

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

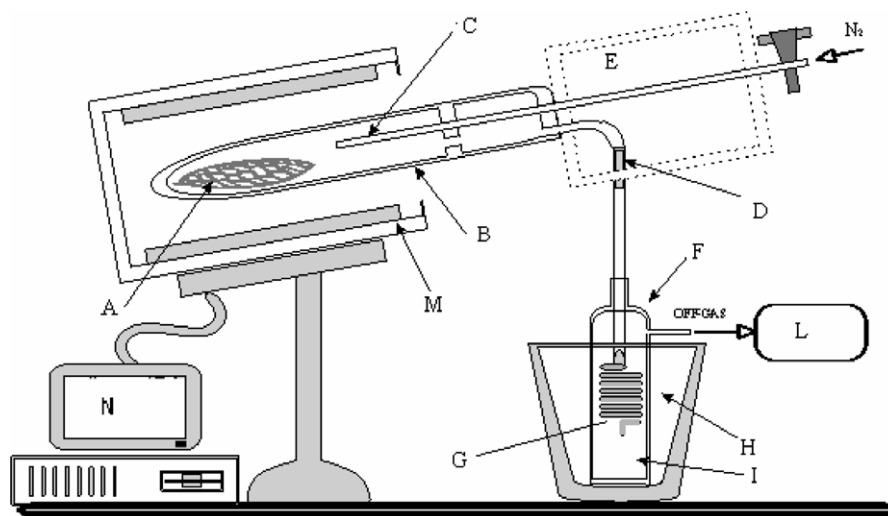
The hydrogenation of PCBs is carried out in a pressure autoclave where the solution of desorbed PCBs and the catalyst are placed. Hydrogen is charged at 0.1–0.5 MPa. The temperature is regulated with a thermo-regulator. The catalyst employed in the hydrogenation is composed of Pd or Rh supported on zirconium-phosphate. 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 dipyrityl (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.

3.2. Effect of the reaction time for the treatment in an electric furnace

Fig. 1b shows the results of the test on spiked and real samples of soil for a variable heating time at constant temperature. The best results were obtained after 60 min of treatment at 573 K. A release of 85% of 2,4,6-trichloro biphenyl from the spiked soil and of 96% of PCBs from the real sample was noted. After 1 h, a slow release was still observed with the maximum decontamination reached after 150 min of heating, when the percentage of desorption was 88%, for the spiked soil, and 98%, for the real matrix. The fact that the sample was not mixed during the heating caused the slow release of PCBs. Therefore, we have developed a rotating reactor and studied its performance in the soil treatment.

3.3. Effect of the reaction time for the treatment using the bench-scale rotating reactor

Fig. 2 shows the effect of the resident time on the contaminated matrix in the bench-scale rotating reactor at the constant temperature of 573 K.

The best desorption was observed after 65 min, with a release of 99% of PCBs using a heating rate of $4\text{ }^{\circ}\text{C min}^{-1}$ from room temperature up to 573 K and a N_2 flow of 500 ml min^{-1} . Two traps cooled at 273 K allow to condense and recover more than 73% of the released PCBs. Lowering the temperature of hexane does not produce a sensible recovery yield. Also adding a third trap does not ameliorate the recovery. As PCBs are almost quantitatively desorbed, the difference of recovered with respect to released is due to PCBs that remain mostly adsorbed on the glass connections. However, comparing the data obtained for the treatment using either the furnace or the

bench-scale rotating reactor, the latter appears more efficient than the treatment in the furnace, as it allows a more complete desorption in a shorter reaction time, and at a lower temperature.

3.4. Effect of the flux of N_2 and of the number of traps on the yield of collection of released PCB using the rotating bench-scale reactor

The great advantage of the rotating reactor is that it allows the recovery of the released PCBs. Table 3 shows that from the real matrix PCBs are released with a yield very close to 100% in the best operative conditions.

The N_2 flow carrying the released PCBs was conveyed into a cold (273 K) trap containing hexane or hexane–acetone. Increasing the nitrogen flow increases the amount of desorbed PCBs, but decreases the quantity of trapped PCBs. A good compromise was found with a flow of 500 ml min^{-1} . Using a single cold trap and acetone/hexane as solvent with a heating rate of 288 K min^{-1} , only 11–18% of the released PCBs were blocked. With two traps the amount of PCBs blocked was almost doubled (32%). The chromatograms shown in Fig. 3 very clearly demonstrate the abatement of PCBs after the treatment of the real matrix and the amount of PCBs recovered using one or two traps, in the best operative conditions (Entry 5, Table 3).

Table 3 shows that reducing the heating rate, and using two traps, a recovery of 73% of PCBs was possible with a release of PCBs equal to 100%. Therefore, a slow releasing rate is better suited for a complete recovery of PCBs and their collection in the cold traps. This issue is still under investigation in order to reach the same efficiency in the collection as in the release of PCBs.

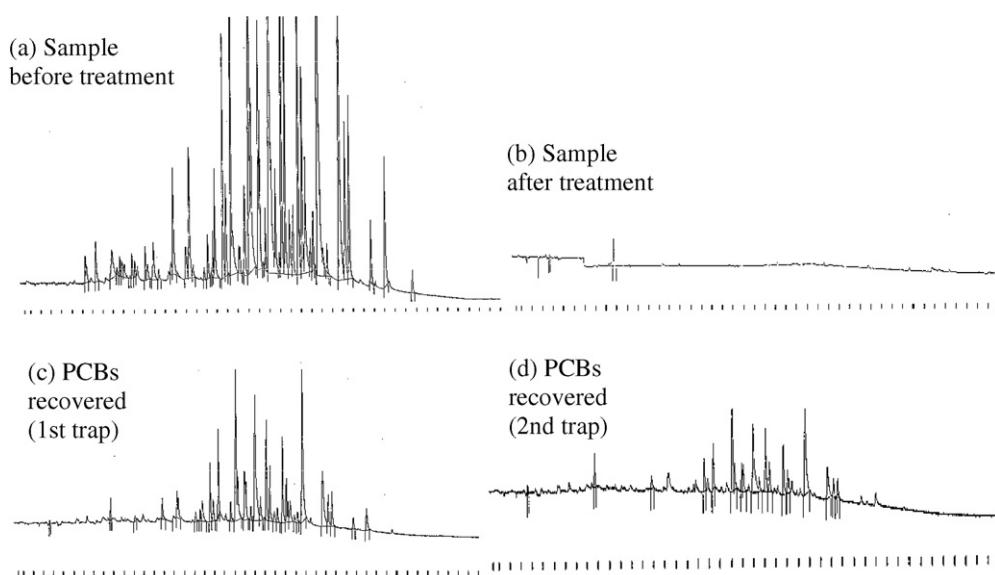
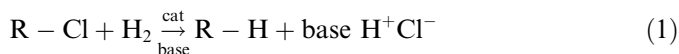


Fig. 3. Chromatograms of PCBs before (a) and after (b) the treatment and PCBs recovered after one (c) or two (d) traps (analyses related to entry 5 Table 3).

3.5. Catalytic reductive dehalogenation of recovered PCBs

The solution containing the recovered PCBs was submitted to a catalytic hydrogenation for the conversion of harmful PCBs into biphenyl that can be easily biodegraded (Borja et al., 2006; Rehmann and Daugulis, 2006). Table 4 shows the results of the different assays carried out for the dehalogenation of the desorbed PCBs.

Different catalysts were used (Table 1): naked ions Pd(II) or Rh(III) supported on ZrPO₄, or Pd(phen)²⁺ or Pd(dipy)²⁺ intercalated in ZrPO₄. The yield of the conversion into C₁₂H₁₀ ranged from 30% to 62% over 3–5 h. Before the use, the catalyst was pre-reduced with H₂. Such preliminary treatment consisted in stirring the catalyst in methyl alcohol under hydrogen for 3 h. This treatment is necessary because the active species in catalysis is the reduced form of the metal (Pd⁰ or Rh⁺¹), that is able to drive the dehalogenation of PCBs (Giannoccaro et al., 2005). The dehalogenation reaction was carried out both in the absence or presence of NEt₃, necessary for trapping the formed HCl. The presence of the base (Eq. (1)) was necessary in order to have an efficient dechlorination process.



When Pd was used as catalyst in absence of NEt₃ no reaction was observed. Conversely, Rh in the absence of the base was able to dehalogenate PCBs, although with a low yield (32%). Pd and Rh in presence of NEt₃ gave comparable results: 62% and 63% of PCBs were dehalogenated, respectively. In any case Rh was more efficient than Pd. In fact, the dehalogenation effect reported above was obtained by carrying out the reaction at 363 K and for 5 h with Pd, while 323 K and 3 h were enough with Rh. The solvent also played a key role.

An analysis of the GC–MS pattern of the residual halogenated compounds, reveals that highly chlorinated species have a slower rate of dehalogenation. A kinetic measurement shows that lower members of the PCBs family are first hydrogenated (their signals disappear within 3 h) while high chlorinated PCBs are then slowly converted into congeners with a lower Cl-content. If the reduction is continued for 24–30 h all Cl-species disappear. A complete dehalogenation was observed after 12 h with Pd or Rh.

4. Conclusions

The thermal desorption of PCBs from a contaminated soil using a bench scale rotating reactor flushed with N₂ resulted to be an efficient technology for soil remediation. The reaction was carried out under controlled temperature conditions (573 K) so that soil was not substantially affected. Either a spiked soil with 3,4,6-trichlorobiphenyl, or a real matrix from a landfill site, were used. The desorption yield reached 100% under the appropriate conditions starting from a PCBs concentration as high as 1739 ppm. The effect of the time of heating, rate of heating, flow of

flushing N₂ were investigated with the rotating reactor technique. This technique was more efficient than the static conditions represented by heating of soil into a furnace. The desorbed PCBs were collected in hexane/acetone 1:1 with a yield higher than 73% when a double cold trap was used, with a slow heating rate (4 °C min⁻¹). The efficiency of recovery depends on the temperature of the cold bath, the geometry of the condenser, the flux of the gas. The solution containing the collected PCBs was then submitted to a catalytic reductive dehalogenation using supported Pd(II), or Rh(III) catalysts. A global dehalogenation efficiency close to 63% was observed in 5 h that was completed in 12 h. The hydrogenation process allows a fast conversion of the low chlorinated compounds, while the high chlorinated ones (decachloro biphenyls) were first partially dechlorinated and transformed into hexa or heptachlorobiphenyls that were then hydrogenated. This technology seems to be quite efficient for PCBs desorption and conversion into non harmful compounds like biphenyl that can be biodegraded. The combined technology appears to be quite promising for the total elimination of PCBs. Its exploitation may depend on the cost of removal and dehydrogenation compared to the cost of technologies used today. A comparative cost analysis should be carried out in order to assess its economic convenience.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2007.07.074](https://doi.org/10.1016/j.chemosphere.2007.07.074).

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