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Catalytic Dechlorination of Aromatic Chlorides Using Fly Ash under Mild Conditions

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Abstract

An efficient dechlorination method for *p*-nitrochlorobenzene, *p*-chloroanisole and 1-chloronaphthalene on municipal waste incinerator fly ash in presence of reducing agents with water/alcohol mixtures was developed. Dechlorination reactions showed higher activity in water/isopropanol mixture at temperature <100 °C. Metal contents of fly ash (copper and lead) played a vital role to enhance dechlorination at low temperature <100 °C. Moreover, the fly ash also provided the surface to accomplish reduction and substitution reactions by adsorbing the chlorinated aromatic compounds, hydrogen and hydroxyl ions. The mechanism of dechlorination was envisaged.

Keywords: dechlorination, fly ash, organic solvents, metals, temperautre

INTRODUCTION

The chlorinated aromatic compounds became a serious environmental contamination problem. Nitrochlorobenzene, chloroanisole and chloronaphthalene and its derivatives which are widely used in the manufacture of explosives, pesticides, and dyes are considered to be highly toxic [1] as these affect skin, eyes and immune system directly [2]. Disposal of chlorinated organic wastes in such a way as to minimize the environmental risks becomes an urgent issue. Conventional incineration of these wastes produces harmful compounds, unless the operating temperature is strictly controlled [3]. Many methods for the detoxification or decomposition of chlorobenzene compounds were consequently developed. For example, the techniques of decomposition by combustion with or without oxygen gas at high temperature [4, 5], vitrification [6], oxidative treatment using supercritical water [7, 8], and dehalogenation by hydroxide using KOH in DMI (1,3-dimethyl-2-imidazolidinone) with heating [9, 10], 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 vaporised dioxins and 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 [11], bioremediations method [12], and mechanochemical systems by energy emissions from collisions between metallic small balls [13] were proposed. However, these methods also present some unfavourable aspects concerning the use of dangerous reducing reagents such as metallic sodium, low decomposition rates, output, or efficiency.

Dechlorination is an effective alternative procedure for decomposing chlorinated organic wastes under relatively mild conditions without the formation of the toxic by-products [14]. It is well known that both chlorination and dechlorination reactions are catalysed by municipal waste incinerator fly ash at elevated

temperatures and proceed simultaneously on the fly ash surface [15–19].

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, and also hydrogen-transfer reactions using hydrogen donors such as alcohols and formats were studied extensively [20].

In recent years, catalytic dechlorination methods have been developed including transfer hydrogenation by means of hydrogen donors such as metal hydrides [21], formic acid, its salts and alcohols [22, 23], which use water or methanol as solvents. The practical application of catalysts to the dechlorination of organic halides is always accompanied by the problem of the deactivation of the catalyst [24]. Hagenmaier *et al.* demonstrated that, under oxygen deficiency, the destruction of PCDD, PCDF and other chlorinated aromatics is a general property of fly ash from waste incineration processes [25, 26]. The authors have proved that dechlorination/hydrogenation of PCDD/PCDF and other chlorinated aromatic compounds on fly ash are catalyzed under certain conditions [27–29].

In the present study, fly ash was used for dechlorination of substituted chlorinated aromatic compounds by applying reducing agents under mild conditions. The effect of metals [30–33], water [34, 35] and organic solvents acting as hydrogen donors [36–39] was studied.

EXPERIMENTAL

The dioxin-free fly ash was taken from the local municipal waste incinerator and metals composition was analysed by acid digestion method. The digestion methodology to analyse metals was based on the USEPA method 3051A (1998). About 0.5 g fly ash sample was digested with a solution of concentrated nitric acid and hydrochloric acid (3 : 1) 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 with double distilled water. Thus prepared sample was kept in polypropylene bottles (soaked in

TABLE 1

Concentration of metals in flyash

Metals	Concentration, mg/kg
Al	3700
As	28
Ba	105
Cd	39.5
Co	11
Cr	53.5
Cu	452
Fe	6340
Mn	453
Pb	1200
Sn	4.95
Sr	157
Zn	3730

dilute acid and washed with double distilled water prior to use).

The clear supernatant solution was analysed for different metals. Most of metals were analyzed using an ICP-AES (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 (500 ppm concentration) to the sample solution in acidic medium. Hg (1 ppt) was determined by a cold vapour atomic absorption spectroscopy (Hirayama mercury analyser, HG-310). Values in pa-

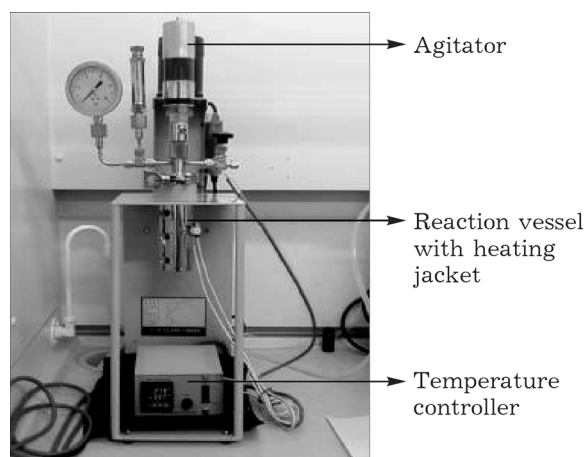


Fig. 1. Mini reactor (MS-100C).

rentheses are the detection limits of each metal in ppb. The metals composition of fly ash is given in Table 1. The surface area of fly ash was $8.1 \text{ m}^2/\text{g}$, whereas the density and porosity was $1.21 \text{ g}/\text{m}^3$ and 68 %, respectively. The surface area of fly ash was measured with a surface area measuring instrument, SURFACE AREA HPP.SA-100 (SHIBATA, Japan). Calcium hydroxide and sulphur were received as industrial chemical material (>99 %). Chlorinated aromatic compounds and organic solvents were received from Wako Pure Chemicals Industries Ltd. (Japan).

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

The experiments were carried out using chlorinated benzene compounds. The chlorinated aromatic compounds in solution form were mixed with fly ash, sulphur and calcium hydroxide and agitated (250 rpm) at 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 then were concentrated by evaporation to 5 mL volume. Dehalogenation products were analysed using a gas chromatogram (HP 5890; Hewlett Packard series II) with internal standard (1-chloro-2,4-dinitrobenzene) for quantitative determination, equipped with a DB-5 column (30 mm \times 0.25 mm i.d.; film thickness: 1 μm) and a quadrupole mass spectrometer (JEOL). Ionisation was performed under 70 eV electron impact conditions (300 μA , 400 V) where the initial temperature of the column was 35 °C, increased to 150 °C at 15 °C/min and then 3 °C/min to 280 °C.

To investigate the dechlorination efficiency, *p*-nitrochlorobenzene, *p*-chloroanisole and 1-chloronaphthalene were used. A series of experiments was performed to optimise the concentration of fly ash, calcium hydroxide and sulphur, water/organic solvent volume ratios and heating time. Simulated solutions of *p*-nitrochlorobenzene (20 mmol), *p*-chloroanisole (25 mmol), 1-chloroanisole (20 mmol) were treated with a mixture of fly ash, calcium hydroxide and sulphur.

TABLE 2

Dechlorination of *p*-nitrochlorobenzene. Solvent: water/alcohol (15/5 mL)

Temperature, °C	Yield, %			Dechlorination, %
	$\text{C}_6\text{H}_4(\text{NO}_2)\text{Cl}$	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_4(\text{OH})\text{NH}_2$	
<i>water/methanol</i>				
40	50	40	5	45
50	45	40	10	55
60	35	60	15	60
70	36	55	15	58
80	40	50	15	55
90	42	50	15	50
<i>water/ethanol</i>				
40	45	40	5	55
50	40	45	10	60
60	32	70	10	65
70	35	65	10	60
80	38	55	15	62
90	40	55	15	60
<i>water/isopropanol</i>				
40	40	35	5	54
50	35	40	10	62
60	25	60	15	75
70	35	55	10	68
80	32	45	10	65
90	37	45	10	63

TABLE 3

Dechlorination of *p*-chloroanisole. Solvent: water/alcohol (15/5 mL)

Temperature, °C	Yield, %			Dechlorination, %
	$C_6H_4(OCH_3)Cl$	$C_6Cl_5(OCH_3)$	$C_6Cl_5(OH)OCH_3$	
<i>water/methanol</i>				
40	55	40	10	45
50	50	40	10	50
60	45	50	10	55
70	45	60	5	55
80	48	60	10	52
90	52	60	10	48
<i>water/ethanol</i>				
40	50	45	5	50
50	50	50	5	50
60	42	60	5	55
70	40	65	5	60
80	42	60	10	58
90	45	60	10	55
<i>water/isopropanol solvent</i>				
40	50	50	5	50
50	45	55	5	55
60	40	60	5	60
70	27	68	5	73
80	40	50	10	60
90	48	42	10	52

TABLE 4

Dechlorination of 1-chloronaphthalene (water/alcohol 15/5 mL)

Temperature, °C	Yield, %, in solvents		
	water/methanol	water/ethanol	water/isopropanol
40	40	45	55
50	45	52	58
60	52	58	60
70	55	60	62
80	58	66	68
90	60	67	70
110	52	55	60

TABLE 5

Dechlorination without fly ash (Cu, 8 mmol; Pb, 5 mmol)

Temperature, °C	Dechlorination, %, of:		
	<i>p</i> -NCB	<i>p</i> -chloroanisole	1-chloronaphthalene
40	40	36	35
50	46	42	35
60	55	50	49
70	58	52	50
80	60	55	52
90	62	58	55
110	50	50	48
130	48	45	42

roxide and sulphur in mixed water/organic solvents at 60–110 °C for different time. Different concentrations of reactants and different mixed water/organic solvents were used. It was found that the best results of dechlorination were obtained with 10 g fly ash, 4 g calcium hydroxide and 6g sulphur in water/isopropanol solvent (v/v 3 : 1). In this paper the results with optimised chemical conditions are mentioned and discussed.

RESULTS AND DISCUSSION

Higher dechlorination (%) of *p*-nitrochlorobenzene was obtained at 60 °C for 3 h (after 3 h dechlorination was constant) and dechlorination products were chloroaniline, and *o/p*-hydroxyaniline.

In case of *p*-chloroanisole, higher dechlorination was achieved at 70 °C for 5 h (after 5 h dechlorination was constant) and the products were anisole and *p*-hydroxyanisole. Whereas, dechlorination of 1-chloronaphthalene was higher at 90 °C for 5 h (after 5 h dechlorination was constant) and product was naphthalene, results were shown in Tables 2–4.

To investigate the role of fly ash metals on dechlorination, experiments were carried out under optimised conditions within the temperature range of 60–150 °C by adding most abundant metals in fly ash (Al, Cu, Fe, Mn, Pb, Zn); results are given in Table 5. According to the experimental results, copper and lead were more effective than other metals under it optimised reaction conditions.

Results suggested that fly ash with calcium hydroxide and sulphur can be used to dechlorinate the chlorinated aromatic compounds. Fly ash from waste incineration plants has a potential to facilitate both reduction and substitution reactions as reported by many researchers [33, 40–42].

Under optimised temperature conditions, the formation of *o/p*-hydroxyaniline and *o/p*-hydroxyanisole suggested that reaction mixture has free hydroxyl ions that substitute the chloride ions under provided conditions.

The resultant products in dechlorination of *p*-chloroaniline revealed that reduction of *p*-nitrochlorobenzene to *p*-chloroaniline was in advance as reported by Xinhua *et al.* [49]. Fur-

thermore *p*-chloroaniline was reduced to aniline and some fraction of *p*-chloroaniline underwent substitution reactions where chloride ions were substituted by hydroxyl ions to give *o/p*-hydroxyaniline (amino phenol).

p-Chloroanisole was reduced to anisole at low temperature as reported by Ukisu *et al.* [48]. In case of *p*-chloroanisole the formation of *o*- and *p*-hydroxyanisole suggested that the reduction and substitution reactions were carried out simultaneously, whereas 1-chloronaphthalene was reduced to produce naphthalene and no substitution reaction occurred to produce naphthol.

Results demonstrated that the dechlorination percentage was changed with a change in organic solvent and it was maximal in isopropanol solvent as reported by Concibido *et al.* [43], with the order as; isopropanol > ethanol > methanol as shown in Fig. 2. As isopropanol is a better hydrogen donor than ethanol and methanol, therefore, an increase in the percentage of dechlorination in isopropanol clearly suggested that organic solvents acted as a hydrogen donor in the catalytic hydrodechlorination of chlorinated aromatic compounds as suggested by Ukisu *et al.* [48]. Thus we concluded that organic solvents acted as hydrogen donors rather than just solvents to dissolve the organic compounds in reaction media, as observed by others researchers [4, 34, 36–39, 46].

Addition of water to organic solvents enhances dechlorination as reported by other researchers [43–45]. The volume of water was optimised and maximal dechlorination was obtained when a relatively high v/v ratio of water with isopropanol (3 : 1) was used. The enhancement in dechlorination, in excess of water, presumed to arise from controlling the solubility of the substrate, the additives and the products as reported by Ukisu *et al.* [46] other than hydrogen source. This argument was supported by the work of other authors [37, 38] who used metals in alcohols to reduce the chlorinated compounds in the absence of water.

Based on dechlorination results it was concluded that calcium hydroxide and sulphur reacted to produce calcium polysulphide which decomposed in the presence of water to provide a mixture of $\text{Ca}(\text{SH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{SH})(\text{OH})$. In the presence of water $\text{Ca}(\text{SH})(\text{OH})$ further produced $\text{Ca}(\text{OH})_2$ and H_2S , where H_2S acted

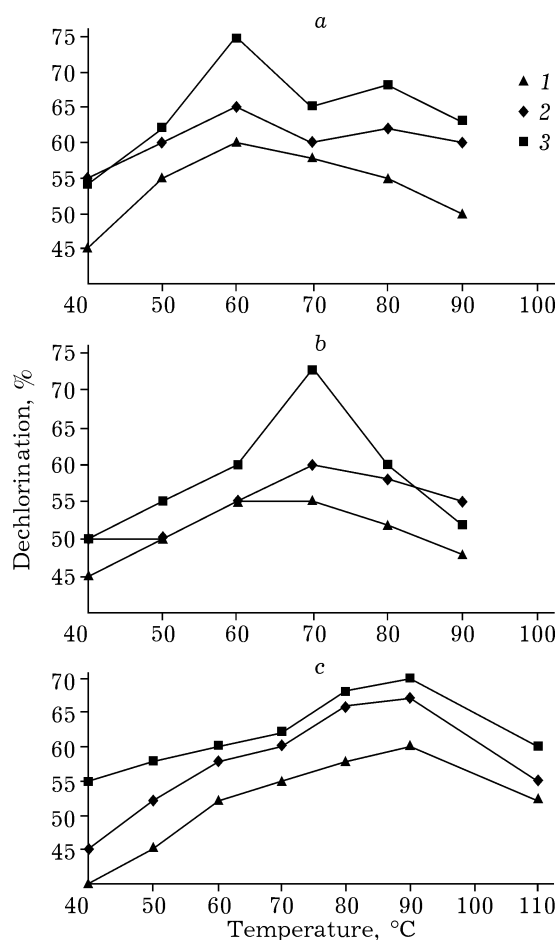
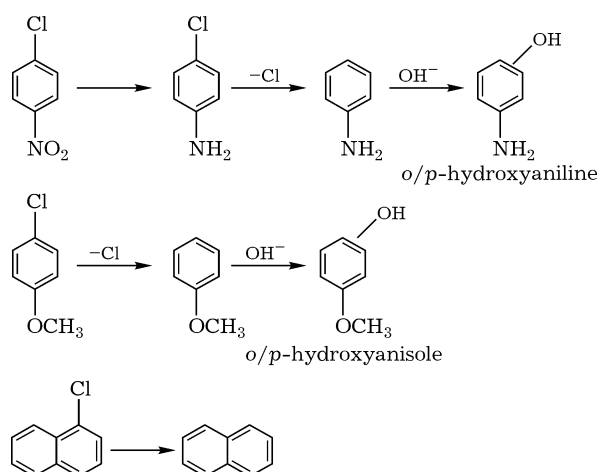
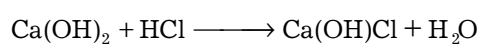
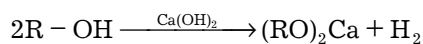
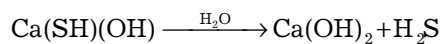
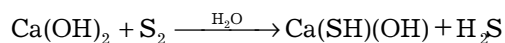


Fig. 2 Dechlorination of chlorobenzene compounds: a - *p*-nitrochlorobenzene, b - *p*-chloroanisole, c - 1-chloronaphthalene.

as a strong reducing agent to reduce chlorinated compounds. The hydroxyl ions were provided by calcium hydroxide that caused nucleophilic substitution. Furthermore, chlorine in chlorinated compounds was substituted by hydrogen which resulted in the formation of aniline, anisole and naphthalene, respectively. The hydrogen atom was supplied by alcohol and the resultant alkoxide ions were quenched by the Ca^{2+} cation. Calcium hydroxide was also used to neutralize the resultant HCl in the reaction mixture and reaction was assumed to proceed as



The dechlorination yield was substantially affected by the change in temperature. Under optimised conditions dechlorination was increased with an increase in temperature. Dechlorination of *p*-nitrochlorobenzene, *p*-chloroanisole and 1-chloronaphthalene was maximized at 60, 70 and 90 °C, respectively. This temperature-dependent phenomenon led us to assume metals content of fly ash played a vital role in dechlorination.

Dechlorination under optimised conditions was increased by the addition of metals as compared to the experiments without metal additives. Metals have a catalytic effect on dechlorination; dechlorination was higher within the temperature range 60 to 110 °C, but it was decreased at 130 to 150 °C, as shown in Fig. 3. According to the experimental results, copper and lead were more effective than other metals under the same optimised reaction conditions. The same observations under different reaction conditions were described by different researchers [31–34]. 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 optimised reaction conditions. Results (Table 6 and Fig. 4) suggested that dechlorination was lower as compared to experiments with fly ash. So it was hypothesized that the surface of fly ash (carbon most important) acted as collector of hydrogen atoms released by alcohol and hydroxyl ions given by a base to facilitate the reduction/substitution of chlorinated compounds. The chlorinated compounds were absorbed on the surface of fly ash particles and

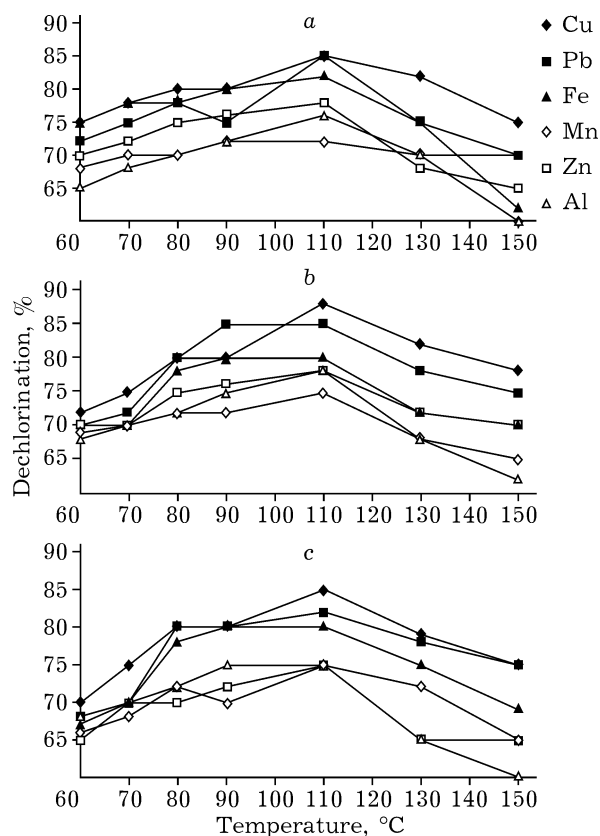


Fig. 3 Dechlorination in presence of metals as additives. For designation see Fig. 2.

are reductively dechlorinated and substituted by OH^- ions.

CONCLUSION

A significant dechlorination of chlorinated aromatic compounds was achieved by applying calcium hydroxide and sulphur in water/isopropanol solution on fly ash under oxygen-deficient conditions. Dechlorination efficiency was enhanced by adding small amount of metals under optimised reaction conditions. At low temperature, the catalytic effect of fly ash was higher at a temperature <100 °C. Furthermore, reducing agents with the hydrogen donor (isopropanol) and water were necessary to carry out dechlorination process effectively. The catalytic potential of fly ash was not only due to its metal content but fly ash also provided the surface to carry out reduction and substitution reactions by adsorbing chlorinated aromatic compounds, hydrogen and hydroxyl ions.

TABLE 6

Dechlorination in presence of metals as additives (Cu, 8 mmol; Pb, 5 mmol; Fe, 9 mmol; Mn, 10 mmol; Zn, 8 mmol; Al, 9 mmol)

Temperature, °C	Dechlorination, %, with					
	Cu	Pb	Fe	Mn	Zn	Al
<i>p-nitrochlorobenzene</i>						
60	75	72	75	68	70	65
70	78	75	78	70	72	68
80	80	78	78	70	75	70
90	80	75	80	72	72	72
110	85	85	82	72	78	76
130	82	75	75	70	68	70
150	75	72	62	60	65	70
<i>p-chloroanisole</i>						
60	72	70	70	69	70	68
70	75	72	70	70	70	70
80	80	80	78	72	75	72
90	80	85	80	72	76	75
110	88	85	80	75	78	78
130	82	78	72	68	75	68
150	78	75	70	65	70	62
<i>1-chloronaphthalene</i>						
60	70	68	67	66	65	68
70	75	70	70	68	70	70
80	80	80	78	72	70	72
90	80	80	80	70	72	75
110	85	82	80	75	75	75
130	79	78	75	72	65	70
150	75	72	69	65	60	62

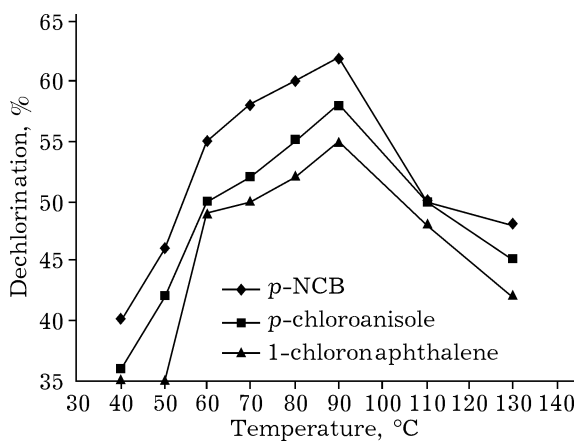


Fig. 4. Dechlorination without fly ash.

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