

Thermal desorption of polychlorobiphenyls from contaminated soils and their hydrodechlorination using Pd- and Rh-supported catalysts

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Abstract

This paper reports about a combined technology for soil remediation from PCBs using the thermal desorption technique coupled with the catalytic hydrogenation of recovered PCBs. The reactor is a bench scale rotating desorption furnace through which nitrogen is flushed and used as carrier gas of desorbed PCBs. The latter are condensed into an hexane or hexane–acetone (1:1 v/v) solution that is then hydrogenated using phosphate-supported Pd or Rh as catalyst. The analysis of the treated soil, under variable operative conditions (temperature and desorption time), shows that the total (99.8%) decontamination from PCBs occurs. The recovery yield of the desorbed PCBs is better than 75% and the subsequent hydrogenation reaches 63% of the collected PCBs in 5 h or 100% in 12 h.

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1. Introduction

PCBs are widely used since 1930 in many industrial processes, that take advantage of their thermal and chemical stability (Cresser and Killham, 1993). They may reach soil either by industrial waste disposal or spilling. Owing to their slow degradation by biosystems such as bacteria (Sierra et al., 2003; Abraham et al., 2005), fungi (Sietmann et al., 2006) or exoenzymes (Takagi et al., 2007), PCBs can accumulate in soil. PCBs can also be transformed into metabolites that may be more toxic than the starting compounds (Hansen and Robertson, 2001).

Noteworthy, of the 209 congeners only a few are classified as toxic compounds. Therefore, alterations of the molecular structure of PCBs, for instance the number of

chlorides, can change their behaviour towards biological systems. The interaction of the PCBs with the many components of soil makes difficult the identification of the fate of PCBs in the environment (Hansen and Robertson, 2001). Several techniques have been proposed for soil remediation (Aresta et al., 2003; Sierra et al., 2003; Lin et al., 2004; Abraham et al., 2005; Borja et al., 2006; Liu and Yu, 2006; Sun et al., 2006; Varanasi et al., 2007). The thermal processes (Ishikawa et al., 2007; Lundin and Marklund, 2007) may produce positive results (Freeman and Harrys, 1997), but at the same time they may cause an unforeseeable modification of the intrinsic molecular structure of main soil components, depending on the operative temperature (Aresta and Tortorella, 1997). In order to prevent structure changes that would make the soil not suitable for uses, for example in agriculture, the decontamination must take place at relatively low temperatures. The desorption of pollutants combined with pyrolysis has

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been used so far. In general, pyrolysis causes the thermal degradation of organic substances, that are converted into primary products such as charcoal, liquids, fuel gas (Bridgewater and Grassi, 1995). Oxygen must be absent, in order to avoid the formation of toxic species like dioxin and similar (Risoul et al., 1999). In this paper we report on the hybrid technique based on the soil thermal treatment under controlled temperature (max 573 K) with a reductive dehalogenation of desorbed PCBs, using Pd- or Rh-catalysts intercalated into a Zr-phosphate layered matrix.

2. Experimental

2.1. Methods and materials

2.1.1. Soil sample

In this work two different soil samples were used: a spiked soil with 16 ppm of 3,4,6-trichloro biphenyl and a real matrix derived from a landfill site for toxic-harmful waste, containing 1739 ppm of a PCBs mixture. Considering the granulometric characteristics (see Table S1 in Supplementary material), the two soil samples can be classified as sandy soils, because for the first and second sample more than 80% and 90% of particles belong to fine sand class, respectively.

2.1.2. Bench-scale rotating plant for thermal treatment

The bench-scale plant developed for the thermal treatment is shown in Scheme 1.

It is formed by a kiln, a reactor, and a cooling system for condensation of volatile compounds, and adsorption traps.

The condensed fraction is blocked by two low temperature traps containing hexane, eventually mixed with acetone. The plant is flushed with N₂ through the reactor (B) which flow is controlled by a flux-meter. The released PCBs are condensed in a trap (F). The temperature is controlled with a thermocouple and a thermo-regulator.

2.1.3. Reductive dehalogenation of desorbed PCBs

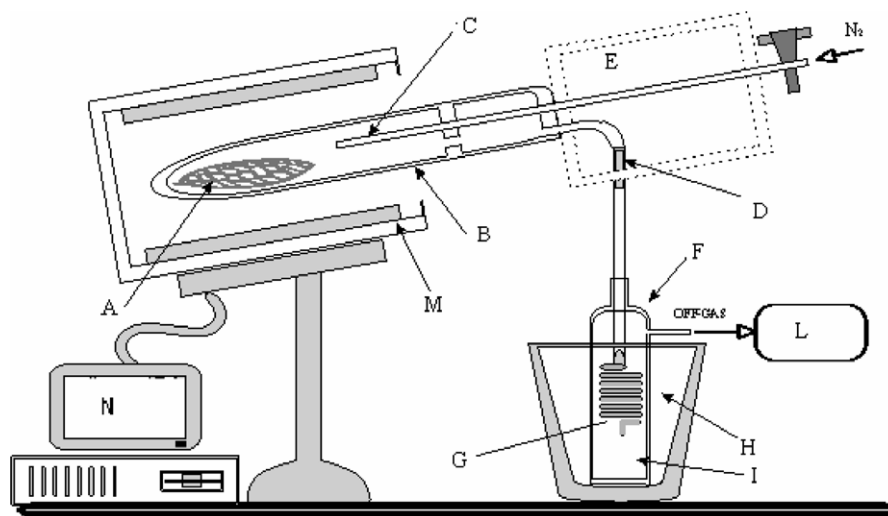
The hydrogenation of PCBs is carried out in a pressure autoclave where the solution of desorbed PCBs and the catalyst are placed. Hydrogen is charged at 0.1–0.5 MPa. The temperature is regulated with a thermo-regulator. The catalyst employed in the hydrogenation is composed of Pd or Rh supported on zirconium-phosphate. In Table 1 the composition of some catalysts is reported. The metal can be either intercalated as naked ions or as complex with 1,10-phenanthroline (phen) or dipyrindyl (dipy).

2.1.4. Analytical methods used for PCBs qualification

The analytical methods used in this work are those recommended by EPA. In particular, for the extraction of PCBs, the US EPA (1995) was used; for the extract clean-up, the US EPA (1996a, 1996b, 1996c) were implemented, and for the determination of PCBs, the US EPA (1996d) was applied using a GC-MS equipment (see below).

2.2. Experimental section

The thermal treatment was carried out in two substantially different ways. The first method was based on the



A	Soil Sample	B	Reactor
C	Inlet	D	Outlet
E	Rotating engine	F	Trap
G	Condenser	H	Cooling solution
I	Adsorption solvents	L	Flux meter
M	Kiln	N	Thermoregulator

Scheme 1. A view of the laboratory scale rotating desorption apparatus.

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