

HYDRODECHLORINATION OF POPs IN SOIL BY NANO SIZE-CALCIUM AND IRON DISPERSION UNDER MILD CONDITIONS

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Introduction

In spite of all regulations and preventive measures, soil contamination with POPs such as polychloro-dibenzo-*p*-dioxins, polychloro-dibenzofurans, and benzene hexachloride (BHC) remains a worldwide issue¹. Due to their toxic properties, any release of POPs into the environment is potentially harmful to all forms of life¹. Therefore, much attention has been devoted to the development of new, cost-effective and environmentally friendly procedures for the hydrodechlorination of POPs. In the scope of eliminating this threat, numerous methodologies have been developed. These include catalytic oxidation², thermal³, photochemical⁴ and purely chemical treatments, such as selective catalytic reduction⁵, catalytic hydrodechlorination⁶ and potassium-polyethylene glycol (KPEG)⁷. In the past decade, catalytic hydrodechlorination with noble metal catalyst methods have been developed⁸. However, these methodologies have some disadvantages in terms of excess energy input, complexity of the system for removing toxic by-products, and/or the efficiency (treatment time, amount, and cost) of dechlorination.

In these circumstances, we found that the use of metallic calcium in a solvent acts as a hydrogen donor and it is very effective for hydrodechlorination of dioxin-like compounds, under mild conditions^{9,10}. We also demonstrated the usefulness of this procedure in the decontamination processes of fly ash or wet soil from PCBs^{11,12}. Our method is based on metallic calcium's numerous advantages (*e.g.* its ability to react slowly with hydrogen donors, its safety in handling). However our method also have some disadvantages related to cost, the use of solvents and the use of some precious metals as catalyst. On the contrary in our method, calcium particles act as a reducing reagent that have been broken down into smaller nano-size particles, dispersing easily in order to use off any solvents and expensive catalyst. The mechanochemical treatment applied to Ca not only activates it (by removing its coating), but it transforms itself into a more reactive, nano-size metallic Ca¹². By using this reduction system, we discovered that the hydrodechlorination of dioxins, PCBs, and dioxin-like compounds in dry soil (moisture: 1-15 wt%) with nano size-calcium which is disperse by stirring at room temperature without any added solvent¹². In the present study we have paid much attention to the hydrodechlorination of aliphatic compounds (BHC *etc.*) as our target.

Benzene hexachloride was initially reported to be a nontoxic benzene derivative, used as a fungicide since 1933. It has ever since been used in a variety of other applications such as for the manufacture of synthetic rubber, fireworks, ammunition and other commercial products, being also a by-product of several chemical manufacturing processes, including the production of other chlorine-containing chemicals¹³. Since it proved to be toxic, causing porphyria cutanea tarda (a liver disease), as well as being a potential carcinogenic¹⁴, BHC was globally banned by the 2001 Stockholm Convention on Persistent Organic Pollutants. However, since its intense use (especially as a fungicide)¹⁵, important quantities of BHC are still persistent in the environment¹⁶.

The use of a nano size-dispersion of calcium and iron toward the decomposition of polychlorinated aromatic compounds (BHC *etc.*) in soil was investigated, the main reason being the multiple advantages of such decomposition process over the existing ones¹⁷⁻¹⁹ (it does not require heating, organic solvents, fancy catalysts or expensive reagents and it does not generate exhaust gases).

Materials and methods

Nano-Fe/Ca/CaO preparation. Nano-Fe/Ca/CaO (dry system) was prepared with iron (Fe), metallic Ca and CaO through planetary ball milling (Retsch PM-100) process. Granular particles of metallic calcium were purchased from Kishida Chemicals (99%, particle size distribution: 1.0–2.5 mm, surface area: 0.43–0.48 m²/g). Fine grade CaO and iron powder (size 0.15 mm) were also commercially obtained with 98 % purity from Kishida Chemicals. Iron powder, metallic Ca and dry CaO (dried at 825°C for 2h), in a 2/2/5 Fe/Ca/CaO ratio, were introduced in planetary ball mill (20 stainless steel balls; 10 mm diameter). Milling was conducted at room temperature and in an Ar atmosphere, for 1 h at 600 rpm to a rotation-to-revolution ratio of 1:2. These conditions for nano-Fe/Ca/CaO preparation (i.e., Fe/Ca/CaO composition, balls to powder ratio and rotation-to-revolution ratio) were established after performing several experiments to ascertain the optimal conditions¹². After milling, samples were collected in glass bottles, filled with Ar and stored for further experiments. Generated hydrogen amount was 28 mL/0.3 g-Fe-Ca/CaO dispersion. Similarly, nano-iron/calcium oxide (Fe/CaO 2/5) and nano-metallic calcium/calcium oxide (Ca/CaO 2/5) dispersions were also separately prepared, under the same conditions, and subsequently used for the treatment of BHC contaminated soil, in order to assess their individual dispersing effect and hydrodechlorination properties. Average particle size of nano-Fe/Ca/CaO and SEM image are shown in Fig. 1. Contaminated soil, containing BHC (initial concentrations 0.1 to 10 ppm) was considered for treatment.

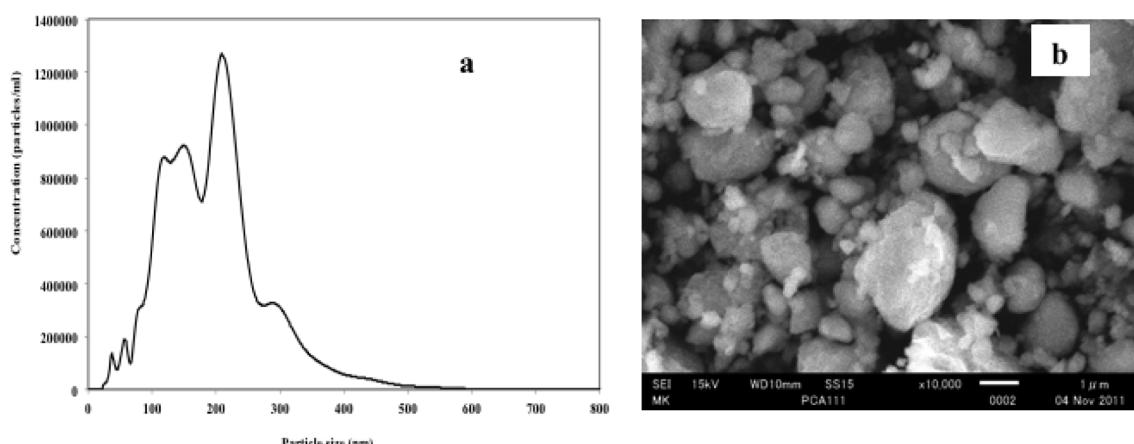


Figure 1. Nano-Fe/Ca/CaO, (a) particle size distribution and (b) SEM microstructure at magnified 10,000 times.

BHC contaminated soil treatment

We have performed a series of experiments using nano-size dispersion of Ca and Fe in CaO (separately or together) in order to assess their hydrodechlorination capacities. In a general experimental procedure, 1 g of BHC-contaminated soil (~ 0.1 to 10 ppm, ~8 wt% of moisture content) and 1 g nano size-Ca/Fe mixture (Fe ~ 2 to 30% in weight) were magnetically stirred for 1 h at room temperature, in order to ensure a proper dispersion. The treated soil was then stored in a dark and thermally controlled environment (room temperature), samples were taken daily for GC/MS analysis. With that purpose, the sample was introduced in an acid solution and the latter was extracted with ethyl ether. The organic solution was submitted to GC/Ms analysis, under the following conditions: GCMS-QP2010 Ultra (SHIMADZU), GC conditions: 30 m column (RXi®-17), I.D.: 0.25 mm, membrane: 0.25 μm, film thickness: 0.25 μm, injection temperature: 200°C, carrier gas: He, flow: 2.2 ml/min, split: 20, GC program: 40°C (5 min) - 250°C (6.6 min), MS range: 50-500.

Results and discussion

The BHC decontamination results of polluted soil treated with Fe/Ca/CaO, Fe/CaO and Ca/CaO individual dispersed mixtures (ratio 10:1~10 = soil:Fe/CaO) are presented in Table 1. The highest rate of hydrodechlorination efficiency was achieved with Fe/CaO dispersion, under mild conditions, after one week a 97.3% hydrodechlorination yield was recorded (Table 1). In the same time, the use of Fe/Ca/CaO and Ca/CaO dispersions, under the same conditions, reached 93.6% and 73.9% efficiencies, respectively (Table 1). In

moistured soil (~18% wt.), the hydrodechlorination was achieved in quantitative yields, water probably plays the role of a hydrogen donor. Lower decomposition yields recorded when Fe/Ca system or only Ca was used may be attributed to a higher rate of Ca surface coating, when dispersed in moisturized soil. Therefore, the coating might influence the decrease in the decontamination efficiency.

An 18% moisture seems a turning point, since over this value, hydrodechlorination yields are dropping, no matter the dispersion system used. Ca/CaO is indeed an efficient hydrodechlorinating system, but its supplement of iron is giving better results in the long run, even in the case of higher moisture content. Since its superior reactivity towards oxidation or hydrolysis, Ca could play a protecting role for Fe, allowing the latter to ensure hydrodechlorination processes even after three weeks after the dispersion occurred. Thus, if Ca/CaO dispersed system is rapidly effective, provided that water content is less than 18% (same for Fe/CaO), by mixing Fe and Ca with CaO we obtained a dispersion system that is not losing its hydrodechlorinating capacity in time, nor in the presence of higher amounts of soil moisture. Thus, this system is opening the door to *in situ* processes, lowering the costs of soil decontamination by eliminating the costs of soil displacement.

Table 1. Decomposition of BHC in contaminated soil treated with Fe/Ca/CaO, Fe/CaO and Ca/CaO dispersions.

Treatment	Soil Moisture Content (%)	Soil Surface Temperature (°C)	Hydrodechlorination yield (%)	
			After 1 week	After 3 weeks
Fe/Ca/CaO	2	22	100	-
	8	138	93.6	93.7
	18	140	86.0	91.1
	24	140	65.5	86.4
	31	91	87.7	100
Ca/CaO	2	31	100	-
	8	141	73.9	88.4
	18	178	100	-
	24	110	30.0	27.3
	31	115	0.0	0.0
Fe/CaO	2	26	96.9	100
	8	31	97.3	98.7
	18	33	100	-
	24	31	37.5	38.3
	31	33	8.5	43.1

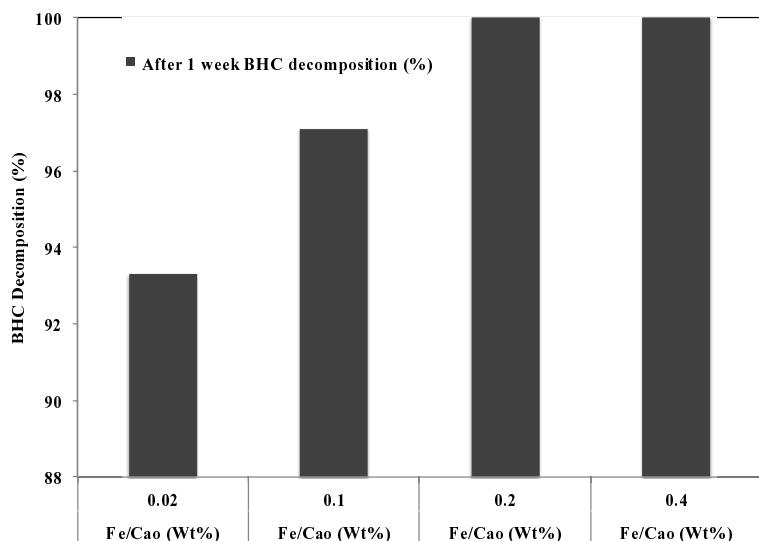


Figure 2. Decomposition of BHC with various proportions of Fe/CaO.

As presented in Fig. 2, BHC contaminated soil treated with various amounts of Fe/CaO dispersion showed that 0.2% in weight is enough to reach complete hydrodechlorination within one week. As a conclusion, it is possible to note that the decomposition of BHC in contaminated soil with nano-Fe/CaO dispersion mixture is the most effective process, the treatment with nano-Ca/CaO is faster, but depends highly on the moisture content of contaminated soil, while the treatment with nano-Fe/Ca/CaO have the best performance, for long-term effects in terms of hydrodechlorination. The dechlorination treatment process does not require external heating, organic solvents, fancy catalysts or expensive reagents, and it does not generate exhaust gases. On the contrary, it only requires a certain amount of water (naturally occurring in outdoor soil), commercially available cheap reagents and a cheap way to disperse the nano-size system into the contaminated soil. Therefore, it is possible to consider this process as an environmental friendly depolluting technique, which could be applicable in *in situ* conditions.

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