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Analysis of thermal processing applied to contaminated soil for organic pollutants removal

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ABSTRACT

The paper presents the results of an experimental study conducted to investigate PAHs behavior during non-oxidant thermal decontamination of soil samples contaminated with petroleum products. The study focused on the assessment of the concentration levels for different PAHs species present in pyrolysis products after the treatment of contaminated soil samples. Pyrolysis experiments were performed using a horizontal tubular reactor. The contaminated soil samples were treated in inert controlled atmosphere (nitrogen). The treatment period varied between 30 and 60 min at a temperature range of 350 °C–650 °C. Chemical analyses were performed to compare the thermal degradation mechanism and the pollutants generation in the flue gases of the pyrolysis process. The present research study identifies and quantifies the concentration level of polycyclic aromatic hydrocarbons from the solid and gaseous phases of the pyrolysis products, as well as from the condensates produced during the process. The amount of the organic contaminants was determined using a GC/MS analyzer and Soxhlet extraction method. The results of the experiments revealed that pyrolysis is an efficient process that could be used to remove the PAHs from contaminated soil. For 650 °C treatment temperature performed for 30 min the thermal process registered a decontamination efficiency superior to 80%. The extension of the treatment period to 60 min increased the decontamination efficiency to more than 90%.

1. Introduction

Due to the anthropogenic activities related to petroleum processing our environment is exposed to polycyclic aromatic hydrocarbons (PAHs) contamination. These organic compounds attach to solid sediments and are omnipresent: in soil, water and air. PAHs existing in these environments lead to potential hazards to human health (Ukiwe et al., 2013). There are several hundred PAHs types in the environment and generally they are found as complex mixtures rather than as individual compounds (HPA, 2008). Only 16 PAHs are classified by the US EPA as priority pollutants based on toxicity, potential for human exposure, frequency of occurrence at hazardous waste sites, and the extent of information available (ATSDR, 2005). Among these, the US EPA considers only seven as probable human carcinogens: benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene and indeno(1,2,3-cd) pyrene (Bojes and Pope, 2007; NTP 2011).

The polycyclic aromatic hydrocarbons are classified as low molecular weights (LMW) or high molecular weights (HMW). The first group is formed by two or three benzene rings, while those with four or more benzene rings represent the class of HMW PAHs. LMW PAHs are fairly soluble in water, but HMW are quite hydrophobic and insoluble (Cerniglia and Heitkamp, 1989). The rate of PAHs absorption into soil organic matter is proportional with the number of the aromatic rings. Various HMW PAHs are recalcitrant under current conditions in the terrestrial environment; consequently their persistence resides over long periods of time (Sims and Overcash, 1983; Ukiwe et al., 2013). So it is more difficult to remove HMW from the soil (Delgado-Balbuena et al., 2013; Stroud et al., 2007). That explains the necessity to develop new processes and technologies in order to increase the degradation rate of the persistent PAH (Chouychai et al., 2009).

There are many applicable technologies for contaminated soil with petroleum hydrocarbon (Ram et al., 1993), but the efficiency of the technologies closely depends on contaminant and soil characteristics as well as on cost limitations (Khan et al., 2004; Reddy et al., 1999; Riser-Roberts, 1998). Over the last years, for the remediation of the petroleum contaminated soils, different processes have been adopted: physical, chemical, biological and thermal methods. Choosing the most appropriate technology for soil decontamination represents a difficult undertaking because many issues must be considered: technical, technological and economical (Kujat, 1999; Reis et al., 2007). Thermal technologies present a scientific and practical interest because they proved high efficiency in removing and degrading organic pollutants.

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According to their operational temperature, thermal treatments can be classified into desorption and destruction techniques. Pyrolysis is part of the second class by fragmenting the organic molecules. Generally, pyrolysis causes the thermal degradation of the organic compounds that are converted into primary products such as charcoal, liquids, and flue gas (Bridgewater and Grassi, 1995). When used for contaminated soils treatment pyrolysis offers the advantages of treatment temperatures superior to pollutant vaporization temperature. Consequently the pollutant (hydrocarbons in this case) undergoes a phase transformation from liquid to gas and leaves the solid matrix of the soil. Therefore pyrolysis can be interesting in this field and requires further study. As for all ex situ thermal treatments, the main advantage of the pyrolysis process is that it requires short times, and there is more certainty about the uniformity of the treatment, due to the capacity to screen, homogenize, and continuously mix the soils. The major disadvantage of the process is related to the energy consumption needed to bring and maintain the contaminated soil at a specific temperature for a minimum residence time to complete the pollutant removal (Bulmău et al., 2013). The energy consumption is the sum of the energy consumed for bringing the soil from ambient temperature to pollutant vaporization temperature, plus the energy necessary to heat the pollutant up to vaporization and energy for heating of soil to the maximum process temperature. Due to this heat demand the pyrolysis of contaminated soil is an endothermic process. Nevertheless, when applied to hydrocarbons contaminated soil, depending on the contamination level (i.e. quantity of hydrocarbons), the released hydrocarbons can be used to generate heat within the process by controlled combustion. Another limitation of the treatment is given by the excavation of soils leading to additional costs. If hydrocarbons are used for heat generation by combustion, the flue gas cleaning system configuration can be reduced to minimum. However thermal treatments offer fast cleanup for heavily contaminated soils with high pollutant removal efficiency (Bulmău et al., 2012a).

The paper provides important information about a thermal process with high efficiency in polycyclic aromatic carbons removal from soil contaminated with petroleum products. The experimental study revealed that pyrolysis could reach over 90% efficiency in PAHs removal from soil.

The main objective of this experimental study is to identify and quantify the concentration levels of different PAHs compounds (pyrene, benzo(a)pyrene, benzo(a)anthracene and total PAHs) existing in a soil contaminated with petroleum products, and to investigate the removal of these organic pollutants from the soil matrix. We have also monitored the amount of PAHs compounds generated in gaseous phase during the thermal treatment. Furthermore, the process results at high temperatures and low temperatures are compared. This piece of information contributed to the assessment of the temperature and the treatment period influences both the efficiency of the contaminants removal from the soil matrix during the thermal treatment, and on products generated by these technologies. The experimental research could provide fundamental data regarding the PAHs removal during the decontamination of the polluted soil, thus helping to establish the behavior of pyrolysis technologies used to remediate contaminated soils.

2. Material and methods

2.1. Samples

The soil used in the study was collected directly from a highly polluted site as a result of anthropogenic activities related to petroleum processing.

The contaminated soil testers were sampled according to STAS 7184/1-75, SR ISO 11074-2:2001 and the improved methodology developed by the National Institute of Research–Development for Agrochemistry and Pedology from Romania, according to the European Union regulations.

An experimental campaign was conducted to establish the properties of the soil and to identify the hydrocarbon pollutants within. The main physical and chemical properties of the soil samples are presented in Table 1.

2.2. Soxhlet extraction of soil contaminants

The Soxhlet extraction method has the advantage of forming emulsions with more rigorous solvent mixtures, for an in-depth analysis of soil/waste mixtures. The analytical method designed to determine the polycyclic aromatic hydrocarbons concentrations was carried out according to the current standard methods in force (EPA Method 3540:1996), applicable to both soil and solid waste, considering ashes (soils decontaminated by pyrolysis) as hazardous solid waste in terms of environmental quality protection. Before being weighed, the solid samples passed through a 2-mm opening sieve. Then the samples were mixed with anhydrous sodium sulfate, placed in an extraction thimble and extracted using the solvent in a Soxhlet extractor. Sample extractions were carried out by Soxhlet method applied by using equipment with 6 benches. Approximately 20 g portions of each contaminated soil sample were extracted with 250 ml of HPLC grade petroleum ether solvent. The extract was concentrated to a small solvent volume and eluted with hexane using Heidolph rotary evaporator. After the concentration step, the samples were cleaned-up, if necessary, or they were transferred to a capped and sealed vial for gas-chromatographic analysis. For the analysis of PAHs, each sample was separately extracted three times and the results are presented as an average of these replicates. In case of the emissions generated by the thermal treatments, the extractions of PAHs compounds collected on quartz fiber filters and polyurethane foam filters (PUF) were performed by Soxhlet extractor using HPLC grade petroleum ether solvent. The extraction procedure acquired a time interval that ranged between 8 and 10 h and it has the same steps as compared with extraction of polycyclic aromatic hydrocarbons from the solid samples.

2.3. Gas chromatography–mass spectrometry (GC/MS) analysis

The qualitative and quantitative analyses were performed by a Shimadzu GCMS-QP2010_Plus system gas chromatograph with a mass spectrometer detector. Polycyclic aromatic hydrocarbons compounds were identified in samples by a combination of retention time and mass spectral match against the calibration standards (Agilent Technologies, 2008 and 2009). Specific parameters, as resulted from standard analyses and individual calibration curves for each of 16 studied compounds (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i) perylene) are presented in Table 2. Calibration curves were obtained using a series of standard solutions, prepared by diluting the standard mix (16 PAHs mix from Supelco) with hexane until it reached the desired concentrations (1; 2; 3 şi 4 ng/μl). Qualitative and quantitative analyses of PAHs were conducted according to the standard procedure

Table 1
Main properties of the soil from the contaminated site.

Soil property	Value	Soil pollutant	Value
pH (–)	7.7	Pyrene concentration (mg/kg$_{dw}$)	0.089
Humidity (%)	16	B(a)P concentration (mg/kg$_{dw}$)	0.050
Density (g/cm^3)	1.5	B(a)A concentration (mg/kg$_{dw}$)	0.257
C organic (%)	13.36	Total PAHs concentration (mg/kg$_{dw}$)	0.989
Humus (%)	23.04	TPH (mg/kg$_{dw}$)	71,000

dw = dry weight.
B(a)P = benzo(a)pyrene.
B(a)A = benzo(a)anthracene.