		23
90	35	50	15		32
120	45	40	5	10	17
150	58	30		12	9
170	60	25		15	5
Water/ethanol solvent (15/5 ml)					
60	65	28	7		17
70	60	30	10		20
80	50	35	15		25
90	30	60	10		35
120	40	40	10	10	20
150	58	32		10	11
170	62	26		12	7
Water/isopropanol solvent (15/5 ml)					
60	55	40	10		20
70	50	33	17		25
80	32	48	20		34
90	18	72	10		41
120	25	65	5	5	32
150	30	62		8	27
170	30	58		12	23

compared to potassium hydroxide and sodium hydroxide provided with the same sulfur contents in water/isopropanol mixture (Tables 5–7). Moreover, the dechlorination (%) with calcium hydroxide was further increased by the addition of sodium hydroxide (Table 8). The consequential products at 60–90°C were chlorobenzene, 2-chlorophenol, and 1,3-dichlorobenzene, whereas at 120–170°C, penta-chloro and hexa-chlorobenzene were produced beside these products. Furthermore, the dechlorination (%) was higher in water/isopropanol mixture as compared to water/ethanol and water/methanol mixtures.

To study the effects of metals on the course of dechlorination, tri-chlorobenzene (0.25 mol/dm^3) was treated with fly ash (4 g), calcium hydroxide (2 g), sodium hydroxide (2 g), and sulfur (4 g) in the mixture of water and isopropanol solvent at 90–150°C (optimized reaction conditions). The main metals of fly ash, such as Fe (15.9 mmol), Cu (15.9 mmol), Mn (18.2 mmol), Pb (4.8 mmol), Zn (15.4 mmol), and Al (18.5 mmol) were added in the reaction mixtures as metals (metallic forms). Results (Table 9) revealed that these metals, in general, and copper and lead, in particular, affect positively at 90°C, as compared to experiments without additives. But at temperatures 120–170°C, these metals, in general, and copper and lead, in particular, adversely affected the dechlorination process as compared to experiments without them prevailing dechlorination products being benzene, chlorobenzene, 2-chlorophenol, penta-chlorobenzene, and hexa-chlorobenzene, as shown in Table 9.

Other series of experiments were carried out without fly ash under optimized reaction condition with metals as additives; results were shown in Table 10.

Discussion

Results demonstrated that the dechlorination percentage was altered through a change in the organic solvent and it was maximum in isopropanol solvent with order as isopropanol > ethanol > methanol, as was reported by Concibido et al. (*32*). An increase

Table 3. Dechlorination of di-chlorobenzene (fly ash, 4 g; calcium hydroxide, 2 g; sulfur, 4 g; and heating for 13 hours).

	Yields (%)					
Temperature (°C)	$C_6H_4Cl_2$	C_6H_5Cl	$C_6H_4(OH)Cl$	$C_6H_4(SH)Cl$	$C_6H_3Cl_3$	Dechlorination
Water/methanol solvent (15/5 ml)						
60	75	20	5			12
70	60	30	10			20
80	40	40	10	10		30
90	20	50	20	10		37
120	28	45	5	5	17	19
150	35	45			20	12
170	30	45			25	10
Water/ethanol solvent (15/5 ml)						
60	60	35	5			20
70	50	35	15			25
80	35	45	20			32
90	20	60	10	10		40
120	25	50	5	5	15	22
150	30	50			20	15
170	30	45			25	10
Water/isopropanol solvent (15/5 ml)						
60	55	35	10			22
70	45	30	25			27
80	15	65	20			42
90	12	68	10	10		44
120	20	55	5	5	15	25
150	25	55			20	17
170	30	50			20	15

in the percentage of dechlorination in isopropanol clearly suggested that organic solvents acted as a hydrogen donor in the catalytic hydrodechlorination of chlorobenzene compounds. It is assumed that the catalytic dechlorination of chlorobenzenes in solution of calcium hydroxide and sulfur in isopropanol involved hydrogen transfer from organic solvent to the aromatic chlorines and displaces a chloride anion from the ring of chlorobenzenes, as suggested by Yuji et al. (*33*). Thus, we concluded that organic solvents acted as hydrogen donors more than to dissolve the organic compounds in reaction media, contradicting observations by other researchers (*2,18,34–37*).

Maximum dechlorination was obtained when a relatively high *v*/*v* ratio of water with isopropanol (3:1) was used. The enhancement in the dechlorination in excess of water (*34,38,39*) presumed to arise from controlling the solubility of substrate, the additives, and the products other than hydrogen source as reported by Yuji et al. (*33*). This argument was supported by the work of other authors (*36,40*) who used metals in alcohols to reduce the chlorinated compounds in the absence of water.

Furthermore, the formation of chlorophenol and chloro-thiophenol suggested that the free hydroxyl and hydrosulfide ions in reaction mixture substituted the chloride ions under specified conditions. Based on dechlorination results, a mechanism was postulated, that calcium hydroxide and sulfur reacted to produce calcium polysulfide which in presence of water decomposed to provide a mixture of $Ca(SH)_2$, $Ca(OH)_2$, and Ca(SH)(OH). In the presence of water, Ca(SH)(OH) further produced $Ca(OH)_2$ and H_2S. On the other hand, the sodium hydroxide reacted with sulfide to produce the Na_2S. In the reaction mixture, the H_2S and Na_2S acted as strong reducing agent to reduce chlorinated compounds. In addition, on the aromatic ring chlorine was substituted by the hydrogen from the hydroxyl group of the alcohols and the alkoxide ions were quenched by the Ca^{2+} and Na^{1+} cations. Furthermore, Ca^{2+} and Na^{1+} ions produced the respective salts with

Table 4. Dechlorination of di-chlorobenzene (fly ash, 4 g; calcium hydroxide, 2 g; sodium hydroxide, 2 g; sulfur, 8 g; and heating for 13 hours).

	Yields (%)					
Temperature (°C)	$C_6H_4Cl_2$	C_6H_5Cl	$C_6H_4(OH)Cl$	$C_6H_4(SH)Cl$	$C_6H_3Cl_3$	Dechlorination
Water/methanol solvent (15/5 ml)						
60	72	20	8			14
70	53	36	11			23
80	33	43	12	12		39
90	18	55	15	12		41
120	25	58	7	5	5	32
150	35	55			10	22
170	35	55			10	22
Water/ethanol solvent (15/5 ml)						
60	58	35	7			21
70	45	37	18			27
80	30	48	22			35
90	12	65	13	10		44
120	25	59	6	5	5	32
150	32	56			12	25
170	32	55			13	21
Water/isopropanol solvent (15/5 ml)						
60	48	40	12			26
70	42	30	28			29
80	10	68	22			45
90	5	75	5	5		52
120	12	70	10		8	36
150	16	66			12	33
170	25	63			12	25

free chloride ions to stabilize them in the reaction mixture.

Moreover, an increase in the dechlorination (%) by addition of the sodium hydroxide along with calcium hydroxide was justified by the fact that the solubility of sodium chloride at temperature >90°C is lower than the calcium chloride. Thus, the addition of sodium hydroxide in the solution of calcium hydroxide and sulfur decreased the free chloride ions in the reaction mixture and consequently decreased the further chlorination. The resultant HCl in the reaction mixture was neutralized by alkali solutions:

$$Ca(OH)_2 + NaOH + S_2 \xrightarrow[\text{metals}]{H_2O} Ca(SH)(OH) + Na_2S + H_2S$$

$$Ca(SH)(OH) \xrightarrow[\text{metals}]{H_2O} Ca(OH)_2 + H_2S$$

$$2R\text{-}OH \xrightarrow[\text{metals}]{Ca(OH)_2/NaOH} (RO)_2Ca + RONa + H_2$$

$$C_6H_nCl_n \xrightarrow[ROH\ +\ H_2O/90^\circ C]{Ca(OH)_2\ \ NaOH\ +\ S_2} C_6H_nCl_{(n-1)} + C_6H_nCl(OH/SH) + HCl$$

$$Ca(OH)_2 + HCl \rightarrow Ca(OH)Cl + H_2O$$

$$Ca(OH)Cl + NaOH + HCl + n\,H_2O \longrightarrow CaCl_2 + NaCl + (n+1)H_2O.$$

The dechlorination yield (%) was substantially affected by the change in temperature. This temperature dependent phenomenon led us to assume that fly ash played a vital role in dechlorination. To find out the effect of metals on dechlorination, the most abundant metals in fly ash (Al, Cu, Fe, Mn, Pb, and Zn) were studied at different temperatures, and the results are shown in Table 2.

Results (Table 9) show that at 90°C, dechlorination was increased by the addition of metals, compared to the experiments without metal additives

Table 5. Dechlorination of tri-chlorobenzene (fly ash, 4 g; potassium hydroxide, 2 g; sulfur, 4 g; and heating for 13 hours).

	Yields (%)							
Temperature (°C)	$C_6H_3Cl_3$	C_6Cl_6	C_6H_5Cl	$C_6H_4(OH)Cl$	$C_6H_4(SH)Cl$	$C_6H_4Cl_2$	C_6HCl_5	Dechlorination
Water/methanol solvent (15/5 ml)								
60	75		20	5				16
70	58		20	5	5	12		24
80	42		25	5	8	20		32
90	27		43	8	10	12		44
120	42		40			12	6	26
130	45	5	32			13	6	15
150	45	13	27			12	5	5
170	48	15	21			14	5	0
Water/ethanol solvent (15/5 ml)								
60	68		30	2				21
70	48		32	4	2	14		30
80	32		38	4	6	20		38
90	22		56	2	5	15		47
120	32		50			10	8	31
130	20	12	50			10	8	16
150	28	12	40			10	10	11
170	32	15	33			10	10	3
Water/isopropanol solvent (15/5 ml)								
60	48		24	10		18		28
70	45		22	10	5	18		30
80	28		39	10	10	15		42
90	18		50	10	8	12		51
120	23		43			28	6	34
130	25	12	31			26	6	12
150	28	17	31			18	6	9
170	30	15	30			15	10	4

(*18,41–43*) but it was decreased at 120–150°C. According to the experimental results, under optimized reaction conditions, copper and lead were more effective than other metals. The effective role of copper under different reaction conditions was described by different researchers (*2,4,5*). A decrease in dechlorination at higher temperature was postulated: at high temperatures (120–150°C), water and alcohol solvent existed in vapor phase that decreased the concentration of OH^- and SH^- ions to substitute chloride ions and consequently the Cl^- ions present in the reaction mixture caused further chlorination. Furthermore, the metals at high temperatures acted as catalysts to perform further chlorination, as observed by other authors (*18,38,42,44,45*).

To investigate the other effects of fly ash, experiments were carried out without fly ash, but copper and lead (most effective metals) were added under optimized reaction conditions. Results (Table 10) suggested that dechlorination without fly ash was lower as compared to experiments with fly ash. Consequently, it was concluded that the particles of fly ash provided the surface for hydrogen released by alcohol and hydroxyl ions given by base to facilitate the reduction/substitution of chlorinated compounds. The chlorinated compounds were adsorbed on the surface of fly ash and were reductively dechlorinated and/or substituted by OH^-/SH^- ions.

Experimental

The dioxins-free fly ash was taken from the fabric filters of local MWI purotherm and its metals composition was analyzed by acid digestion method. The digestion methodology to analyze metals was based on the USEPA method 3051A 1998. About 0.5 g fly ash sample was digested with 9 ml concentrated nitric acid and 3 ml concentrated hydrochloric acid in a microwave sample preparation system (multiwave 3000, Anton Paar GmbH, Austria). Digested fly ash sample was filtered by syringe membrane filter (0.45 μm) and diluted to 100 ml by adding double distilled

Table 6. Dechlorination of tri-chlorobenzene (0.25 M; fly ash, 4 g; sodium hydroxide, 2 g; sulfur, 4 g; and heating for 13 hours).

	Yields (%)				
Temperature (°C)	$C_6H_3Cl_3$	C_6H_5Cl	$C_6H_4(OH)Cl$	$C_6H_4Cl_2$	Dechlorination
Water/methanol solvent (15/5 ml)					
60	72	28			18
70	55	25	10	10	26
80	35	35	10	15	40
90	22	50	10	18	46
120	35	44		21	36
130	40	40		20	33
150	45	33		22	30
170	48	27		25	26
Water/ethanol solvent (15/5 ml)					
60	65	30	5		23
70	50	35	10	15	25
80	30	45	10	15	41
90	15	69	4	12	52
120	35	55		10	36
130	40	40		20	33
150	40	42		20	32
170	45	30		30	25
Water/isopropanol solvent (15/5 ml)					
60	45	30	10	15	31
70	38	37	10	15	36
80	20	55	13	12	49
90	12	68	8	12	54
120	18	60		22	47
130	22	50		28	42
150	30	40		30	36
170	35	35		30	33

water. Prepared sample was kept in polypropylene bottles (soaked in acid and washed with double distilled water prior to use).

The clear supernatant solution was analyzed for different metals. Most of metals were analyzed using an inductively coupled plasma optical emission spectroscopy (Perkin-Elmer Optima 3100 RL) for Al (45 ppb), Cd (3 ppb), Cr (7 ppb), Cu (5 ppb), Fe (4 ppb), Pb (42 ppb), Mn (1 ppb), Sr (103 ppb), and Zn (1 ppb). As (2 ppb) and Sn (2 ppb) were determined by a polarized Zeeman Atomic Absorption Spectrophotometer (graphite furnace atomizer, Hitachi Z-2000) by adding Pd/Mg mixture (concentration 500 ppm) to the sample solution in acidic medium. Hg (1 ppt) was determined by a cold vapor atomic absorption spectroscopy (Hiranuma mercury analyzer, HG-310). The values given in parentheses are detection limits of each metal in ppb. The surface area of fly ash was 8.1 m^2/g, whereas the density and porosity were 1.21 g/m^3 and 68%, respectively. The surface area of fly ash was measured with a surface area measuring instrument, Surface Area HPP.SA-100 (Shibata, Japan). Alkalis and sulfur were received as industrial chemical materials (>99%). Chlorinated aromatic compounds and organic solvents were received from Wako Pure Chemicals Industries Ltd.

The experiments were carried out in a mini reactor (MS-100C) equipped with reaction vessel (100 ml, 5 Mpa), mini agitator (90–1500 rpm), and electric heating jacket with digital temperature controller (200°C max.) as shown in Figure 1.

The experiments were carried out by using chlorinated benzene compounds. The simulated solutions of chlorinated aromatic compounds were mixed with fly ash, sulfur, and different alkaline solutions (KOH, NaOH, and $Ca(OH)_2$) and agitated (250 rpm) at

Table 7. Dechlorination of tri-chlorobenzene (fly ash, 4 g; calcium hydroxide, 2 g; sulfur, 4 g; and heating for 13 hours).

	Yields (%)						
Temperature (°C)	$C_6H_3Cl_3$	C_6Cl_6	C_6H_5Cl	$C_6H_4(OH)Cl$	$C_6H_4Cl_2$	C_6HCl_5	Dechlorination
Water/methanol solvent (15/5 ml)							
60	72		25	3			18
70	46		32	10	12		36
80	18		50	12	20		48
90	15		60	10	15		51
120	30		49		16	5	34
130	25	10	45		15	5	22
150	30	15	35		15	5	10
170	30	18	32		15	5	5
Water/ethanol solvent (15/5 ml)							
60	67		30	3			22
70	45		35	10	10		33
80	16		50	10	24		48
90	9		70	4	16		55
120	25		60		10	5	40
130	20	10	50		15	5	25
150	25	12	43		10	10	13
170	30	15	35		10	10	5
Water/isopropanol solvent (15/5 ml)							
60	40		35	10	15		35
70	27		42	13	18		43
80	11		61	16	12		55
90	5		70	15	10		60
120	10		54		30	6	42
130	10	10	50		25	5	28
150	15	15	40		25	5	16
170	20	15	40		15	10	10

different temperatures for different durations in aqueous/organic solvent mixtures.

The experimental products were extracted twice with ether with 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. Dehalogenation products were analyzed using a gas chromatogram (HP 5890; Hawlett Packard series II) with internal standard (1-chloro-2, 4-dinitrobenzene) for quantitative determination, equipped with DB-5 m column (30 m × 0.25 m × 1 μm) and a quardrupole mass spectrometer (JEOL). Ionization was performed under 70 eV electron impact conditions (300 μA, 400 V) where the temperature initially was 35°C, ramped at 15–150°C/min and then at 3–280°C/min.

A series of experiments were performed to optimize the concentration of fly ash, alkaline solutions, sulfur, water/organic solvent volume ratios, and heating time. It was found that dechlorination was non-significant (less than 10%) without sulfur and alkali solutions. A significant dechlorination percentage was obtained in presence of sulfur, alkali solutions, and organic solvent/aqueous media. Higher dechlorination percentage was achieved with 4 g fly ash, mixture of alkaline solution (2 g calcium hydroxide and 2 g sodium hydroxide), and 4 g sulfur in water/organic solvent (v/v 3:1). Reaction mixtures for dechlorination of chlorobenzene compounds were heated at different temperatures from 11 to 17 hours. Experimental results suggested that the maximum dechlorination percentage was achieved by heating for 13 hours; heating more than 13 hours did not change the dechlorination results. In this paper, experimental results with optimized reaction conditions (concentration of sulfur, alkalis, and volume of organic solvent/aqueous media at 13 hours heating) were mentioned and discussed.

Experimental yields are presented in Tables 1–10, where the contents of chloro-compound substrates and dechlorinated products are expressed in wt% and the extend of dechlorination was expressed

Table 8. Dechlorination of tri-chlorobenzene (fly ash, 4 g; calcium hydroxide, 2 g; sodium hydroxide, 2 g; sulfur, 4 g; and heating for 13 hours).

	Yields (%)						
Temperature (°C)	$C_6H_3Cl_3$	C_6Cl_6	C_6H_5Cl	$C_6H_4(OH)Cl$	$C_6H_4Cl_2$	C_6HCl_5	Dechlorination
Water/methanol solvent (15/5 ml)							
60	58		37	5			28
70	42		44	14			38
80	17		60	11	12		51
90	15		63	12	10		53
120	22		60		13	5	49
130	28	5	56		11	5	26
150	27	6	48		12	7	25
170	28	6	47		12	7	24
Water/ethanol solvent (15/5 ml)							
60	51		42	7			32
70	36		42	14	8		40
80	13		60	12	15		53
90	8		78	4	10		58
120	18		67		10	5	44
130	15	3	67		10	5	41
150	18	5	60		12	5	35
170	22	5	54		12	5	33
Water/isopropanol solvent (15/5 ml)							
60	28		49	15	8		45
70	20		56	18	6		51
80	9		69	16	6		58
90	5		80	5	10		60
120	8		78		10	4	52
130	10	2	72		12	4	47
150	12	3	71		10	4	45
170	15	3	65		12	5	41

Table 9. Dechlorination of tri-chlorobenzene (0.25 M) in presence of metals as additives (fly ash, 4 g; calcium hydroxide, 2 g; sodium hydroxide, 2 g; sulfur, 4 g; water/isopropanol, 15/5 ml; heating for 13 hours).

Additives (metals)	Temperature (°C)	$C_6H_3Cl_3$ (%)	C_6H_5Cl (%)	$C_6H_4(OH)Cl$ (%)	C_6H_6 (%)	$C_6H_4Cl_2$ (%)	C_6HCl_5 (%)	Dechlorination (%)
Cu	90		78	4	16	2		71
Fe	90	4	76	6	12	2		67
Mn	90	5	75	11	6	3		64
Pb	90	4	78	2	14	2		68
Zn	90	5	74	12	7	2		65
Al	90	5	72	12	8	3		65
Cu	120	6	68	8	14	4		66
Fe	120	8	66	8	10	8		62
Mn	120	10	65	10	5	10		58
Pb	120	8	65	9	12	6		63
Zn	120	10	62	8	6	10	4	60
Al	120	8	64	6	8	10	4	62
Cu	150	10	71	6	5	8		45
Fe	150	8	69	10	6	7		47
Mn	150	10	67	9	8	6		47
Pb	150	12	68	8	6	8		42
Zn	150	10	70	7	7	6		47
Al	150	8	64	14	8	6		48

Note: metals added: Cu (8 mmol); Fe (9 mmol); Mn (9 mmol); Pb (9 mmol); Pb (5 mmol); Zn (8 mmol); Al (19 mmol).

Table 10. Dechlorination of chlorobenzene (0.25 M) without fly ash with metals as additives (calcium hydroxide, 2 g; sodium hydroxide, 2 g; sulfur, 4 g; water/isopropanol 15/5 ml; and heating for 13 hours).

	Dechlorination (%)	
Temperature (°C)	Dichlorobenzene	Trichlorobenzene
60	20	38
70	21	44
80	35	48
90	38	50
120	30	42
150	25	31
170	20	23

Note: metals added: Al (3.7 mg/g); Cu (0.4 mg/g); Fe (6.0 mg/g); Mn (0.5 mg/g); Pb (1.2 mg/g); Zn (3.7 mg/g).

as the percent of chlorine lost by dechlorination relative to the original chlorine contents in the substrates by following formula:

$$\text{Dechlorination}(\%) = [(\text{Cs} - \text{Cp})/\text{Cs}] \times 100,$$

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

Conclusion

Dechlorination of chlorinated aromatic compounds on fly ash was enhanced by adding sodium hydroxide to the calcium hydroxide and sulfur solution. Fly ash, under oxygen deficient conditions, has potential to catalyze the dechlorination in water/isopropanol solution at 90°C. Catalytic potential of fly ash was not only due to its metal contents, but it also provided the surface to carry out reduction and substitution reactions by adsorbing the chlorinated aromatic compound, hydrogen, and hydroxyl/thiol ions. At low temperature (90°C), catalytic effect of fly ash can be ascribed to the effect of metals but the catalytic effect of these metals was adverse at high temperature. Besides the metals, reducing agent with hydrogen donor (isopropanol) and water was required to carry out dechlorination process by fly ash. Furthermore, these mild conditions were acquirable on industrial scale to dechlorinate and/or detoxify the chlorobenzene liquid and/or solid wastes as well.

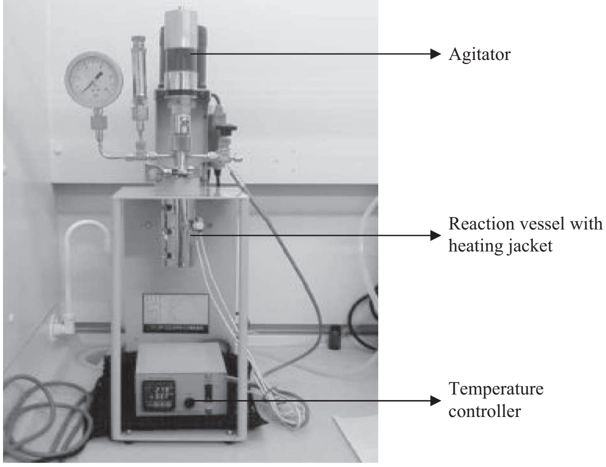

Figure 1. Mini reactor (MS-100C).

References

(1) Vikelsoe, J.; Johansen, E. Estimation of Dioxin Emission from Fires in Chemicals. *Chemosphere* **2000,** *40*, 165–175.
(2) Purchase, I.F.H. Inter-Species Comparisons of Carcinogenicity. *Br. J. Cancer* **1980,** *41*, 454–468.
(3) Hagenmaier, H.; Horch, K.; Fahlenkamp, H.; Schetter, G. Destruction of PCDD and PCDF in Refuse Incineration Plants by Primary and Secondary Measures. *Chemosphere* **1991,** *23*, 1429–1437.
(4) US Congress, Office of Technology Assessment. *OTA-BP-O-93*; US Government Printing Office: Washington, DC, 1991.
(5) Sako, T.; Sugeta, T.; Otake, K.; Sato, M.; Tsugumi, M.; Hongo, M. Decomposition of Dioxins in Fly Ash with Supercritical Water Oxidation. *J. Chem. Eng. Jpn* **1997,** *30*, 744–747.
(6) Weber, R.; Yoshida, S.; Miwa, K. PCB Destruction in Subcritical and Supercritical Waters Evaluation of PCDF Formation and Initial Steps of Degradation Mechanisms. *Environ. Sci. Technol.* **2002,** *36*, 1839–1844.
(7) Lapierre, R.B.; Guczi, L.; Kranich, W.L.; Weiss, A.H. Hydrodechlorination of Polychlorinated Biphenyl. *J. Catal.* **1978,** *52*, 230–238.
(8) Tavoularis, G.; Keane, M.A. Gas-Phase Catalytic Dehydrochlorination and Hydro-Dechlorination of Aliphatic and Aromatic Systems. *J. Mol. Catal. A: Chem.* **1999,** *142*, 187–199.
(9) Forni, P.; Prati, L.; Rossi, M. Catalytic Dehydrohalogenation Polychlorinated Biphenyls Part II: Studies on a Continuous Process. *Appl. Catal. B: Environ.* **1997,** *14*, 49–53.
(10) Bumpus, J.A.; Tien, D.M.; Right, S.D. Oxidation of Persistent Environmental Pollutants by a White Rot Fungus. *Aust. Sci.* **1985**, *228,* 1434–1436.
(11) Hutchins, R.O.; Zipkin, R.E.; Taffer, I.M. Reductions of Alkyl and Aryl Halides with Magnesium and Methanol. *Synth. Commun.* **1989,** *19*, 1519–1522.
(12) Murena, F.; Schioppa, E. Kinetic Analysis of Catalytic Hydrodechlorination Process of Polychlorinated Biphenyls (PCBs). *Appl. Catal. B: Environ.* **2000,** *27*, 257–267.
(13) Aresta, M.; Dibenedetto, A.; Pastore, T. Mechanochemistry: Old Technology with New Applications to Environmental Issues. Decontamination of Polychlorobiphenyl-Contaminated Soil High-Energy Milling in the Solid State with Ternary Hydrides, In *Environmental Chemistry*, edited by E. Lichtfouse,

J. Schwarzbauer and D. Robert (Springer-Verlalg, Berlin, Germany, 2005)

(14) Schetter, G.; Horch, K.; Stuetzle, R.; Brunner, H.; Hagenmaier, H. Low Temperature Thermal Treatment of Filter Ash from Municipal Waste Incinerators for Dioxin Decomposition on a Technical Scale. *Organohalogen Compd.* **1990,** *3*, 165–168.

(15) Hagenmaier, H.; Brunner, H.; Haag, R.; Kraft, M. Copper Catalyzed Dechlorination/Hydrogenation of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Other Chlorinated Aromatic Compounds. Environ. *Sci. Technol.* **1987b,** *21*, 1085–1088.

(16) Alonso, F.I.; Beletskaya, P.; Yus, M. Metal-Mediated Reductive Hydrodehalogenation of Organic Halides. *Chem. Rev.* **2002,** *102*(11), 4009–4091.

(17) Johnstone, R.A.W.; Wilby, A.H.; Entwistle, I.D. Heterogeneous Catalytic Transfer Hydrogenation and its Relation to Other Methods for Reduction of Organic Compounds. *Chem. Rev.* **1985,** *85*, 129–170.

(18) Rodriguez, J.G.; Lafuente, A. A New Advanced Method for Heterogeneous Catalysed Dechlorination of 1,2,3-, 1,2,4-, and 1,3,5-Trichlorobenzenes in Hydrocarbon Solvent. *Tetrahed. Lett.* **2002**, *43,* 9645–9647.

(19) Tundo, P.; Perosa, A.; Selva, M.; Zinovyev, S.S. A Mild Catalytic Detoxification Method for PCDDs and PCDFs. *Appl. Catal. Environ.* **2001**, *32,* L1–L7.

(20) Hitchman, M.L.; Spackman, R.A.; Ross, N.C.; Agra, C. Disposal Methods for Chlorinated Aromatic Waste. *Chem. Soc.* **1995**, *24,* 423–430.

(21) Pekek, V.; Hetflejg, J.; Katanek, F. Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Combustion Processes. *Chem. Listy* **1995,** *89*, 343–353.

(22) Vogg, H.; Metzger, M.; Stieglitz, L. Recent Findings on the Formation and Decomposition of PCDD/PCDF in Municipal Solid Waste Incineration. *Waste Manag. Res.* **1987,** *5*, 285–294.

(23) Hagenmaier, H.; Brunner, H.; Haag, R.; Kunzendorf, H.J.; Kraft, M.; Tichaczeck, K.; Weberrub, U. Stand der Dioxinanalytik. *VDI Berichte* **1987c,** *634*, 61–89.

(24) Ishida, M.; Shiji, R.; Nie, P.; Nakamura, N.; Sakai, S. Full-Scale Plant Study on Low Temperature Thermal Dechlorination of PCDDs/PCDFs in Fly Ash. *Organohalogen Compd.* **1996,** *27*, 147–152.

(25) Trumpf, R.; Christmann, A.; Hagenmaier, H. Decontamination of Filter Ash from Municipal Refuse Incineration Plants. *UTA Int.* **1998,** *4*, 82–90.

(26) Zook, D.R.; Rappe, C. In *Dioxins and Health-Environmental Sources, Distribution and Fate of Polychlorinated Dibenzodioxins, Dibenzofurans and Related Organochlorines* edited by A. Schecter, (Plenum: New York) 1994. pp. 79–113.

(27) Jan, S.; Vladimir, P.; Rene, E.; Jiri, H. Dechlorination of Hexachlorobenzene on MWI Fly Ash. *Chemosphere* **1999,** *39*(14), 2391–2399.

(28) Weber, R.; Nagai, K.; Nishino, J.; Shiraishi, H.; Ishida, M.; Takasuga, T.; Konndo, K.; Hiraoka, M. Effects of Selected Metal Oxides on the Dechlorination and Destruction of PCDD and PCDF. *Chemosphere* **2002,** *46*, 1247–1253.

(29) Ghaffar, A.; Tabata, M. Optimized Catalytic Dechlorination of Chlorobenzene Compounds on Fly Ash; Role of Metals, Aqueous/Organic Solvents and Temperatures. *Appl. Catal. B: Environ.* **2009,** *86*, 152–158.

(30) Ghaffar, A.; Tabata, M. Dechlorination/Detoxification of Aromatic Chlorides Using Fly Ash Under Mild Conditions. *Waste Manag.* **2009**, *29*(12), 3004–3008.

(31) Ghaffar, A.; Tabata, M. Dechlorination of *p*-Nitrochlorobenzene by Using the Fly Ash; Effects of Metals; Mixed Solvents and Temperatures. *Reac. Kinet. Catal. Lett.* **2009**, *97*(2), 35–41.

(32) Concibido, N.C.; Okuda, T.; Nakano, Y.; Nishijima, W.; Okada, M. Enhancement of the Catalytic Hydrodechlorination of Tetrachloroethylene in Methanol at Mild Conditions by Water Addition. *Tetrahed. Lett.* **2005,** *46*(21), 3613–3617.

(33) Ukisu, Y.; Miyadera, T. Catalytic Dechlorination of Aromatic Chlorides with pd/c Catalyst in Alkaline 2-propanol: Activity Enhancement by the Addition of Methanol. *React. Kinet. Catal. Lett.* **2006,** *89*(2), 341–347.

(34) Guo, B., Takehito, T., Tadashige, K., Yoshiharu, M., Masashi, T. Organic Reaction in Water. Part 2. A New Method for Dechlorination of Chlorobiphenyls Using a Raney Ni–AI Alloy in Dilute Aqueous Alkaline Solution. *Tetrahed. Lett.* **1998**, *39,* 5991–5994.

(35) Yoshiharu, M.; Taizouda, N. Approach to Highly Efficient Dechlorination of PCDDs, PCDFs, and Coplanar PCBs Using Metallic Calcium in Ethanol Under Atmospheric Pressure at Room Temperature. *Environ. Sci. Technol.* **2004,** *38*, 1216–1220.

(36) Yoshiharu, M.; Satoko, N.; Cristian, S.; Alina, M.; Simion, T.Y.; Keisuke, M.; Keiko, I.; Masashi, T. Dehalogenation of Aromatic Halides Using Metallic Calcium in Ethanol. *Environ. Sci. Technol.* **2001,** *35*, 4145–4148.

(37) Schoonenboom, M.H.; Zoetermeijer, H.E.; Olie, K. Dechlorination of Octachlorodibenzo-*p*-Dioxin and Octachlorodibenzofuran on an Alumina Support. *Appl. Catal. B: Environ.* **1995,** *6*, 11–20.

(38) Hoke, J.B.; Gramiccioni, G.A.; Balko, E.N. Catalytic Hydrodechlorination of Chloro-Phenols. *Appl. Catal. B: Environ.* **1992,** *1*, 285–296.

(39) Xia, C.; Xu, J.; Wu, W.; Liang, X. Pd/C-Catalyzed Hydrodehalogenation of Aromatic Halides in Aqueous Solutions at Room Temperature Under Normal Pressure. *Catal. Commun.* **2004,** *5*(8), 383–386.

(40) Hagenmaier, H.; Michael, K.; Hermann, B.; Roland, H. Catalytic Effects of Fly Ash from Waste Incineration Facilities on the Formation and Decomposition of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans. *Environ. Sci. Technol.* **1987**, *21,* 1080–1084.

(41) Yang, Z.; Xia, C.; Zhang, Q.; Chen, J.; Liang, X. Catalytic Detoxification of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans in Fly Ash. *Waste Manag.* **2007,** *27*, 588–592.

(42) Hanspaul, H.; Hermann, B.; Roland, H.; Michael, K. Copper-Catalyzed Dechlorination/Hydrogenation of

Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Other Chlorinated Aromatic Compounds. Environ. *Sci. Technol.* **1987,** *21*, 1085–1088.

(43) Feng, Z.; Jiping, C.; Haijun, Z.; Yuwen, N.; Xinmiao, L. The Study on the Dechlorination of OCDD with Pd/C Catalyst in Ethanol–Water Solution Under Mild Conditions. *Chemosphere* **2007,** *68*, 1716–1722.

(44) Leona, V.; Vladimir, P.; Vera, P.; Jindrich, K.; Michal, B.; Karel, S. Dechlorination Ability of Municipal Waste Incineration Fly Ash for Polychlorinated Phenols. *Chemosphere* **2004,** *56*, 935–942.

(45) Jan, S.; Vladimir, P.; Roman, G.; Milan, L.; Vera, P. Dechlorination of Polychlorinated Biphenyls, Dibenzo-*p*-dioxins and Dibenzofurans on Fly Ash. *Chemosphere* **2000,** *41*, 1881–1887.