BEHAVIOUR OF PCBs IN REMEDIATION BY OXYGEN FREE THERMAL TREATMENTS OF AN ARTIFICIALLY CONTAMINATED SOIL

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Samples of a soil artificially polluted with PCBs were decontaminated using thermal treatments in inert atmosphere. Laboratory experiments were carried out at 400°C, 600°C and 800 °C and two retention times: 30 and 60 minutes. This paper investigates the fate of PCB compounds during the thermal remediation method. Results revealed that increasing the treatment temperature and time good results concerning the contaminated soil remediation were obtained. Pyrolysis technologies as methods for decontamination of PCBs polluted soil ensured, with some exceptions, an efficiency of over 99%.

Keywords: contaminated soil, PCBs, pyrolysis, temperature, retention time, efficiency

1. Introduction

Polychlorinated Biphenyls (PCBs) belong to a broad group of man-made organic chemicals that are known as Persistent Organic Pollutants (POPs) [1]. PCBs are classified as probable human carcinogens and produce a wide spectrum of adverse effects in animals and humans, including reproductive toxicity, teratogenicity and immunotoxicity. These are some reasons because in 1985, the use and marketing of PCBs in the European Community were very heavily restricted. Also, in order to secure better protection from the effects of dioxins and PCBs on human health and on environment, it has been deemed necessary to develop a Community strategy for dioxins, furans and PCBs [2].

From inventories made in Romania some representative areas related to the existence of soils contaminated with persistent toxic pollutants (PTP) due to historical or existing pollution have resulted [3]. Since 2001 information on PCBs concentration in environmental samples from Romania are available, but these cover just some regions at national level. Analysis of the PCBs concentrations in soil and sediment samples have been done on tasters from industrialized and remote areas in Eastern, Western and Southern Romania [4,5]. The interaction of the PCBs with many components of the soil makes difficult the evaluation of

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PCBs fate in environment [6]. In recent years, at international level, an increasing concern about treatments and disposal of contaminated sediment or soil due to accumulated dioxins (PCDDs, PCDFs) and PCBs [7, 8]. Several techniques have been proposed for soil remediation [9-14]. The search for identification of the most efficient technologies has motivated fundamental research on thermal treatment for cleaning of contaminated soils. The thermal processes [15, 16] may produce positive results [17], 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 [18]. According to their operational temperature, thermal treatments can be classified into desorption and destruction techniques. Pyrolysis is part of the second class. Generally, pyrolysis causes the thermal degradation of organic substances that are converted into primary products such as charcoal, liquids, fuel gas [19].

This paper presents the results of the experimental studies on laboratory scale pyrolysis treatments applied to soil contaminated with PCBs. The main objective of the paper was to obtain information on the fate of PCB compounds during such thermal treatment and to find significant information that could be applied in the large scale of a pilot scale pyrolyzer.

2. Methods and materials

2.1. Soil samples

The contaminated soil treated in the experimental campaigns was collected from one of the most contaminated area of Romania. The polluted soil is historically contaminated with heavy metals due to industrial activities realized for almost 60 years and artificially polluted with PCB - containing transformer oil (the unnaturally contamination was realized only for the laboratory experiments). Some characteristics of the contaminated soil, the concentration of the metals and the concentration of the PCB compounds analyzed in the present laboratory study are listed in table 1.

Table 1

Characteristics of the contaminated soil

Characteristic	Value	Concentration	Value	Concentration	Value
pH (-)	7.78	**Pb** (mg/kg_{dw})	2305	**PCB_{28}** (mg/kg_{dw})	1.3595
W (%)	4.93	**Cd** (mg/kg_{dw})	75	**PCB_{52}** (mg/kg_{dw})	0.5251
C organic (%)	4.73	**Be** (mg/kg_{dw})	903	**PCB_{126}** (mg/kg_{dw})	-
Nt* (%)	0.182	**Cr^{tot}** (mg/kg_{dw})	82	**Total PCBs** (mg/kg_{dw})	0.4662
P_{AL}* (%)	36	**Ni** (mg/kg_{dw})	72		
K_{AL}* (%)	323				

2.2. Experimental set-up and thermal treatments conditions

Oxygen free thermal treatments were performed using a laboratory scale experimental set-up existing in the Renewable Source Laboratory from Power Engineering Faculty, University POLITEHNICA of Bucharest. It is formed by a tubular fixed bad NABERTHERM, type RO 60/750/13 (fig. 1). In order to identify the PCBs emissions from the oxygen free thermal treatment experiments, an isokinetic automatic portable sampling system ISOSTACK Basic HV was used. This system was connected to the outlet for the gas discharge generated from the thermal treatments applied to the contaminated soil.

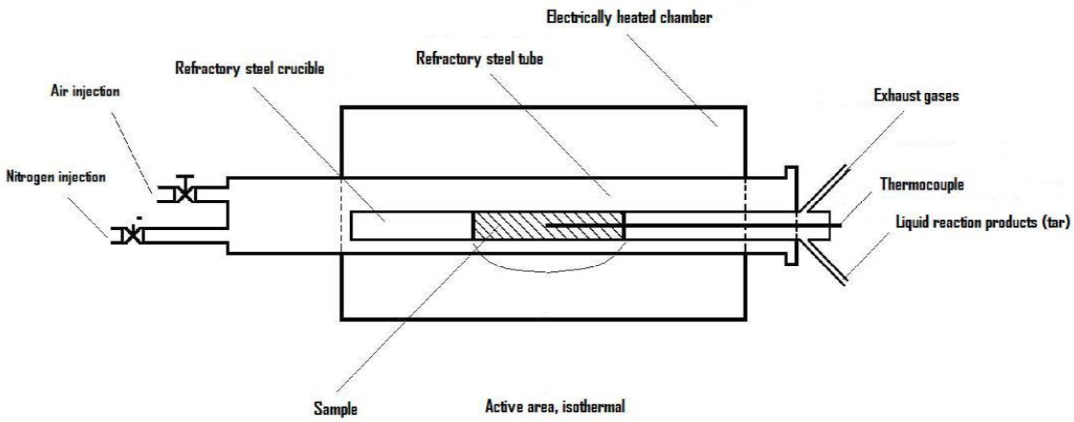


Fig. 1. Tubular electric furnace diagram

The pyrolysis tubular reactor is external electrical heated and represents an adaptable device allowing the reproduction of the thermal degradation processes of solids wastes in conditions of incineration, pyrolysis and gasification. Consequently, the treatment atmosphere can be oxidant or reductive depending on the thermo-chemical process applied to the solid material [20]. The active zone, the heated one, measure about 750 mm and the maximum process temperature can rise to approximately 1200°C. The pyrolysis reactor is working in a discontinuously mode; so small batches (600g) of PCB contaminated soil were separately heated ensuring an inert atmosphere (1 l/min of nitrogen flow) at different temperatures: 350°C, 400°C, 600°C and 650°C. The thermal treatments have been applied for 30 minutes and 60 minutes retention time.

2.3. Methods and standards for sampling and analysis

The sampling method was based on STAS 7184/1-75, SR ISO 11074-2:2001 and improved methodology developed by the National Institute of Research-Development for Agrochemistry and Pedology (ICPA), Bucharest. PCBs concentrations were identified according to the current standard methods in force (SR EN 10382:2007, SR EN 15308:2008, EPA Method 3540:1996) applicable to both, contaminated soil and remediated soil-ash produced by the thermal treatments. Samples from emissions were taken using an isokinetic automatic portable sampling system of particulate emissions (ISO 9096, EN 13284-1, EN 1948-1) – Isostack Basic HV. Particle and gas phase were iso-kinetically sampled on quartz fibber filters, respectively on polyurethane foam (PUF) (SR ISO 12884:2008, SR EN 15549:2009). All samples have been extracted using the Soxhlet and rotary evaporator equipment and then transferred to a capped and sealed vial for gas-chromatographic analysis. A GCMS QP2010 Plus Shimadzu equipment was used in order to identify the concentration of the PCBs from the untreated contaminated soil and also from ashes. Concentrations of the PCBs compounds were identified by a combination of a retention time and mass spectral match against the calibration standards.

3. Results and discussions

Results from the laboratory experiments are summarized in Table 2. Here are presented the concentration of the PCBs compounds from the contaminated soil and from ashes generated during the pyrolysis treatments.

Table 2

Concentration levels of PCB compounds in contaminated soil and ashes generated by the pyrolysis experiments

Sample	Pyrolysis conditions		Concentration of the PCB compound [mg/kg$_{dw}$]			
	Temperature [C]	Time [min]	PCB 28	PCB 52	PCB 126	Total PCBs
Contaminated soil	-	-	1.3595	0.5251	0.0026	4.4662
Ash	400	30	0.0492	0.0135	0.0020	0.1184
	600		0.0039	0.0001	0.0009	0.0133
	800		0.0023	0	0.0002	0.0099
	400	60	0.0093	0.0027	0.0000	0.0276
	600		0.0016	0	0.0000	0.0062
	800		0.0007	0	0.0000	0.0045

3.1. Effect of the pyrolysis temperature and retention time on PCBs concentration from the decontaminated soils

Comments about results must start considering the national legislation which establishes thresholds in case of soil contamination (Order 756/1997 for approving the Rules on assessment of the environmental pollution). According this, the intervention thresholds for sensible use is 1 mg/kg$_{dw}$. In case of the soil analysed in the present paper, the initial concentration of □PCBs is four times bigger than the legal limit. In the actual paper we have choose to study organic pollutants as PCB28, PCB52 and total PCBs that are regulated by the named national order, exception makes PCB126, the present regulation not covering this pollutant. So, PCB28 and PCB52 levels existing in the ashes produced by pyrolysis treatments applied for 30 minutes (the most short experiment time, where we detected higher level of PCBs concentration than for pyrolysis applied for 60 minutes) were compared with the national reference levels (these have the same alert level for sensitive use: 0.002 mg/kg_{dw}). We have observed that for all process temperatures, the pyrolysis of the PCBs contaminated soil ensured concentrations of PCB28, PCB52 in soil below the reference levels. Exception was only in case of the pyrolysis applied at 400°C, when the resulted ash contains concentrations of PCB28 (0.0492 mg/kg_{dw}) and PCB52 (0.0135 mg/kg_{dw}) higher than the reference limit.

In the Order no. 756/1997 in case of total PCBs, the alert level for sensitive use in soil is 0.25 mg/kg_{dw}. The experiments results showed that all ashes produced by non-oxidant thermal treatments, no matter the temperature applied, contain concentration of total PCBs under the alert level for sensitive (fig. 2).

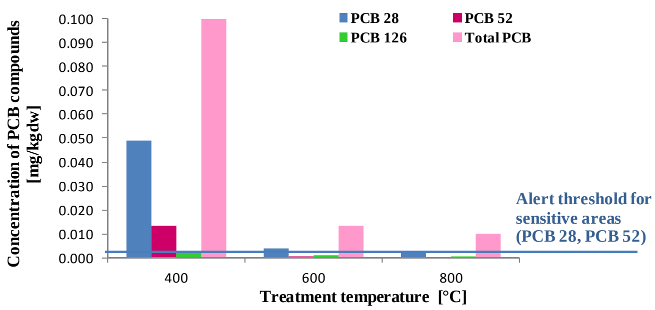
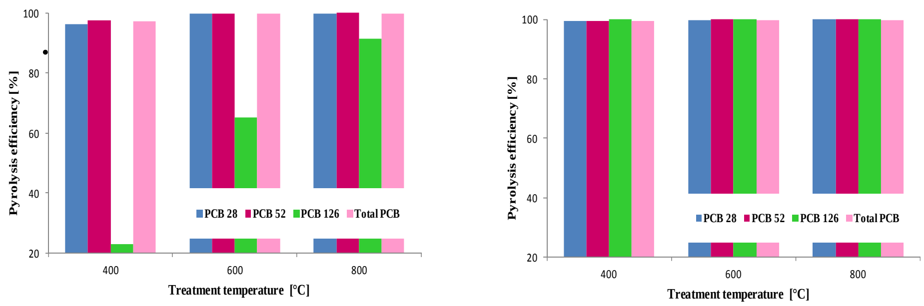


Fig. 2. Concentration levels of PCB 28, PCB 52, PCB 126 and total PCB in soil and ashes generated by the pyrolysis experiments applied for 30 minutes long

3.2. Effect of the pyrolysis parameters on treatment efficiency

Figures 3.a and 3.b put in evidence the thermal treatment efficiencies in removal of PCB28, PCB52, PCB126 and total PCBs from soil. Results of the pyrolysis experiments process illustrated an efficiency for removal of PCBs compounds from soil between 96.38% and 99.99% as a consequence of keeping of the contaminated soil in the reactor for different retention times (30 minutes, respectively 60 minutes) at different process temperatures (400°C, 600°C and 800°C). Exception is made by the PCB126 for which the elimination efficiency of the thermal treatments applied for 30 minutes to the contaminated soil have revealed lower values: 23.08% (400°C), 65.38% (600°C) and 91.54% (800°C). All these aspects evidence the importance of the process time in removal of PCB126 from polluted soil. The results of our experiments showed also that the mechanism of PCB 126 removal from contaminated soil is working well for all final temperatures attended in the pyrolysis reactor if the non-oxidant thermal treatments are applied for 1 hour. As we can observe in the next graphs, for the pyrolysis technologies a maximum level of the efficiency was obtained (99,99 %).



(a) treatment time = 30 minutes (b) treatment time = 60 minutes

Fig. 3. Efficiency of the pyrolysis technologies applied for PCBs removal from contaminated soil for different remediation time

3.3. Effect of the pyrolysis parameters on pyrolysis emissions

The results concerning the emissions showed that the concentration level of PCBs compounds analyzed in the present papers is strongly influenced by the temperature if this increases from 400°C to 600°C. This process parameter has an important influence on PCBs concentration in the flue gases generated during the pyrolysis thermal treatment. Contrary, the retention time has no influence on emissions; doubling the remediation time the PCBs concentration in emissions maintain the same trend: increasing pyrolysis temperature from 400°C to 600°C conduct to increasing of the concentration level in emissions; when the process temperature is increased from 600°C to 800°C the PCBs concentration is decreasing (fig. 4).

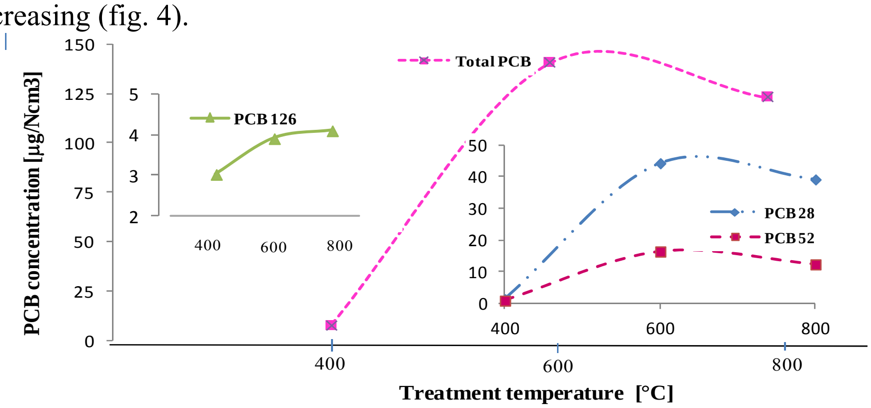


Fig. 4. Concentration level of PCBs in emissions generated by the soil pyrolysis applied for 30 minutes retention time

This tendency is available for PCB28, PCB52 and total PCBs. For example, the concentration of PCB28 in the flue gases increases with almost 96%. Not the same behaviour was observed if the pyrolysis temperature was raised from 600°C to 800°C (a decrease of 11.6% was registered). From the results presented in the figure from below it could be observed that devolatilisation is the main mechanism for PCB126 removal from the contaminated soil under operational conditions applied in our experiments, phenomena revealed in studies realized by other authors [21] for a similar soil matrix. Opposite, the concentration of PCB126 from emissions generated by all pyrolysis process is almost the same no matter the time of the thermal decontamination process (the biggest difference between concentrations is 0.36%).

6. Conclusions

Behaviour of PCB28, PCB52, PCB126, and total PCBs has been assessed applying different operational conditions of the pyrolysis treatment. With respect to the process temperature of the thermal technologies, the experiments results demonstrated that pyrolysis is an efficient method for removal of PCB28, PCB52, PCB126 and total PCBs from contaminated soils. Generally, an efficiency of over 99% was obtained, independently of the process parameters. Exception to this affirmation makes PCB126 that appear to be more difficult to be eliminated from soil at 600°C and 800°C in case of pyrolysis applied for 30 minutes, when the efficiencies were 98,077% and 98.462%. The results of the experimental campaign demonstrate the potential of oxygen free pyrolysis as an alternative technology to either prevent formation of PCB complex or minimize the release of these organic compounds into the environment.

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