PYROLYSIS PROCESS OF PENTACHLOROPHENOL IN SANDY SOIL AT LOW TEMPERATURES

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Introduction

An-Shun Site of SouthernTaiwan has been famous with pentachlorophenol (PCP), mercury (Hg) and polychlorinated dibenzo dioxins and furans (PCDD/Fs) in soil. The high content of PCP (0.312 – 110 mg/kg), PCDD/Fs (36,000 ng I-TEQ/kg) and Hg (0.212 – 12,000 mg/kg) in soil around the factory [1] is due to chlorination of the non-substituted phenol to produce chlorophenols. Several technologies including thermal, chemical treatments and electrolysis have been developed recently. Thermal treatments are still considered as the prior techniques for simultanous removal of PCP, dioxins and Hg with high concentration. Incineration/combustion which are normally related to use high temperature in oxygen environment are proved as efficient techiniques. However, energy cost and possible toxic dioxin formation in gas phase during PCP/chorophenol combustion have limited the usage of these techniques[2]. In the other hand, incineration at the high temperature results in the “dead soi”which can not be used to vegetate anymore. Hence, understanding the pyrolytical process for PCP at relatively low temperature range (200-400^{0}C) is nessesary to optimize pyrolysis parameters, reduce the energy cost and off-gas release. In this study, the investigation of PCP removal from sandy soil under nitrogen condition has been examined. The pyrolytical parameters including temperature and heating time were investigated to achieve the maximun removal efficiency of PCP froms soil. In addition, by-products of PCP pyrolysis in off gas and soil phase were collected and analyzed to clarify the pathways of PCP removal from sandy soil during PCP pyrolysis. At the inital results under our experimental conditions, almost PCP (>90%) can be removed from soil at 350^{0}C for 10min. Temperature strongly affects the removal rate and by-product releases. Finally, while pyrolysis and desorption are the main pathways, the lower chlorinated phenols detected in gas phase and soil phase has shown the dechlorination phenomenon and no any toxic dioxins or furans were found during PCP pyrolysis.

Materials and methods

Sandy soil samples, similar to matrix of An-Shun soil, were collected. Firstly, they were air dried and Soxhlet wash with n-hexane for 5h and then further air-dried before use. The basic compositions of soil were as following: sand: 90%, pH 7.9, moisture 0.78%.

The artificial PCP contaminated soil was prepared by spiking an appropriate amount of PCP in acetone solution into the pretreated soil. The soil was vigorously homogenized for several hours. Due to potential interactions between soil constituents and the contaminant, separated runs of the clean and contaminated soil are conducted to indentify products inherent to the soil itself in addition to the contaminant. A one day aging period was selected to reach PCP equilibrium condition in soil[3]. The actual value of PCP in soil was verified by Soxhlet extraction with hexane, and then analyzed by GC/MS. The contamination level was within 90 ± 5% mg PCP/kg. Batch pyrolysis system is shown in Fig. 1.

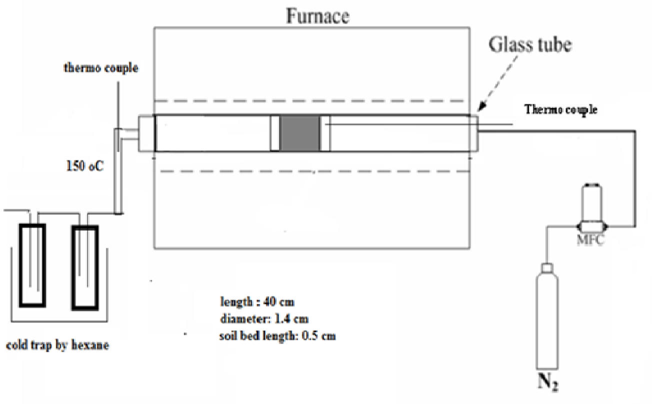

Fig. 1: Experimental apparatus

Results and discussion:

1. Removal of PCP from soil

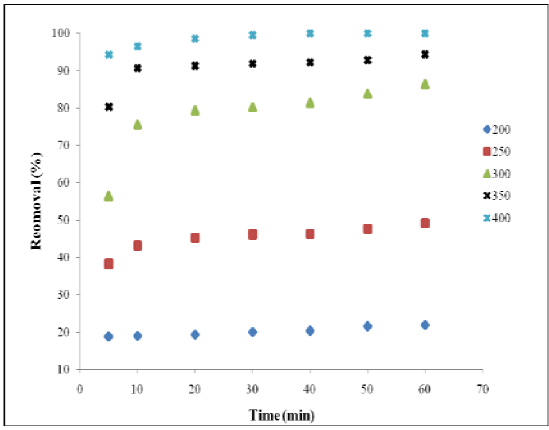

Fig. 2: Effect of temperature and time on PCP removal from soil

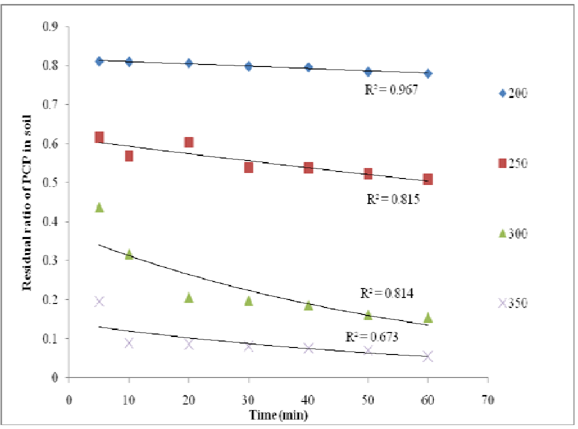

Fig. 3: Residual ratio of PCP as function of time and temperature

The removal efficiency was calculated by the difference between the initial concentration and residual in soil after thermal treatment. Figure 2 shows the dynamics of PCP removal from with time at temperatures of 200^{0}C, 250^{0}C, 300^{0}C, 350 ^{0}C and 400 ^{0}C, respectively. As expected, the contaminant residual in soil decrease with treatment time and significantly reduce with temperature. PCP was removed rapidly at the first 10 min possibly due to the low specific surface area and low porosity of coarse sand that increase the contaminant desorption processes. Clearly, PCP removal was increased dramatically at 300^{0}C above and 350^{0}C is sufficient to remediate PCP from sandy soil.

PCP residual in soil decreases with time and the rate of PCP desorption decribed as slopes of curves increase with temperatures of 200^{o}C, 250^{0}C, 300^{0}C and 350^{0}C, respectively (Fig. 3). The significant loss (>70%) was observed in the region of 200 – 300^{0}C, which is supposed to be the vaporization of PCP. And then the removal rate was much lower (~ 20%) is obtained in the temperature range of 300^{0}C – 400^{0}C which is contributed to PCP pyrolysis occuring with possible formation of involatile products. The rapid decline at the beginning is supposed due to evaporation of PCP from the particle surface, and then internal diffusion is rate-limiting[4]. The correlations of the first order model and experiment data seem good for low temperature and decrease with increasing temperature. Hence, other mechanisms possibly occur to control desorption process.

2. Analysis of temperature effect on byproduct release in gas and soil phases

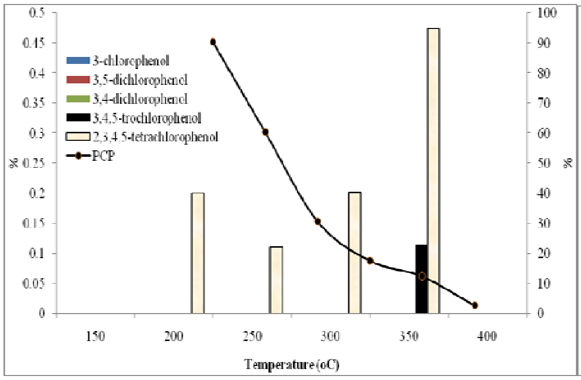

Fig. 4: Effect of temperature on release of PCP byproducts in soil phase

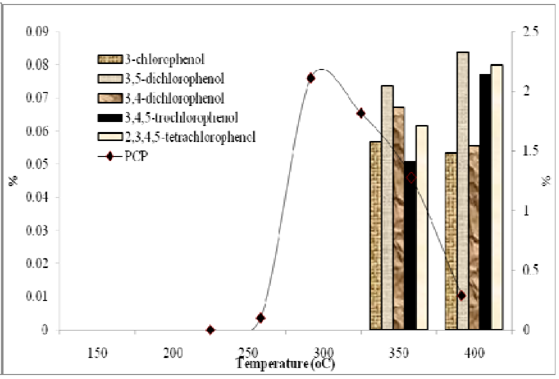

Fig. 5: Effect of temperature on release of PCP byproducts in gaseous phase

By-products of PCP after thermal treatment in gaseous and soil phases were extracted and identified by GC/MS. Due to the poor detection limit of GC/MS for chlorinated phenols, it is difficult to analyze all by-products. It is worthwhile to consider peak sizes to estimate contributions of lesser chlorophenols compared to initial mother PCP in gaseous phase as well as soil phase as presented in Fig. 4 & 5.

Clear evidence of significant removal by vaporization mainly of PCP from soil into gaseous phase in the range of 150-300^{0}C was observed. Due to PCP pyrolysis in temperature range of 300-400^{0}C^5 , PCP release decreased and disappeared in both phases at 400^{0}C. Meanwhile the lesser chlorophenols started to produce at 200^{0}C with 2,3,4,5-tetrachlorophenol at soil phase and then the number of lower chlorophenols increase with temperature. Finally they vaporized into gaseous phase at 350^{0}C and 400^{0}C as shown in Fig.5. vaporization of PCP into gaseous phase at 250^0, 300^{0}C, 350^{0}C and 400^{0}C are only about 2.5%, 1.8%, 1.3% and 0.28%, respectively while 30%, 17%, 12% and 0.7% of PCP were retained in soil, the other amount has been not indentified yet. However, detection of many involatile compounds such as biphenyl compounds in soil phase has proved the phenyl intermediate radical formation during PCP pyrolysis. Hence the PCP loss is possibly due to intermediate radical formation. Further results need to be confirmed by analysis of chlorine balance.

The lower chlorinated phenols were detected as an obvious evidence of PCP dechlorination during pyrolysis. However, this process occurred partially and slightly because phenol, cyclohexanol/cyclohexanone, the final products of dechlorination, were not detected in this procedure.

3. Analysis of time effect on chlorophenol releases in gas and soil phases

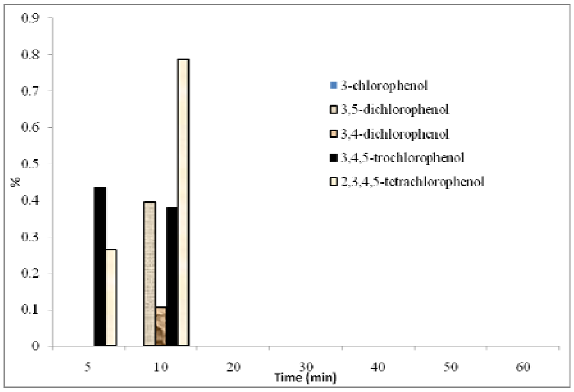

Fig. 6: Effect of time on release of PCP byproducts in soil phase at 350^{0}C, 0.25 slpm

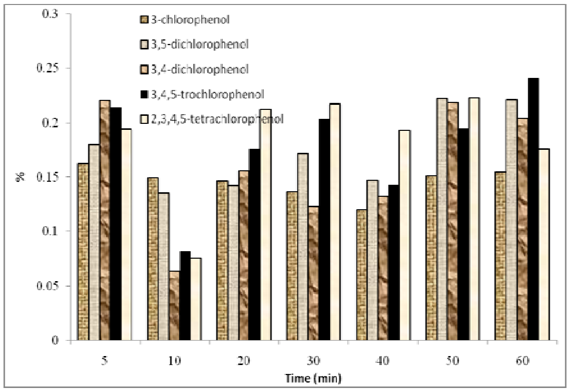

Fig. 7: Effect of time on release of PCP byproducts in gaseous phase at 350^{0}C, 0.25 slpm

To clarify how the dechlorination process occurs, effect of time on chlorophenol releases in gaseous and soil phases were investigated and shown in Fig. 7 & 8. Dechlorination process occurred rapidly at the first 5min and vaporized into gaseous phase due to higher temperature than boiling point of chlorophenols. After 10 min, only 2,3,4,5-tetrachlorophenol was detected in soil phase and disappeared at 60 min. All chlorophenol compounds have been moved into gaseous phase for longer treatment time (Fig. 8). The pattern of lower chlorophenol is quite similar at each treatment time. Obviously, the order of chlorophenol appearance in gaseous and soil phases is followed as tetrachlorophenol, trichlorophenol, dichlorophenol and monochlorophenol, respectively.

4. Possible mechanisms of PCP removal from sandy soil

Three pathways for PCP removal at relatively low temperature (200^{0}C – 400^{0}C) have been proposed in this study: (1) desorption; (2) catalysis by sandy soil via dechlorination, (3) vapor phase pyrolysis to release intermediate radicals and then reaction/catalysis with volatile products in soil.

According to previous results of time effect on chlorophenol existence in soil and gaseous phases, dechlorination clearly happens at ortho-chloro position firstly to form 2,3,4,5-tetrachlorophenol and 3,4,5-tricholophenol and then dichlorophenol and monochlorophenol formation at the lower rate (Fig. 9). In addition, formation of cyclohexasiloxane, cyclotetrasiloxane and cyclotrisiloxane detected by GC/MS chromatography has shown the crosslink of PCP and SiO_2 present in sandy soil. Hydrogen bonding between hydroxyl functional group of PCP and O-atom of SiO_2 makes energy distribution of PCP molecule change, especially at ortho-cloro position which are more easily dissipated than the other positions. As a result, 2,3,4,5-tetrachlorophenol and 3,4,5-trochlorophenol were found in most of cases.

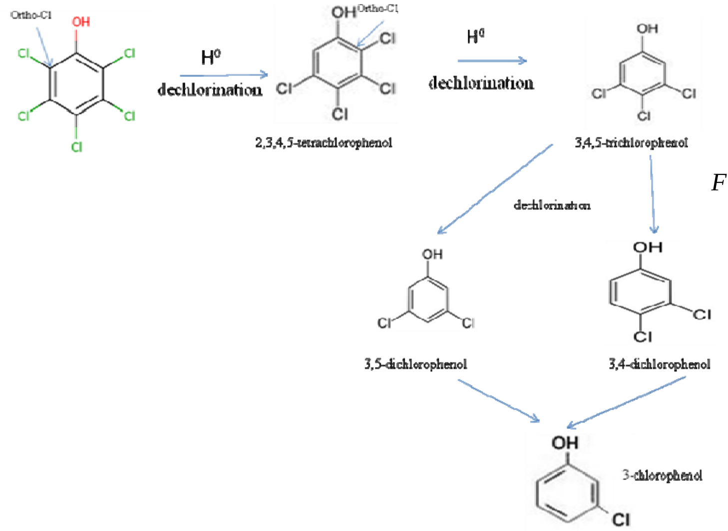

Fig. 8: Dechlorination process of PCP in sandy soil at 200^0C – 400^0C

As mentioned above, there are some biphenyl compounds present in gaseous and soil phases due to unpredictable formation of intermediate radicals during PCP pyrolysis at different conditions. Hence vapor and soil phases' pyrolysis are supposed to contribute potentially the significant imbalance of carbon and chlorine. However, the toxic dioxins and furans (17 most toxic congeners) were analyzed by HRGC/HRMS to identify any possible further toxic compounds and no any ones were found in this pyrolysis condition. Further research needs to be conducted in order to clarify this phenomenon.

Acknowledgements:

The authors gratefully acknowledge Mr. Hung, Pao-Chen for his help and comments. The authors are pleased to acknowledge the financial support provided by the National Science Council (NSC 98-2221-E-008-019-M Y3) of the Republic of China.

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