

Evaluation of the Emissions from the Pyrolytic Treatment of PAHs Soil Contaminated Soil

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Abstract – The present paper examines the emissions of polycyclic aromatic hydrocarbons (PAHs) resulted from the thermal treatment through pyrolysis process of contaminated soil with petroleum products. Specifically, across the experimental work, the process temperature influence on PAHs and Phenanthrene emissions and remediation degree during the thermal treatment were investigated. The pyrolytic treatment of the contaminated soils was performed at different temperatures and time: 400°C for 60 min; 600°C for 30 min and 800°C for 30 min. The obtained results revealed that non-oxidative atmosphere at temperatures between 400°C and 800°C reduced PAHs and Phenanthrene to below regulatory standards. More than that, it was evidenced that, when the initial concentration of the contaminants in soil is not too high (content of PAHs in soil was 26.811 mg/kg_{d.w.} respect to 25 mg/kg_{d.w.}, while for Phenanthrene initial concentration in soil was 19.264 mg/kg_{d.w.} respect to 5 mg/kg_{d.w.} from the regulation in force) even a low-temperature of 400°C for the pyrolysis process ensure an efficiency in removing PAHs and Phenanthrene higher than 99%. It was evidenced that, increasing the process temperature with 200°C and respectively with 400°C, respect to the selected pyrolysis conditions as appropriate (400°C for 60 minutes), has no relevance in terms of reducing contaminants from the contaminated soil. This is an important advantage considering that lower temperatures are requiring lower energy costs and soil fertility is not affected as in case of soil incineration or other thermal treatment methods.

Keywords: Soil pollution, Remediation, Polycyclic aromatic hydrocarbons, Pyrolysis.

1. Introduction

Worldwide, contamination of soils with petroleum products pose significant risks both for environment and human health. In Romania soil contamination was estimated at 201 contaminated and 1183 potentially contaminated sites. At national level, the main economic sectors with important impact on soil quality are mining and metallurgical industries, chemical industry, oil industry and old pesticide deposits [1].

Contamination of soil with petroleum products is a major environmental problem because of pollution with dangerous pollutants as heavy metals (Zn, Fe, Mn, Pb, Ni, Cr, Cu, Cd, Hg, As), polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPHs) and polychlorinated-biphenyls (PCBs) [2] [3].

For the remediation of contaminated soils, many methods such as thermal, chemical, microbial or physicochemical procedures are used. These methods can be used alone or in combination, on site or off-site application [4] [5].

Compared to other soil remediation thermal methods as incineration and thermal desorption, the pyrolysis method has the advantage of obtaining a good quality of the remaining soil, which allows using it for different purposes [6] [7].

In this context, the current paper presents the obtained results by using the pyrolysis method for remediation of soil contaminated with PAHs by petroleum hydrocarbon release. The research objective was to illustrate the remediation degree concerning the removal of PAHs and Phenanthrene from contaminated soils at different operating temperatures, as well as associated retention times of the material (contaminated soil) in the reactor.

2. Material and methods

2.1. Soil sampling and main characteristics

Soil samples were collected from a contaminated site (of about 1000 m²) accidentally polluted with crude oil. We selected soil sampling following the simple random sampling design [8]. So, 5 samples were chosen (according to the regulation in force [9]) and mixed together to form a unique and homogenous sample. Soil characterization was performed according to current analytical standards as illustrated in Table 1. We performed elemental analysis of TPHs content in soil (Table 2) using HPLC model Agilent 1200 with Fluorescence Detector, from Agilent Technologies (California, USA) and having as support the analytical procedures from the Romanian standard SR ISO 13877:1999 [10]. Table 2 indicates also the references values concerning the allowed concentrations of the contaminants in soil according to the national regulation in force [11].

Table 1: Physicochemical properties of raw soil.

| Parameter | Units | Determined values | Methods |
|--------------------------------------|------------|-------------------|-------------------|
| pH (aqueous extract 1:5) | unit. pH | 7.84 | SR ISO 10390:2015 |
| Potassium – K (aqueous extract 1:5) | mg/kg d.w. | 17.11 | ISO 9964-1:1993 |
| Phosphorus – P (aqueous extract 1:5) | mg/kg d.w. | 13.22 | STAS 7184/7-87 |
| Total nitrogen | mg/kg d.w. | 1.73 | SR ISO 11261:2000 |
| K | mg/kg d.w. | 6302.85 | EPA 7000A:1992 |
| Total phosphorus | mg/kg d.w. | 290.16 | STAS 7184/14-79 |
| Total organic carbon | % d.w. | 12.52 | STAS 7184/21-82 |
| Humus | % d.w. | 21.59 | |
| Chlorides (aqueous extract 1:5) | mg/kg d.w. | 336.85 | STAS 7184/7-87 |

Table 2: PAH content of raw soil.

| Parameter analyzed | Units | Determined values | Normal value | Alert thresholds | Intervention thresholds |
|------------------------|------------|-------------------|--------------|------------------|-------------------------|
| ΣPAH* | mg/kg d.w. | 26.811 | <0.1 | 25 | 150 |
| Naphthalene | mg/kg d.w. | 0.467 | 0.02 | 5 | 50 |
| Acenaphthene | mg/kg d.w. | 0.063 | - | - | - |
| Fluorene | mg/kg d.w. | 1.522 | - | - | - |
| Phenanthrene | mg/kg d.w. | 19.264 | <0.05 | 5 | 50 |
| Anthracene | mg/kg d.w. | 0.009 | <0.05 | 10 | 100 |
| Fluoranthene | mg/kg d.w. | 0.427 | <0.05 | 10 | 100 |
| Pyrene | mg/kg d.w. | 0.898 | <0.05 | 10 | 100 |
| Benzo-a-anthracene | mg/kg d.w. | 2.026 | <0.02 | 5 | 50 |
| Chrysene | mg/kg d.w. | 0.286 | <0.02 | 5 | 50 |
| Benzo-b-fluoranthene | mg/kg d.w. | 0.284 | <0.02 | 5 | 50 |
| Benzo-k-fluoranthene | mg/kg d.w. | 0.064 | <0.02 | 5 | 50 |
| Benzo-a-pyrene | mg/kg d.w. | 0.211 | <0.02 | 5 | 50 |
| Dibenzo-a,h-anthracene | mg/kg d.w. | 0.135 | - | - | - |

| Parameter analyzed | Units | Determined values | Normal value | Alert thresholds | Intervention thresholds |
|------------------------|------------|-------------------|--------------|------------------|-------------------------|
| Benzo-ghi-perylene | mg/kg d.w. | 0.054 | <0.05 | 10 | 100 |
| Indeno-1,2,3-cd-pyrene | mg/kg d.w. | 0.100 | <0.02 | 5 | 50 |

*ΣPAHs – represents the concentration of the 16 EPA-designed priority PAHs

2.2. Experimental framework

The thermal treatment of the contaminated soil was performed using a laboratory tubular batch reactor designed and operated within Renewable Energy Sources Laboratory from University POLYTECHNIC of Bucharest (NABERTHERM, type RO 60/750/13). The pyrolysis reactor is working in a discontinuously mode and the process temperature can be adjusted between 20 – 1300 °C. The refractory steel tube is 60 mm in diameter with a total length of 750 mm and the isothermal active zone of the crucible is 300 mm (zone where the material/soil sample is placed) [12]. The main components of the tubular batch reactor are illustrated in Figure 1.

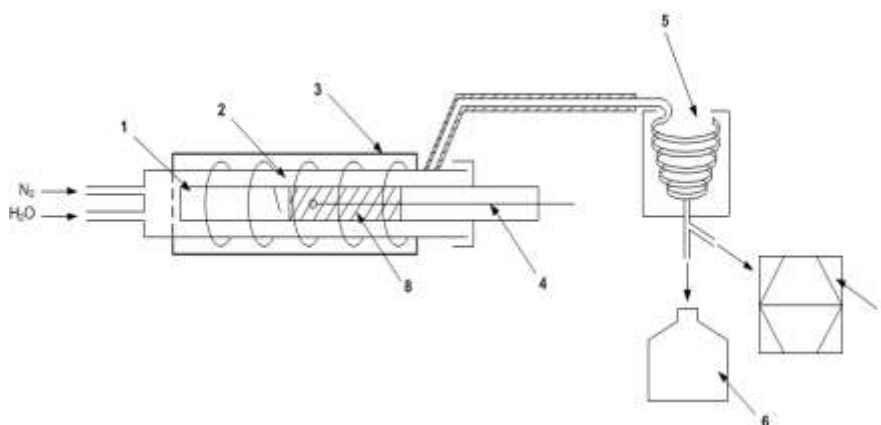


Fig. 1: Tubular batch reactor [12] [13] [14].

1. Refractory steel crucible; 2. Refractory steel tube; 3. Electrically heated chamber; 4. Thermocouple; 5. Condensable hydrocarbons fraction separation system; 6. Collector; 7. Gas analysis system; 8. Sample.

The process parameters used for the pyrolytic treatment of the contaminated soil are presented in table 3.

Table 3: Process parameters of the pyrolytic treatment.

| Treatment type | Temperature | Time |
|-----------------------------|-------------|--------|
| Low - Temperature pyrolysis | 400 °C | 60 min |
| Low - Temperature pyrolysis | 600 °C | 30 min |
| Mid - Temperature pyrolysis | 800 °C | 30 min |

During the experimental work treated soil samples and emission from the thermal treatment were investigated. In order to quantify concentrations of PAHs from emissions from the thermal process, solid and gas phase samples were collected using an isokinetic automatic portable sampling system ISOSTACK Basic HV was used (TCR Tecora). The sampling system has been described in previous works [7] [15]. The working principle of the analytical device is based on isokinetic sampling conditions of a gas volume and deposition of toxic compounds. In this way, the gas phase of the contaminants was sampled on the PolyUrethane Foam Sampler (PUF) and while the solid phase was collected on a quartz filter element, according to EN1948 [16]. Subsequently, the collected samples were sent to a specialised and accredited laboratory for quantitative determinations of PAHs.

3. Results and discussions

From Table 2, where the characterisation of the contaminated soil is evidenced comparing with the allowed concentrations level according to the regulation in force, could be noticed that for Σ PAHs and Phenanthrene compounds the concentration level in soil is higher than the established thresholds. Concerning Σ PAHs, the concentration in soil is with almost 2 mg/kg_{d.w} higher than the acceptable limit of 25 mg/kg_{d.w}, while for Phenanthrene, the determined concentration is almost 4 times higher than the established limit: 19.264 mg/kg_{d.w}, compared with 5 mg/kg_{d.w}. With regard to the other investigated PAHs, concentrations of chemicals as Naphthalene, Benzo-a-anthracene, Chrysene, Benzo-b-fluoranthene, Benzo-k-fluoranthene and Benzo-a-pyrene are exceeding only the normal values (Table 2). According to the regulation in force, special measures are required when alert or intervention thresholds are surpassed at least for one contaminant. As consequence, for the evaluation of the achieved results, the attention was mainly focused on Phenanthrene and Σ PAHs.

The obtained results after soil pyrolysis at different temperatures (400°C, 600°C and 800°C) indicates that the PAHs removal from soil reaches values higher than 98%, exception Naphthalene for which the remediation degree was around 95%. On the other hand, as it was observed also by other authors [6], the removal of PAHs from the contaminated soils (or the conversion of the contaminated soil in “char”) through the pyrolysis process starts between 300°C and 350°C, proceeds rapidly in the 400-450°C range and is usually complete before 500°C. This is sustained also by the results achieved through the illustrated experimental work: initial concentration of Σ PAHs in soil is 26.811 mg/kg_{d.w}, after the pyrolytic treatment at 400 °C for 60 minutes is decreasing to 0.046 mg/kg_{d.w}. (the remediation degree is higher than 99%), while process temperatures equal with 600°C and 800°C are not having important influence on the concentration of the contaminants in treated soil (Σ PAHs concentration in soil 0.043 mg/kg_{d.w}. respectively, 0,040 mg/kg_{d.w}). An overview on the behavior of compounds according to the process temperature and retention time is illustrated in Figure 2 (for PAHs for which initially concentration in soil exceeded the normal values) and Figure 3 a) (for Σ PAHs). It was chosen the graphical representation only for the contaminants for which concentration in soil after the pyrolytic treatment is higher than 0.001 mg/kg_{d.w}.

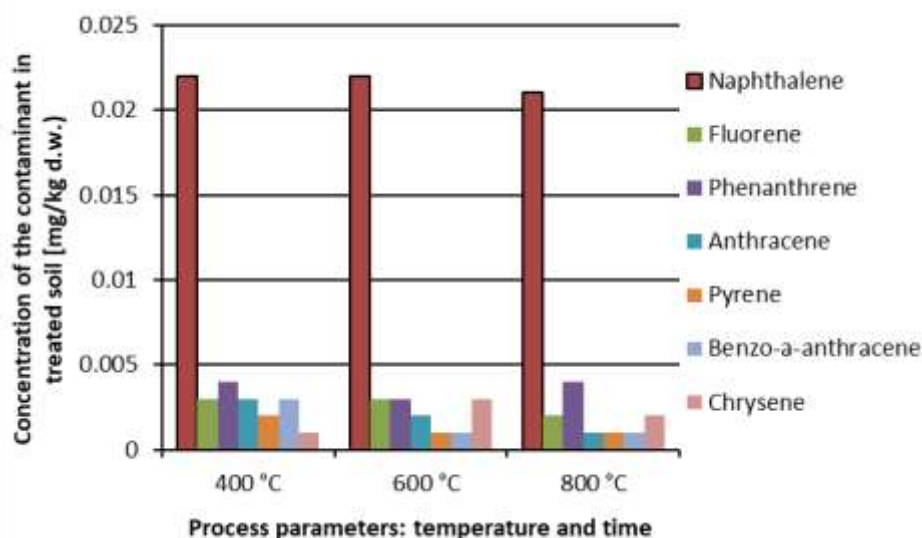
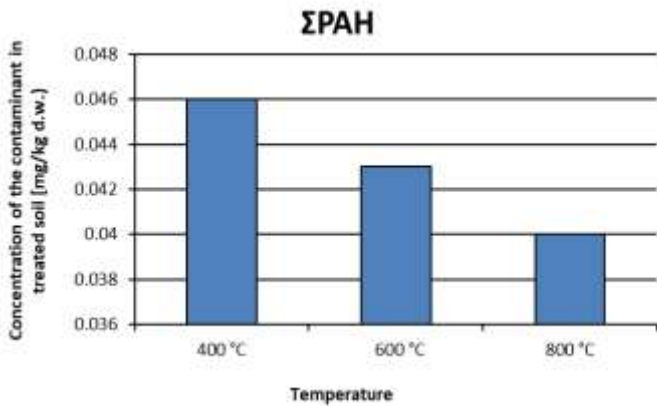
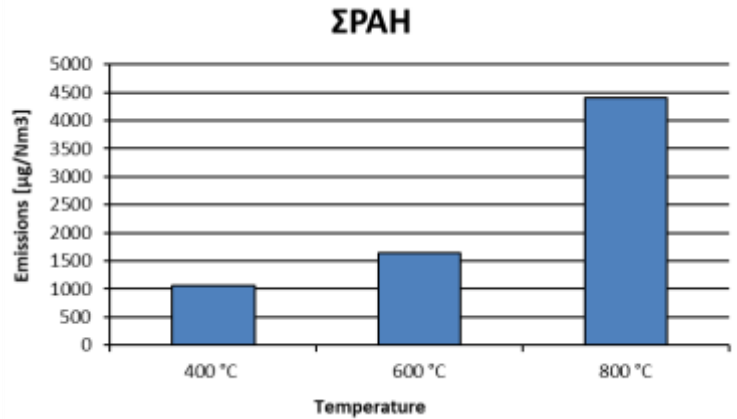


Fig. 2: Concentration of PAHs in treated soil after pyrolysis at different temperatures.

Even if there are different publications on pyrolysis treatment on hydrocarbon contaminated soils, just limited information is provided on emissions that are resulting when the pyrolytic treatment is applied for removal of hydrocarbons (specifically PAHs) from soil. For this reason, the experimental work followed also to determine the emissions of PAHs during the thermal treatment of the contaminated soil. Figure 3 and Figure 4 are illustrating concentrations of Σ PAHs and Phenanthrene in soil and emissions (simultaneously) for different process temperatures.

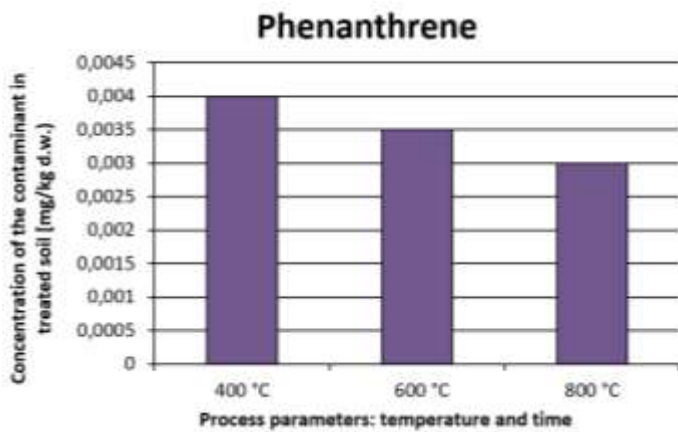


a) ΣPAHs in treated soil at different temperatures

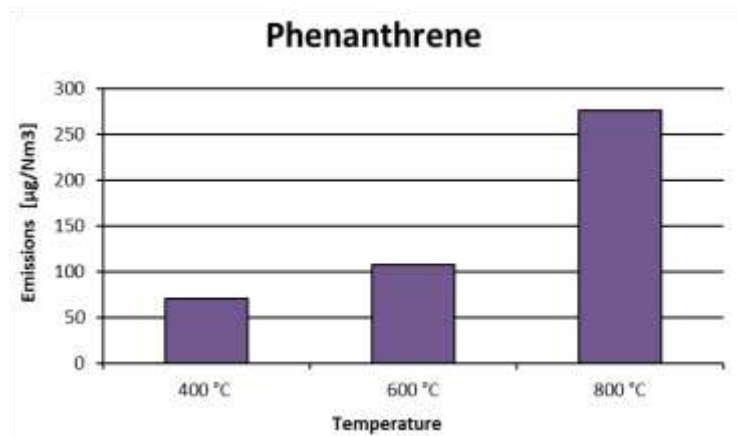


b) ΣPAHs emissions at different temperatures

Fig. 3: Concentration of ΣPAHs in treated soil and ΣPAHs emissions during the pyrolysis treatment.



a) ΣPAHs in treated soil at different temperatures



b) ΣPAHs emissions at different temperatures

Fig. 4: Concentration of Phenanthrene in treated soil and Phenanthrene emissions during the pyrolysis treatment.

The figures above indicate that, increasing process temperature, has as consequence the fact that the concentrations of the contaminants in treated soil are decreasing (over 99%), while the emissions of ΣPAHs and Phenanthrene are increasing. The obtained results concerning the concentrations of ΣPAHs, in treated soil at 400°C for 60 minutes indicates that the selected pyrolysis conditions were appropriate. The same trend is followed also in case of every single investigated compound. Increasing the process temperature with 200°C has no relevance in terms of reducing contaminants from the contaminated soil and additionally requires more energy consumption, reducing in the same time the fertility of the treated soil, as demonstrated by other authors [6]). So, higher process temperature in the pyrolysis process showed that high emissions factors of ΣPAHs can be obtained: 1059.71 $\mu\text{g}/\text{Nm}^3$ at 400°C, 1646.75 $\mu\text{g}/\text{Nm}^3$ at 600°C and 4398.94 $\mu\text{g}/\text{Nm}^3$ at 800°C. Between the studied elements were highlighted especially: Fluorene (567.16 $\mu\text{g}/\text{Nm}^3$ at 400°C; 882.23 $\mu\text{g}/\text{Nm}^3$ at 600°C and 1473.42 $\mu\text{g}/\text{Nm}^3$ at 800°C), Benzo-a-anthracene (151.48 $\mu\text{g}/\text{Nm}^3$ at 400°C; 175.86 $\mu\text{g}/\text{Nm}^3$ at 600°C and 797.56 $\mu\text{g}/\text{Nm}^3$ at 800°C) and Phenanthrene (70.34 $\mu\text{g}/\text{Nm}^3$ at 400°C; 107.05 $\mu\text{g}/\text{Nm}^3$ at 600°C and 275.77 $\mu\text{g}/\text{Nm}^3$ at 800°C).

4. Conclusion

The pyrolytic process used as treatment method of the contaminated sites with crude oil requires attention also from the environmental point of view. It must be avoided that the compounds in the treated soil are subsequently found in the emissions generated by the application of the remediation method.

The present research was mainly focused on the emissions of PAHs resulted from the pyrolysis treatment of contaminated soil with hydrocarbons. In the pyrolysis process (400°C) it was shown that concentration of PAHs in soil are decreasing significantly being maintained in the same time the soil fertility. Increasing the temperature of the process does not provide a significantly lower level of contaminants in the soil, but it influences in the sense of increasing the level of emissions of contaminants resulting from the thermal treatment of the polluted soil.

These kinds of information are very useful for the decision makers who must to identify opportunities to increase process sustainability together with the efficiency of removing contaminants as PAHs from contaminated soils.

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