A NOVEL APPROACH FOR THE REMEDIATION OF PCBS CONTAMINATED SOIL WITH NANO-METALLIC CA/CAO DISPERSION MIXTURE IN DRY CONDITION

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Introduction

Rapid industrialization, increased urbanization, modern agricultural practices and inappropriate waste disposal methods have caused contamination of soils with polychlorinated biphenyls (PCBs) and it has become a major environmental concern in many parts of the world.[1] According to a notice by Ministry of Environment, Japan, there are about 27.2 million ha of contaminated land in Japan.[2] For the purpose of preventing adverse effects on public health caused by soils contaminated with toxic substances, in japan the soil contamination countermeasures act went into effect in February 2003. PCBs contaminated soils are notoriously hard to remediate. Hence, its remediation is recognized to be one of the most difficult problems to be solved by taking advantage of suitable technologies. General methods proposed for PCBs removal and/or degradation in soils are physical, chemical, and microbial.[1] Among the physical methods, the most prominent are high temperature incineration,[3] ultra sonication,[4] and photochemical degradation.[5] While chemical methods can be classified into two main categories dechlorination (DC)[6] and hydrodechlorination (HDC) processes.[7] A more recent approach in the struggle against the presence of PCBs in soils is the microbial one. Unfortunately this field has proven rather difficult. Starting from those laboratory methods, several industrial processes have been developed for the decomposition of PCBs in soil to fulfill the requirements of an advanced, powerful, and safe detoxification.[8] Moreover, the equipment required for these methods is expensive, energy consuming and often engendering a high risk of generation of other organic pollutants suchas, dioxins.

While, mechanochemical dechlorination process (MDP) were also used for the degradation of PCBs.[9] Our recent investigations have also shown that the mechanochemical treatment of contaminated fly ash with PCDDs, PCDFs and PCBs in the presence of a mixture of metallic Ca and CaO is the most effective since dechlorination is total, no traces of chlorinated compound was detected after the treatment of a sample.[10] We assume that, during the hydrodechlorination process using metallic Ca applied to a polluted soil, moisture in soil can act as hydrogen source. If moisture can be an advantage in a hydrodechlorination mixing process, we expect that polluted soil with polychlorinated compounds can also be successfully treated with metallic Ca and CaO mixture. Therefore, in the present work, initielly, the use of metallic Ca and CaO dispersion mixture toward decomposition of PCBs in decomposed granite soil was investigated. While, furthermore, the use of nano-metallic Ca and CaO dispersion mixture toward decomposition of PCBs in three diffrent (decomposed granite, clay and field soils) was investigated in dry conditions. The main reasons being the multiple advantages of such a degradation process, it does not require heating, organic solvents, fancy catalysts or expensive reagents, also it does not generate exhaust gases.

Materials and methods

Experimental design and the treatment

In a typical experiments, three diffrent (decomposed granite soil (0~10% moisture, 0.52% organic substances), clay (ca.18% moisture, 4.5% organic substances) soil and field soil (ca.18% moisture, 16.97% organic substances) samples are used. On the other hand, nano-metallic Ca/CaO (dry system) was prepared with metallic Ca and CaO through planetary ball milling process. Granular particles of metallic calcium was purchased from Kishida Chemicals. (99%, particle size distribution: 1.0-2.5 mm, surface area: 0.43–0.48 m^2/g). Fine grade CaO was also commercially obtained with 98% purity from Kishida Chemicals. Room temperature under Ar gas atmosphere, metallic Ca and dry (825^oC for 2h) CaO composition (Ca/CaO = 2/5) were introduced in the

planetary ball mill (Retsch PM-100; 20 pieces SUS, 32g/ball). Stirring was carried out at 600 rpm to a rotation-to-revolution ratio of 1 to 2. After stirring samples were collected in glass bottles, Ar gas was filled and stored to be used further treatment experiments. Mixture of nano-particle metallic calcium in CaO (2.80 mmol of metallic Ca/g-mixture) and average particle size of nano-metallic Ca/CaO was 206 nm. A standard solution containing 0.13 mg of a PCB (an equimolecular mixture solution of Kanechlor-300, Kanechlor-400, Kanechlor-500, and Kanechlor-600) in hexane was sprayed and thoroughly mixed to 100 g of soil. A mixture of 1 g of polluted soil showing an average PCBs concentration of $1300x10^{-3}$ mg kg^{-1}.

While, we started our PCBs contaminated soil treatment studies with two different treatment process initally, PCBs contaminated decomposed granite soil (1.0g, 31 ppm PCBs), metallic Ca (0.01g, 0.25mmol, size 0.5-1 mm) and dried CaO were introduced into a stainless-steel pressure reactor, under 0.1Mpa N_2 gas atmosphere. The mixture was stirred by a magnetic stirrer for 2 hr at 400 rpm and heated at 260°C, 280°C and 300°C respectively. Further, in second exprement, 9g of PCBs contaminated (decomposed granite, clay and field) soils having various moistures (0, 1, 4.4 and 9.6) were grinded with 1g or 7.5g of nano-Ca/CaO (metallic calcium raio: 11.9% in total nano-calcium weight, 2.80mmol ~ 21mmol) for 24hr into a ceremic mortar, under room temperature. After treatmen the reaction mixture was poured into 1M nitric acid and extracted twice using dichloromethane under vigorous shaking. After the separation from the aqueous layer, the combined organic phases were washed with distilled water until the pH of the aqueous layer became neutral. The dichloromethane layer was dried on anhydrous $MgSO_4$, then filtered and concentrated to 10 ml. Analyses of soil samples for PCBs determination were performed according to Japanese Industrial Standard (JIS) methods.[11-12] PCBs analysis was performed by a gas chromatograph (GC-17A; Shimadzu Co.) equipped with agilent HP-5 (length 30 m, inside diameter 0.32 mm, film thickness 0.25 μm) column and ^{63}Ni-ECD detector. These experiments were repeated three times, giving similar results.

Results and discussion

Metallic Ca and CaO treatment for PCBs decomposition in soil in wet condition

Initielly, PCBs contaminated decomposed granite soil was mixed only with CaO by a magnetic stirrer for 2hr into a stainless-steel pressure reactor, under an atmosphere of N_2 gas at 0.1Mpa. The experimental results are presented in Table 1. As presented in Table 1, with CaO treatment, the rate of PCBs decomposition was in average 81.1, 90.8, and 96.4% at 260, 280 and 300°C respectively in the presence of N_2 gas at 0.1MPa. After the treatment with CaO, approximately 1% of metallic Ca (particle size 0.5-1 mm) was added to the CaO treated soil samples and the results was also presented in Table 1. After the combined treatment of CaO and metallic Ca at 260°C, PCBs decomposition was increased to 95.2% when compared with CaO alone treatment (81.1%), about 14.1% increased. Similarly, combined treatment was also performed at 280°C, about 95.0% reduction of PCBs was observed. On the other hand only 90.8% was observed in CaO treatment. An additional 4.2% reduction was observed with the combined treatment. While at 300°C the PCBs reduction was about 95.7% with combined treatment. Whereas, with alone CaO treatment also showed better PCBs reduction about 96.4%. Normally, at high temperatures (about 300ºC) CaO alone also gives good PCBs reduction (similar to metallic Ca/CaO mixture). However, at low temperatures around 260ºC metallic Ca/CaO mixtures shows better PCBs reduction. Indeed, assuming a radicalic hydrodechlorination process, metallic calcium is more prone to generate free electrons than its oxide, which, in return, is available for the trapping of chlorine atoms formed in the process.[10] Therefore, the combined treatment with metallic Ca and CaO at 260ºC and 280ºC was found to be effective in the dechlorination of PCBs. After CaO treatment PCBs residual amount remained at 18.9% for 260ºC, 9.2% for 280ºC and 300ºC for 3.6%, it decreased sharply with increasing of the processing temperature. Whereas, after CaO and metallic Ca treatment PCBs residual amount remained at 4.8% for 260ºC, 6% for 280ºC and 4.3% for 300ºC, which continued constant (Table 1). Further, subsequent reducing amount of metallic Ca contact to PCBs also reduces the rate of dechlorination reactions.

The decomposition of PCBs in contaminated soil with metallic Ca and CaO mixture is the most effective treatment process. Moisture in soil acted as a hydrogen source for hydrodechlorination in a magnetic stirring process. The decomposition was due to dechlorination. Further, metailic Ca and CaO can increase effectively the number of collisions and mutual refinement. The hydrodechlorination efficiency was over 95%. Treatment at 260ºC and 280ºC of combined with metallic Ca and CaO was found to be effective in the decomposition of PCBs. The metallic Ca particle size is about 0.5-1 mm this relatively large, hence the occurrence of dechlorination reaction with metalic Ca destroy sharply with the increase of treatment temperature. Therefore,

the finer metalic Ca surface area is the more capable of reacting with PCBs, therefore it can be assumed that the reaction can further promote decomposition of the PCBs polluted soils.

Table. 1. The percent of total PCBs decomposition and residual ratio at different temperature. Each value is the average of three measurements.

	CaO treatment		CaO and metallic Ca treatment	
Temperature ^{o}C	Total PCBs decomposition Avg (%)	Residual ratio (%)	Total PCBs decomposition Avg (%)	Residual ratio (%)
260	81.1	18.9	95.2	4.8
280	90.8	9.2	95.0	5.0
300	96.4	3.6	95.7	4.3

Nano-metallic Ca and CaO treatment for PCBs decomposition in various soils in dry condition

Further research was done using with nano-metallic Ca/CaO (particle size was 206 nm) in dry condition. In second exprement, 9g of PCBs contaminated decomposed granite soil having various moistures (0, 1, 4.4 and 9.6) were grinded with 1g or 7.5g of nano-Ca/CaO (metallic calcium raio: 11.9% in total nano-calcium weight, 2.80mmol ~ 21mmol) for 24hr into a ceremic mortar, under room temperature. The experimental results for decomposition of total *non-ortho, mono-ortho* and total coplanar PCBs are presented in Fig. 1. As presented in Fig. 1, with nano-metallic Ca/CaO treatment, the rate of total PCBs decomposition was about 97, 59, 60 and 29% in 0, 1, 4.4 and 9.6% soil moisture content, respectively. Onthe other hand, the influence of initial moisture in soil and remaining metallic calcium after treatment was presentd in Figure 2. As shown in Fig. 2, higher dechlorination efficiency by preliminary drying of soil was observed. While, as presented in Table 2, the total *non-ortho* and total PCBs dechlorination efficiency in clay soil (ca.18% moisture, 4.5% organic substances) was observed tob e 71.5 and 63.2% respectively. Whereas, the total *non-ortho* and total PCBs dechlorination efficiency in case of field soil with 17 of organic substances and 18% of moisture is much lower than the non-organic soils (decomposed granite and clay soil). On the other hand, the use of excess CaO as a dry reagent was effective for the dechlorination to reach 55.4% of efficiency. The hydrodechlorination is sensitive to moisture content, its efficiency decreasing along with the increase of moisture. To counteract this effect, the ratio of Ca/CaO should be modified in favor of the metallic calcium.

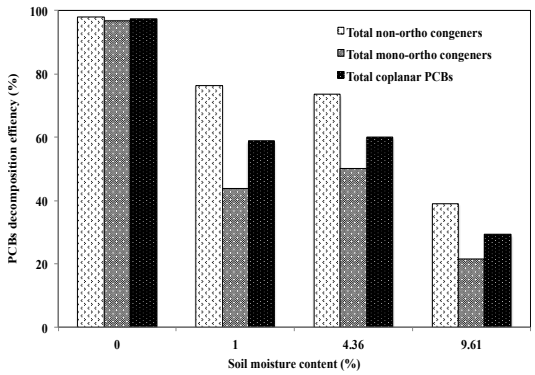

Fig. 1. Decomposition of non-ortho, mono-ortho and total coplanar PCBs in decomposed granite soil.

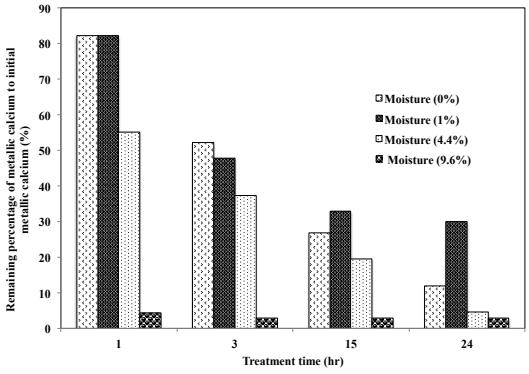

Fig. 2. Remaining quantity of metallic calcium during the treatment in decomposed granite soil with various moisture contents.

The mixture (=1g) of 2.80 mmol of metallic calcium and 15.9 mmol of calcium oxide is very effective for the dechlorination of PCBs in 9g of decomposed granite soil (with a moisture content up to 9.61% wt. = 48.1 mmol) under mild conditions such as room temperature and atmospheric pressure, at a reaction time of 24 hours,

without any external heating. In the dechlorination of PCBs in "non-organic soil" such as clay or decomposed granite soil, the hydrodechlorination efficiency for *non-ortho*- and *mono-ortho*-units reached over 60-97%, under dry conditions. On the other hand, the dechlorination efficiency of PCBs in "organic soil" such as field soil with 16.97 of organic substances and 18% of moisture is lower than the one of non-organic soil. However, the use of excess CaO as a dry reagent was effective for the dechlorination to reach 55.4% of efficiency. The hydrodechlorination is sensitive to water content, its efficiency decreasing along with the increase of moisture. To counteract this effect, the ratio of Ca/CaO should be modified in favor of the metallic calcium. Furthermore, this treatment method does not require high heating, organic solvents, fancy catalysts or expensive reagents, and it does not generate exhaust gases. On the contrary, it requires only electricity, cheap and commercially available reagents and eventually water. Therefore, this treatment process is considered to be an environmental friendly depolluting technique.

Table 2. Decomposition of non-ortho, and total coplanar PCBs in Clay and field soils with various CaO additions.

	Clay soil		Field soil	
Amount of added CaO	Dechlorination efficiency for *non-ortho* type	Total dechlorination efficiency for all PCBs	Dechlorination efficiency for *non-ortho* type	Total dechlorination efficiency for all PCBs
0% (0g)	66.90%	$\simeq 0$	(3.8)*	$\simeq 0$
16.7 (2g)	46.00%	23.50%	31.10%	~10%
50% (10g)	62.00%	48.50%	56.4	55.40%
Nano-Ca (1g → 7.5g (CaO:6.6g))	71.50%	63.20%	--	--

*Increment value.

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