

# Efficiency of PAHs Removal from Soils Contaminated with Petroleum Products Using Ex-situ Thermal Treatments

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*In order to gain a better understanding of Polycyclic Aromatic Hydrocarbons compounds (PAHs) removal from contaminated soil and improving the efficiency of the thermal treatment used for soil remediation, this paper presents results from the experimental laboratory research. Pyrolysis experiments were carried out using contaminated soil samples from two different soil matrixes, having two different levels of oil contamination. The polluted soil samples were heated for 1 hour in an inert atmosphere, at different temperatures: 350, 400, 600 and 650°C. Solid (initial contaminated soils and ashes) and gas pyro-products were sampled. The analytical determinations of PAHs, and respectively of pyrene compound, were performed by GC/MS technique. This paper aims to provide scientific information on optimal treatment conditions in order to increase the remediation efficiency of the pyrolysis technologies applied to oil contaminated soil, particularly for removal of pyrene from polluted soils.*

*Keywords: soil, PAHs, decontamination, pyrolysis, efficiency*

Soil pollution represents a widespread and challenging problem threatening environment, groundwater resources and human health throughout the world [1], while petroleum hydrocarbons is one of the most common chemical contaminants found in the environment [2]. EEA reports indicate that industrial activities are responsible for over 60% of Europe's soil pollution (the oil sector accounts for 14% of this total), mineral oil being one of the main harmful contaminants for the soil from Europe (almost 34%).

An important class of petroleum hydrocarbons are polycyclic aromatic hydrocarbons (PAHs). They have frequently recalcitrant properties i.e. difficult to biodegrade and will persist in the environment. Petroleum crude oil, coal, processed fossil fuel deposits and even smoking contains important amounts of PAHs [3, 4]. Abundance and persistence of the PAHs in some polluted

environmental compartment such as sediments [5], surface waters [6], airborne particulate matter [7] and drinking water [8] have been reported by different authors. They have the potential to bind to particulates in soil and sediments rendering them less available to degrade in soils; this problem has become a major concern to environmental researchers [9]. There are several hundred of PAHs, which usually arise as complex mixtures rather than as individual compounds. The US EPA has classified 16 of the PAHs (table 1) as priority pollutants based on toxicity, potential for human exposure, frequency of occurrence at hazardous waste sites, and the extent of information available. They are non-volatile, characterized by low solubility in water and they tend to be sorbed to the solid matrix having organic carbon content. As a result, remediation of PAHs contaminated soils has proved to be very costly and energy intensive.

Polycyclic aromatic hydrocarbons	Structure [number of rings]	Molecular weight [g/mole]	Solubility [mg/l]
Naphtalene	2	128.17	31
Acenaphthene	3	154.21	3.8
Acenaphthylene	3	152.20	16.1
Anthracene	3	178.23	0.045
Phenanthrene	3	178.23	1.1
Fluorene	3	166.22	1.9
Fluoranthene	4	202.26	0.26
Benzo(a)anthracene	4	228.29	0.011
Crysene	4	228.29	0.0015
Pyrene	4	202.26	0.132
Benzo(a)pyrene	5	252.32	0.0038
Benzo(b)fluoranthene	5	252.32	0.0015
Benzo(k)fluoranthene	5	252.32	0.0008
Dibenz(a,h)anthracene	6	278.35	0.0005

**Table 1**  
US EPA'S 16 PRIORITY-POLLUTANT PAHS AND  
PHYSICO-CHEMICAL PROPERTIES (ATSDR,  
2005)

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Soil properties	Soil	
	<i>naturally contaminated</i>	<i>artificially contaminated</i>
Humidity [%]	16	4.64
Density [g/cm <sup>3</sup> ]	1.5	1.3
C <sub>org</sub> [%]	13.36	4.73

**Table 2**  
GENERAL CHARACTERISTICS OF THE SOILS

Over the last years, petroleum contaminated soils were treated by different processes such as physical, chemical, biological and thermal methods. The choosing of the most appropriate method for soil decontamination represents a difficult mission because there must be taken into account many factors: technical, technological and economical factors [10-12]. For remediation of the polluted sites, thermal decontamination technologies present a significant scientific and practical interest because they can provide high destruction and removal efficiencies for organic pollutants. The present paper analyses the decontamination of oil polluted soil by oxygen-free thermal treatments. The pyrolysis remediation experiments illustrated in the present paper followed the pre-establish steps: thermal treatments at different temperatures; emissions and ashes sampling during/after 1 hour experiment time; solvent (petroleum ether – C<sub>6</sub>H<sub>14</sub>) extraction by Soxhlet for ashes and emission samples (quartz fiber filters for emission particulate matter and polyurethane filters (PUF) for gaseous emissions; samples being taken according to SR ISO 12884:2008 and EN 1948-1), and GC/MSD analytical determination of individual 16 PAHs compounds; quantification and validation of the obtained results (SR EN 14039:2005, SR EN 15549:2009, US EPA 8270:1998, US EPA 3540:1996)].

In the present paper the experimental results are discussed taking into consideration the following information: (1) pyrene and PAHs concentrations evolution in ashes and emission samples (gaseous phase samples on PUF and particulate matter phase sampled on quartz fiber filter); (2) legislative allowed limits established by the Romanian legislation [Order 756:1997 for approval of regulation concerning environmental pollution assessment]; (3) evaluation of pyrene and PAHs efficiency removal from polluted soil as resulted after analysing the ashes versus primary contaminated soil contents of PAHs. The aim of this laboratory study was to evaluate the optimal treatment conditions in order to increase the decontamination efficiency of the pyrolysis technologies applied to oil contaminated soil, particularly for removal of pyrene from polluted soils.

Pyrene was used as an indicator in the laboratory experimental campaign because it represents one of the frequent PAHs, especially in PAH mixtures (according to ATSDR - Agency for Toxic Substances and Disease Registry), with important carcinogenic potential. Consequently, the experiments were conducted also to assess the influence of the thermal treatments operational conditions on removal of pyrene from contaminated soils.

## Experimental part

### Soils samples

In the present laboratory study two soils from the centre of Romania were analyzed. The first is historically contaminated with heavy metals (Pb, Cd, Ni, As, Zn, Cu, Fe, Mn, Cr, Co, Hg, As and Be) due to industrial activities

realized for almost 60 years and artificially polluted with oil (artificially contaminated soil samples). The second type of soil is a historically polluted due to the human activity related to the petroleum processing (naturally contaminated soil samples). The general parameters values for initial characterization of soils taken for experiments development are presented in table 2.

In terms of chemical composition, oil is a mixture of hydrocarbons with very complicated molecules of different sizes, starting from hydrocarbons with low molecular mass (as for example methane) up to very high molecular masses (> C<sub>40</sub>). Since oil composition varies from one naturally deposit to another, these two types of soils contaminated with petroleum products, had different PAHs content. Considering only the sum of 16 PAHs measured compounds (EPA 16 list of compounds), concerning the characterization of the PAHs content, after the analytical determination, for the PAHs content in the case of naturally contaminated soil samples it was established a percentage of 0.011% from total petroleum hydrocarbons content measured classically (gravimetric), while for the artificially contaminated soil of about 0.058%. In this way it is resulting that PAHs content is 5.3 times bigger for the second type of soil samples.

This kind of information is important to be mentioned if we are taking into consideration that the improving of the thermal treatment remediation efficiency to remove the polyaromatic compounds (especially focused on pyrene) from soils contaminated with petroleum products it has to cover different kind of contamination degrees.

### Pyrolysis reactor

Thermal treatments of the contaminated soils were performed adopting a laboratory scale experimental set-up. It is about a horizontal reactor NABERTHERM, type RO 60/750/13 (fig. 1) and allows reproducing different thermal treatments of solids (i.e. incineration, pyrolysis or gasification). In order to identify PAHs and pyrene concentration level from pyrolysis emissions, an isokinetic automatic portable sampling system ISOSTACK Basic HV has been attached.

The pyrolysis tubular reactor is external electrically heated and consists in a compact bench furnace, provided with a work tube made of Sillimantín 60. The active zone, the heated one, measure about 750 mm and the maximum process temperature can rise to approximately 1200°C. The device is equipped with a control pad that permits to set the process temperature, residence time and heating rate. The pyrolysis reactor is working in a discontinuously mode; as a consequence small batches (600g) of oil contaminated soil were introduced into the furnace in a crucible with tubular parallelepiped form of refractory steel W4541 (size: 100 cm long, 4 cm wide and 3 cm in height). The test samples were separately heated at different temperatures: 350, 400°C, 600°C and 650°C for 1 hour retention time. Through one inlet of the reactor a flow of nitrogen was continuously introduced in order to ensure the inert atmosphere.

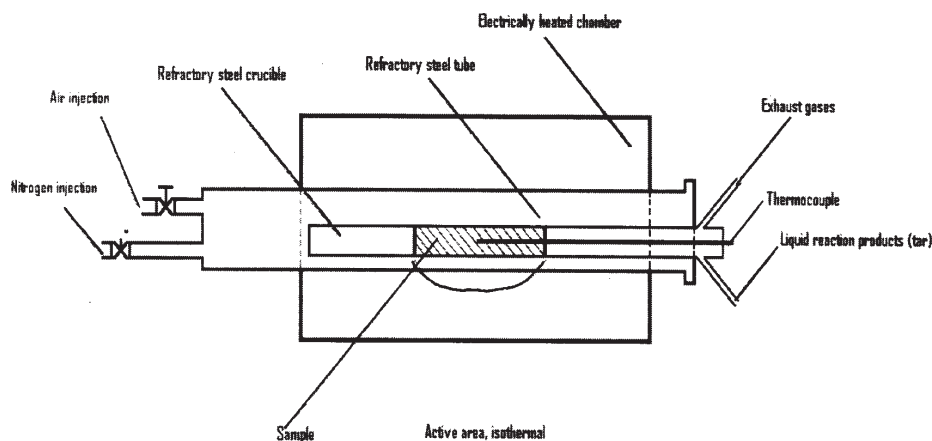


Fig. 1. Diagram of the pyrolysis tubular reactor

Process parameter	Value	Unit
Soil mass	600	g
Temperature	350 – 650	°C
Process time	1	h
Nitrogen flow	1	l/min

Table 3  
PYROLYSIS PROCESSES PARAMETERS

The following pyrolysis conditions have been applied for the laboratory scale experiments (table 3).

#### Methods and standards for sampling and analysis

Soil samples were taken according to 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.

Determination of the polycyclic aromatic hydrocarbons concentrations was performed according to the current standard methods in force (SR EN 14039:2005, EPA 8270:1998; EPA Method 3540:1996) applicable to both, soil and solid waste, considering ashes resulted from thermal treatment of contaminated soils as hazardous solid waste in terms of the environmental quality protection.

The solid soil samples were passed through a sieve of approximately 2 mm openings in thickness and an approximate 20 g portion was weighted if their humidity allowed. For not losing part of the semi-volatile compounds, if the samples had too much humidity, they were only weighted and mixed with sodium sulphate as sample drying agent. Sodium sulphate has the only role to reduce the humidity of the sample and does not interfere into the PAHs analysis.

An approximate 20 g portion of ash from pyrolysis sample of contaminated soil was sampled for PAHs content analysis

Emission samples were sampled using an isokinetic automatic portable sampling system of particulate emissions (ISO 9096, EN 13284-1, EN 1948-1) – Isostack Basic HV from Tecora, having heated inlet for emissions sampling, temperature measuring sensors and gas inlet flow and volume monitor module.

Particle and gas phase were iso-kinetically sampled on quartz fiber filters, respectively on polyurethane foam (PUF) (SR ISO 12884:2008, SR EN 15549:2009) trap with flow rates between 3.034 l/min and 3.224 L/min.

All samples, as initial contaminated soil, ashes resulted from pyrolysis experiments, quartz fiber filters and PUF after emission sampling, have been extracted with 250 mL of HPLC grade petroleum ether using 6 benches Soxhlet equipment (SR EN 14039:2005; US EPA 8270:1998; US EPA 3540:1996; SR ISO 12884:2008; SR EN 15549:2009). When analysing solid waste and soil/waste mixtures which

form emulsions, Soxhlet extraction is more reliable and advantageous technique in comparison with more rigorous solvent mixing extraction techniques.

The extract was concentrated to a low solvent volume using Heidolph rotary evaporator and eluted with hexane ( $C_6H_{14}$ ). After concentration step samples were clean-up (SR EN 14039:2005), if necessary, or were transferred to a capped and sealed vial for gas-chromatographic analysis and were analyzed by GCMS QP2010 Plus Shimadzu equipment. Separations were performed on a GC - QPLOT 5MS (cross-linked 5% phenyl-methyl-silicone) column (30.0 m x 0.25 mm i.d x 0.25 $\mu$ m). Helium with purity of 99.99995% has been used as carrier gas due to its highest sensitivity for detecting low concentrations.

PAHs were identified by a combination of a retention time and mass spectral match against the calibration standards [13, 14].

#### Legal normatives for compliance

For results discussion, important references have been taken into consideration; it is about: thresholds established for soil by *Order 756/1997* for approving the Rules on assessment of the environmental pollution, together with technical conditions for atmospheric protection of *Order 462/1993* (Annex 1 - General preventive rules limiting emissions of pollutants into the atmosphere), in relation to the incineration of waste (incineration of the polluted soil) and emissions limits from *Governmental Decision 128/2002* on the incineration of waste amended by *Government Decision 268/2005*, *Order No. 756/2004* approving the technical update on the incineration of waste and *Government Decision 427/2010*.

#### Results and discussions

The results obtained from non-oxidant thermal treatments refers to the concentration of the pyrene and total PAHs (all 16<sup>th</sup> analyzed compounds sum) from initial contaminated soils, pyrolysis ashes samples (decontaminated soil) and pyrolysis emissions. The values of the pyrene and total PAHs concentration determined in the initial contaminated soils samples and in the decontaminated soils samples, produced at different treatment temperatures, in comparison with legal admissible limit as stated in *Order 756/1997* are presented in table 4.

Type of sample	Sum of all 16 PAHs concentrations (mg/kg dry weight)	Pyrene concentration (mg/kg dry weight)
<b>Naturally contaminated soil thermal treatment experiment</b>		
Naturally contaminated soil	0,989	0,089
Ash resulted from pyrolysis at 350 °C	0,843	0,042
Ash resulted from pyrolysis at 650 °C	0,043	0,002
<b>Artificially contaminated soil thermal treatment experiment</b>		
Artificially contaminated soil	8,329	0,155
Ash resulted from pyrolysis at 400 °C	0,043	0,001
Ash resulted from pyrolysis at 600 °C	0,037	0,001
<b>Admissible limits values for soil establish by Order 756/1997</b>		
Normal	<0,10	<0,50
Alert threshold for sensitive areas	7.5	5
Alert threshold for less sensitive areas	25	10
Intervention threshold for sensitive areas	15	10
Intervention threshold for less sensitive areas	150	100

Comparing with allowed limits from enforce Romanian legislation, the values obtained from analyses of soil contaminated samples and ashes from pyrolysis experiments indicate:

-the concentration values of total PAHs from soil are above the normal concentration limit, but less than alert threshold limit for sensitive areas, established by legislation, for both types of contaminated soil samples;

-the concentration values of pyrene in soil are under the normal value established by legislation, for both types of contaminated soil samples;

-after pyrolysis process, all measured concentration values, of total PAHs, as well as of pyrene compound, are under the normal value established by Order 756/1997 for soils, except only the concentration level of total PAHs from the ash generated by the pyrolysis of the naturally contaminated soil at 350°C, that exceeds the normal concentration limit of 0.10 mg/kg<sub>dw</sub>.

#### The influence of the process temperature on pollutant compounds removal

Results indicate considerably decreasing of total PAHs concentration from ashes with temperature enhance, and a much slower increasing rate for pyrene compound. In this case, results showed that for naturally contaminated soil, the rising of the treatment temperature conducted to an increasing of the process efficiency of about 81%, while for the artificially contaminated soil the efficiency remained the same (about 99%) for both temperatures.

Figures 2 and 3 reflect very clear that optimal pyrolysis temperature, for a good removal of pyrene and total PAHs from contaminated soil, is above 400°C.

Figures 4 and 5 suggest the following conclusion: at the beginning stage, as a normal physical reaction, the removal of pyrene and total PAHs from soil is due to a primarily, rapid, very strong volatilization of the compounds, in both cases, for all considered experimental temperatures. As suggested from both experimental results, the optimal removal efficiency of the pyrolysis technology is around of 400°C in case of artificially soil thermal treatment, and respectively 600°C for the naturally

**Table 4**  
CONCENTRATION LEVELS OF TOTAL PAHs AND PYRENE IN SOIL AND ASHES GENERATED BY THE PYROLYSIS EXPERIMENTS IN COMPARISON WITH LEGAL ADMISSIBLE LIMIT AS STATED IN ORDER 756/1997

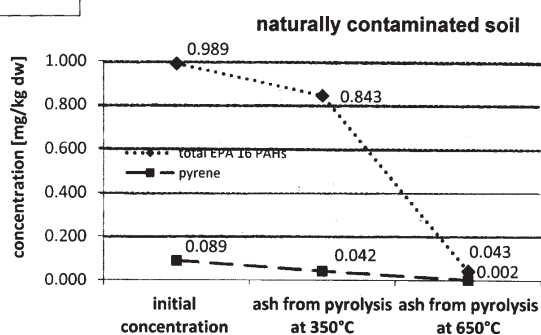


Fig. 2. Concentration of pyrene and total PAHs from naturally contaminated soil and from pyrolysis ashes

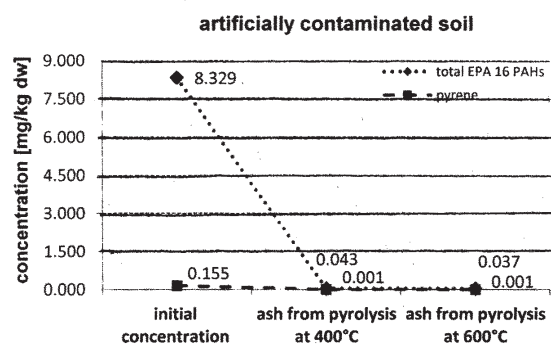


Fig. 3. Concentration of pyrene and total PAHs from artificially contaminated soil and from pyrolysis ashes

contaminated soil remediation, taking into consideration the cost-efficiency analyses.

#### The influence of the soil chemical composition, of ashes and gaseous emissions

Results indicate that the removal of pyrene and total PAHs compounds depends on contamination type and on degree of soil contamination. For example, in case of the artificially contaminated soil, the initial content of total PAHs from soil was 8.4 times higher than the concentration level from the naturally contaminated soil, and the concentration of pyrene was 1.7 times bigger (table 4).

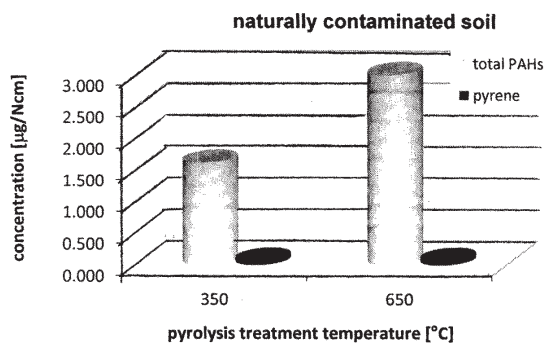


Fig. 4. Concentration level of pyrene and total PAHs from pyrolysis emissions function of the treatment temperature – naturally contaminated soil

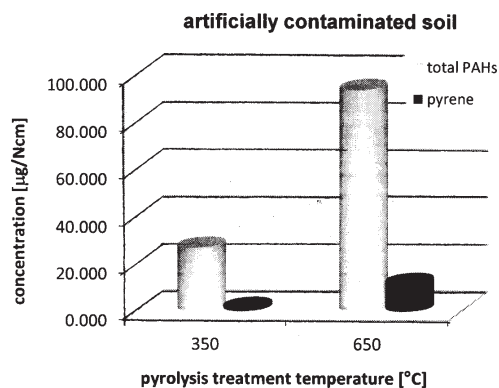


Fig. 5. Concentration level of pyrene and total PAHs from pyrolysis emissions function of the treatment temperature artificially contaminated soil

Type of sample	Sum of all 16 PAHs concentrations (mg/kg dry weight)	Pyrene concentration (mg/kg dry weight)
<b>Thermal treatment of the naturally contaminated soil</b>		
Emissions from pyrolysis at 350 °C	1.613	0.060
Emissions from pyrolysis at 650 °C	3.016	0.067
<b>Thermal treatment of the artificially contaminated soil</b>		
Emissions from pyrolysis at 400 °C	27.055	1.344
Emissions from pyrolysis at 600 °C	93.977	11.778
<b>Emission limits - Order 462/1993</b>	<i>Total PAH</i> ≤ 150 mg/m <sup>3</sup>	pyrene = 100 µg/m <sup>3</sup>
<b>Reference values from literature</b>	<i>Total PAH</i> ≤ 10 µg/m <sup>3</sup>	pyrene = 0.1 µg/m <sup>3</sup>
G.D. 128/2002; G.D. 268/2005 and G.D. 427/2010 don't specified any emission limits		

**Table 5**  
AVERAGE CONCENTRATION LEVELS OF TOTAL PAHS AND PYRENE IN EMISSIONS SAMPLES FROM PYROLYSIS EXPERIMENTS (µg/N m<sup>3</sup>)

Emission samples were kept iso-kinetically as was described in the previous chapter of this paper (ISO 9096:2003, EN 13284-1:2002, EN 1948-1) using Isostack Basic HV equipment. The system automatically measured the effluent flow rate and registered the gases temperature, the pressure and total sampled volume. Sampling time has been correlated with sampling flow and, in order to assure the representative recommended sample volume, having in mind that the volatilization and degradation processes of PAHs have different rates and the emission gases composition varies in time during the pyrolysis procedure. Sampled volume, normalized under standard conditions (20° C temperature and 1 atm pressure), was used to compute the pollutant concentration level as a ratio from the total amount captured during the sampling and measured by GC technique and total normal sampled volume of emission, according to standards (SR ISO 12884:2008, SR EN 15549: 2009). To confirm the accuracy of the emission values reported in this work, an average over few replicate sampling lines has been considered. The pollutants emission average concentrations, expressed in µg/N m<sup>3</sup>, as they resulted from experiments, are presented in the table 5 and are compared to the legislative stipulations (Order 462/1995).

Computing, in total emission (meaning PUF and PF emissions; table 5), the percentage of pyrene concentration against the total PAHs concentration it might be observed that by increasing the temperature from 350 to 650°C the percentage of pyrene in the emissions decrease from 3.72 to 2.22% for the naturally contaminated soil pyrolysis.

By contrary, in case of the pyrolysis treatment applied to the artificially contaminated soil, the increasing of the process temperature from 400 to 600°C had led to the rising of the pyrene percentage in the emissions from an initial value of

4.97 to 12.53%. Since the temperature ranges are relatively similar in these two experimental studies, this obviously suggests that the difference in evolution is given by the difference of initial type and level of contamination.

In case of the artificially contaminated soil, the composition of oil mixture contains other higher amounts of aromatic compounds, which degrade faster and easier than pyrene, finally the level for total PAHs decreasing by degradation, and removal also, from emissions, quicker than pyrene, which persistency and resistance to degradation is well known.

Less removal of pyrene compound from contaminated soils it should be correlated with the sequential degradation of larger molecules of PAH compounds (e.g., benzo[a]pyrene (C<sub>20</sub>H<sub>12</sub>), benzo[ghi]perylene (C<sub>22</sub>H<sub>12</sub>), indeno(1,2,3-cd)pyrene (C<sub>22</sub>H<sub>12</sub>), etc.), with known fragmentation compounds such as triphenylene (C<sub>18</sub>H<sub>12</sub>), cyclopenta[hi]acephenanthrylenes (C<sub>18</sub>H<sub>10</sub>) and cyclopenta[cd]pyrene (C<sub>18</sub>H<sub>10</sub>)[15], and with generation of additional by-product.

Comparing the emissions values resulted from the experiments with en force Romanian legislative limits and reference values from specific literature, it might be concluded that all measured values from experiments are far under limits established by Order 462/1993, under the indicative values from literature for naturally contaminated soil experiments and far beyond for artificially polluted soil experiments (10 times for total PAHs and 100 times for pyrene as a comparison with value for pyrene). Additionally, it must be also said that samples from emissions were collected before the flue gas cleaning system.

## Conclusions

This research targets only the removal of above mentioned sixteen polyaromatic hydrocarbon compounds by using the pyrolysis as thermal treatment for soil decontamination.

Although, other compounds could result due to the subsequent fragmentation of these polyaromatic hydrocarbons, this is beyond the aim of the present paper.

The efficiency in removal of pyrene and of all the 16 PAHs compounds from contaminated soils with petroleum products is rising with the increasing of the pyrolysis temperature.

The experimental results reveal a lower degradation rate for pyrene compound in contrast with total PAHs, depending on initial mixture composition of the petroleum products from contaminated soil and the degradation of larger molecules compounds.

As suggested from the above experimental results and considering the economical perspective concerning the reduction of energy consumption in thermal treatment, we conclude that the optimal temperature of the pyrolysis processes in order to attend maximum efficiency for removing the pyrene and PAHs from the artificially contaminated soil is around 400°C and from the naturally polluted soil is about 650°C.

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