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Dechlorination of chlorobenzene compounds on flyash; effects of metals, aqueous/organic solvents and temperatures

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ABSTRACT

Dechlorination of chlorobenzene compounds on flyash by using a solution of calcium hydroxide and sulfur in aqueous/organic solvent at 60–170 °C, under oxygen deficient conditions was studied. High percentage of dechlorination was obtained under certain reaction conditions. The results suggested that at 90 °C, metals in general and copper and lead in particular enhanced the catalytic potential of flyash for dechlorination by hydrodechlorination and substitution reactions. But at high temperatures (120–170 °C), dechlorination process was adversely affected by these metals. The effects of water, organic solvents, temperatures and heating time, were studied and reactions conditions were optimized to get maximum dechlorination.

1. Introduction

Chlorinated organic compounds are widely used in the chemical and electronic industries. Disposal of chlorinated organic wastes in such a way as to minimize 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 DMI (1,3-dimethyl -2-imidazolidinone) 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 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 method [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, 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 [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 have also 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], 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 deactivation of the catalyst [18]. It is well known that both halogenation and dehalogenation reactions are also catalyzed by municipal waste incinerator (MWI) fly ash at elevated temperatures and proceed simultaneously on the flyash surface [19–23]. Hagenmaier et al. demonstrated that, under oxygen deficiency, the destruction of PCDD, PCDF and other chlorinated aromatics is a general property of flyash from waste incineration processes [24,25]. The authors have proved that dechlorination/hydrogenation of PCDD/PCDF and

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other chlorinated aromatic compounds on fly ash are catalyzed under certain conditions [26]. This catalytic property of flyash is being applied for low temperature decontamination of flyash during industrial scale operations [27,28].

The present study was focused on dechlorination of simulated solutions of the chlorinated aromatic compounds by using flyash and applying reducing agents under mild conditions. The effect of metals [29–32], water [33,34] and organic solvents acting as hydrogen donors [18–37] on dechlorination of chlorobenzene compounds has been reported by different authors. We also tested the effects of water/organic solvents, temperatures, metals and heating time on dechlorination and reactions conditions were optimized to get maximum dechlorination.

2. Experimental

The dioxins-free fly ash was taken from the local municipal waste incinerator and its metallic 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 flyash sample was filtered by syringe membrane filter (0.45 μm) and diluted to 100 ml by adding double distilled 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 the metals were analyzed using an Inductively Coupled Plasma Optical Emission Spectroscopy (PerkinElmer 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 metallic composition of flyash is given in Table 1. Calcium hydroxide and sulfur was received as industrial chemical material (>99 %). Chlorinated aromatic compounds and organic solvents were received from Wako Pure Chemicals Industries Ltd.

3. Apparatus and procedures

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

Table 1
Concentration of metals in flyash

Metals	Concentration (mg/kg)
Al	3670
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
Zn	3730

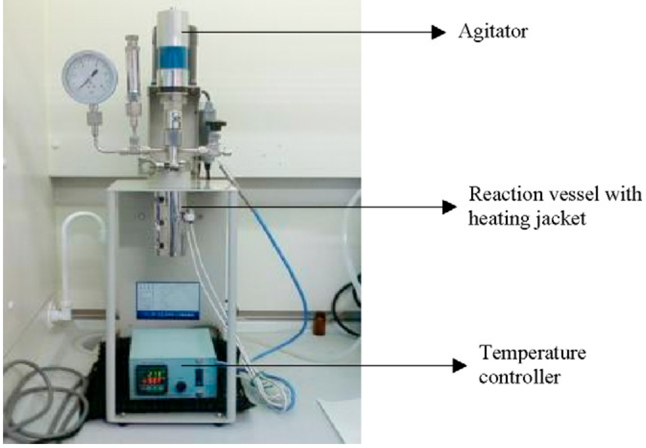

Fig. 1. Mini reactor (MS-100C).

The experiments were carried out by using chlorinated benzene compounds. The simulated solutions of chlorinated aromatic compounds were mixed with flyash, sulfur 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 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 determina-

Table 2
Dechlorination of chlorobenzene (flyash (4 g); calcium hydroxide (2 g), sulfur (4 g), heating for 13 h)

Temperature (°C)	Yield (%)	
	C_6H_4 (OH)Cl	$C_6H_4Cl_2$
2.1. Water/methanol solvent 15/5 ml		
40	–	–
50	10	
60	25	
70	38	
80	47	
90	49	
120	30	10
150	22	25
170	18	38
2.2. Water/ethanol solvent 15/5 ml		
40	–	–
50	12	
60	45	
70	52	
80	58	
90	61	
120	38	15
150	35	20
170	20	25
2.3. Water/isopropanol solvent 15/5 ml		
40	–	–
50	15	
60	35	
70	60	
80	62	
90	68	
120	38	20
150	30	30
170	25	38