REDUCING CANCER RISK FROM ENVIRONMENTAL EXPOSURE TO PAHs THROUGH THE PYROLYSIS TREATMENT OF CRUDE OIL CONTAMINATED SOIL

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Contaminated soils with crude oil are a global concern as this type of pollution has harmful effects on human's health and environment. In the framework of the current research work, human health risk associated with exposure to soil contaminated with PAHs is assessed. The results concerning the human health risk from the investigated site indicated an unacceptable risk for population and a soil remediation solution is required. The pyrolysis treatment it has been chosen for its advantages, and after applying the non-oxidant process, the carcinogenic risk is decreasing considerable. Furthermore, the treated soil treated could be reintroduced in natural circuit.

Keywords: contaminated soil, Polycyclic Aromatic Hydrocarbons, pyrolysis, carcinogenic risks, organic contaminants.

1. Introduction

The environment pollution involves the pollution of soil, air, water surface and groundwater. The contamination of one of these ecosystems can affect the others. Soil is an important life environment for microorganisms, plants, or for animals. Soil pollution could lead to the damage or to the destruction of them and can affect the health of terrestrial animals or humans [1], [2], [3].

Through the anthropogenic activities which are the most damaging causes of soil pollution it can be remembered the agricultural practices (the use of pesticides, insecticides, fertilizers, and herbicides), industrial activities, urbanization and other activities that are generating waste or sewage sludge [4],

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[5]. Soil pollution with petroleum products is resulting after industrial activities of drilling, extraction, transport, and processing of crude oil. The main sources of contamination with crude oil are oil spills and oil industry. Over time, there has been more oil spills in countries as United States of America, Kuwait, Iran, Mexico, Russia, etc. [6].

Contaminants as Total Petroleum Hydrocarbons (volatile and semi-volatile organic compounds) and Heavy Metals (Arsenic, Cadmium, Chromium, Nickel, etc.) are the contaminants of concern related to soil contaminated with crude oil. From the Total Petroleum Hydrocarbons group of compounds, contaminants of interest from the point of view of environmental pollution are: Monocyclic Aromatic Hydrocarbons (BTEX - benzene, toluene, ethylbenzene, and xylene) and Polycyclic Aromatic Hydrocarbons (PAHs). These are known as contaminants of concern, because of their toxic's characteristics [7].

Soil polluted with crude oil and petroleum products could lead to harmful effects on the environment (underground or surface waters, atmosphere, and biosphere) and human health. Humans can be affected by the contaminants from polluted soil directly (dermal contact, accidentally soil ingestion or inhalation) or indirectly (consumption of contaminated vegetables or animal products, recreational activities, etc.) [8], [9], [10]. These effects could be reduced or eliminated through application of the appropriate soil remediation techniques. The contaminated soil can be treated by using different processes as thermal (e.g. pyrolysis and incineration) [11], [12], [13] and biological remediation (phytoremediation and bioremediation) [14], [15], 16].

As pyrolysis has shown efficiency in removing organic contaminants in soils and oily sludges [17] the present paper is illustrating the remediation degree related to polycyclic aromatic hydrocarbons (PAHs) from crude oil contaminated soils using one of the existing thermal methods. Specifically, the chosen method is pyrolysis, which presumes a chemical decomposition at high temperature in oxygen absence [18].

By the thermal treatment of the contaminated soil is resulting a remediated soil with a high content of carbon, liquid matter (liquid matters) and different emissions (Fig. 1.) [19].

In current work, the authors focused on the advantages of using pyrolysis to treat the oil contaminated soils. Particularly, the attention was paid to apply pyrolysis as a treatment for contaminated soil in order to remove PAHs. Other important aspects of the pyrolysis process are the performing conditions, such as temperature. In order to reintroduce the soil in the natural circuit, its chemical and bio-physical properties must be maintained, and this it is not possible in case of higher temperatures as those used across the combustion process (incineration).

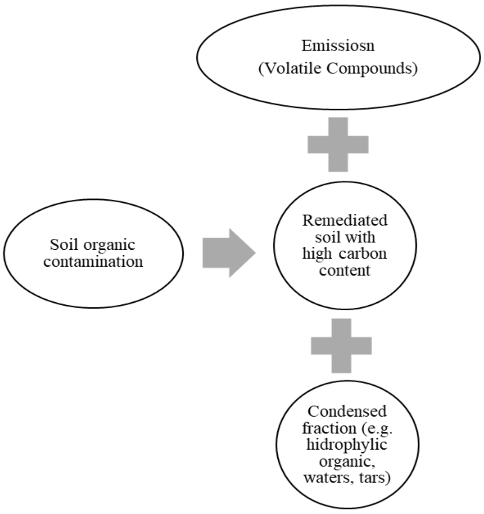

Fig. 1. Pyrolysis process [19]

In order to evaluate the remediation degree, different process temperatures were tested (400 °C, 600 °C and 800 °C) as well as different retention times (30 min and 60 min) [20].

2. Materials and Methods

2.1. Soil Sampling

In order to develop the experimental work, the soil samples were collected from a bioremediation platform, from Prahova County, Romania according to the Ministerial Order No. 184 from 21 September 1997 for the approval of the Environmental Balance Sheet Procedure [21]. The contaminated soil was placed on a concrete surface before of being decontaminated using the most common remediation technique in Romania (bioremediation). The number of sampling points were established taking into consideration the national regulation in force. According to the previously mentioned Ministerial Order [21] a minimum number of sampling points for an of 1000 m^2 is equal with four. In the present work, five soil samples were collected from an area of 1000 m^2. For soil sampling, basic soil sampling tools as soil probes were used. Subsequently, samples were transferred to a suitable container in order to be sent to an analytical accredited laboratory.

2.2. Investigation methods

The methods of investigation designated in the framework of the present scientific study were divided into two important phases: (1) the first step was dedicated to the chemical analysis of contaminated soil, according to the Romanian regulation in force and actual national and international analytical standards, while the second phase (2) consisted in the evaluation of reducing cancer risk from environmental exposure to PAHs through the pyrolysis treatment of crude oil contaminated soil. Both steps are decision phases for human health risk assessment and for application of remediation treatment to soil [22].

After the chemical analysis of contaminated soil with crude oil were performed, in soil were identified inorganic chemicals (heavy metals) and organic compounds (BTEX – benzene, toluene, ethylbenzene, and xylene; PAHs – Polycyclic Aromatic Hydrocarbons). In the framework of the present work the attention is focused on PAHs.

In order to do an evaluation of harmful effects on different environments or on human's health, the first step is to compare the concentration levels of analyzed contaminants with legal thresholds from the national regulation (according to Ministerial Order 756/1997 [23]), that are divided in: normal values, warning (alert) levels, and intervention levels. These values are specific for each contaminant and they are different for each considered scenario: industrial, residential, recreational, commercial, agricultural.

In the framework of the present study, the investigated scenario is the industrial one. The industrial scenario involves a less sensible use of soil and the exposure pathways considered for the human health risk assessment because of human exposure to the contaminated site are accidentally soil ingestion and dermal contact (specific to workers) [24]. The investigated compounds are the contaminants of concern, which are responsible for cancer occurrence to humans, according to The United States Environmental Protection Agency (U.S. EPA) and World Health Organization (WHO) [25], [26]. A special attention was paid to Benzo[a]pyrene, which is considered the most toxic compounds from PAHs group [27].

3. Results and Discussions

The decision of soil remediation was considered because of soil pollution level according to the legal values of Romanian regulation and because of the achieved the results in terms of carcinogenic risk for human health estimated for the investigated site. In order to be able of estimating human health risks, a software tool named REMPET was used. REMPET was developed in the framework of a PhD thesis across a research project financed by the National Authority for Scientific research (ANCS) Romania [28]. The main information concerning the software structure is designed in Fig. 2.

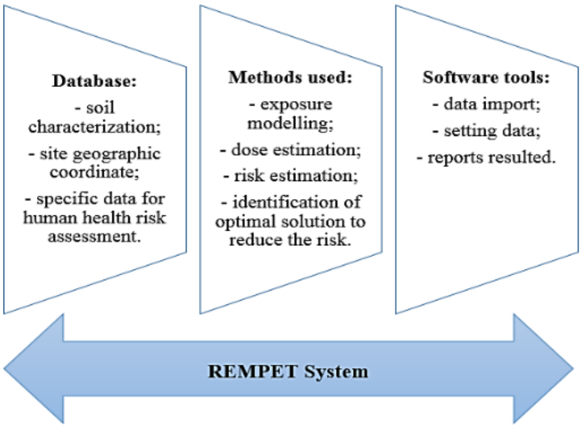

Fig. 2. REMPET software tool

Therefore, REMPET is a decision-making tool that provides rational and scientifically feasible solutions for the optimal management of contaminated sites with petroleum products, having as criteria for selecting the optimal remediation method following the next aspects: health risk assessment; cost analysis for proposed remediation technologies for decontamination; identifying the optimal solution soil remediation (between the tested solutions); land use planning for certain uses.

3.1. Regulation report

After the analytical phase, the chemical concentration of each contaminant from soil contaminated with crude oil was identified. The achieved results are presented in Table 1.

Table 1

Initial concentrations of PAHs

Chemical	Chemical concentration [mg/kg$_{d.m.}$]
Acenapthene	0.240
Anthracene	0.002
Benzo[a]anthracene	0.172
Benzo[b]fluoranthene	0.172
Benzo[k]fluoranthene	0.116
Benzo[g,h,i]perylene	0.030
Benzo[a]pyrene	0.115
Crysene	0.123
Dibenzo[a,h]anthracene	0.176
Fluoranthene	0.010
Fluorene	0.023
Indeno[1,2,3-c,d]pyrene	0.098

Chemical	Chemical concentration [mg/kg$_{d.m.}$]
Naphtalene	0.033
Phenanthrene	0.011
Pyrene	0.070
Total PAHs	**1.239**

Using REMPET, the concentration levels of each contaminant of concern is easily compared with legal thresholds from the Romanian regulation in force (Table 2).

Table 2

Measured concentration and legal values for PAHs according to Romanian regulation

Chemical	Normal Value	Warning level -Less Sensible (mg/kg dm)	Intervention level –Less Sensible (mg/kg dm)	Chemical Concentration
Anthracene	0.05	10	100	0.0020
Benz[a]Anthracene	0.02	5	50	0.1720
Benzo[a]pyrene	0.02	5	10	0.1150
Benzo[b]fluoranthrene	0.02	5	50	0.1720
Benzo[g,h,i]fluoranthrene	0.02	5	50	0.0000
Benzo[k]fluoranthrene	0.02	5	50	0.1160
Benzoperilen	0.02	10	100	0.0300
Chrysen	0.02	5	50	0.1230
Fluoranthene	0.02	10	100	0.0100
Indeno [1,2,3-cd] pyrene	0.02	5	50	0.0980
Phenanthrene	0.05	5	50	0.1100
ΣPAHs	0.1	7.5	150	0.948

From Table 2 it can be noticed that the values for warning or for intervention level are not exceeded.

From Fig. 3 the results show that the normal values are higher than initial chemical concentrations measured in analyzed soil, but taking in account that PAHs, and especially Benzo[a]pyrene are very toxic for humans it was decided to proceed to the next step and to estimate the cancer risk:

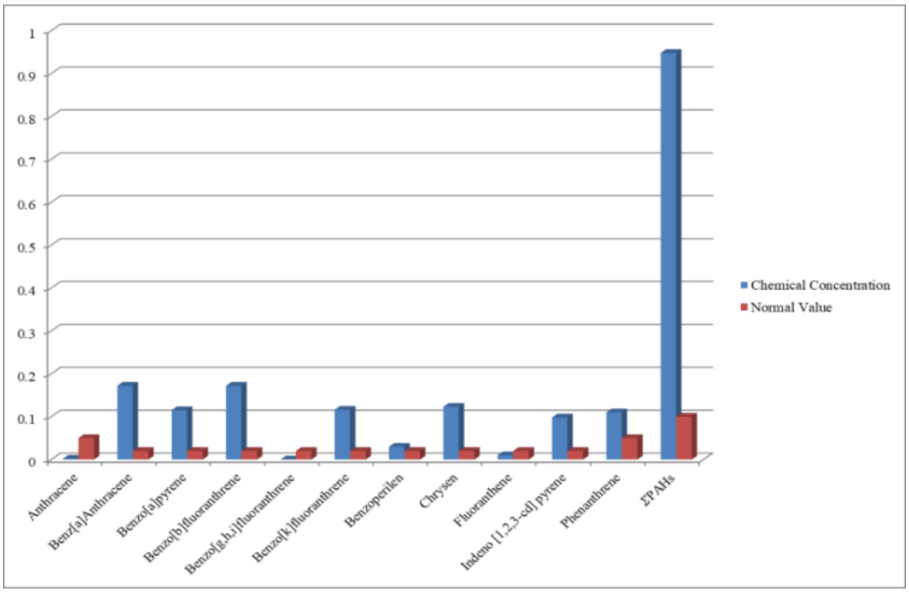

Fig. 3. Comparison between initial concentrations and normal value

3.2. Human health risk assessment

Human health risk assessment is a complex process characterized by four important steps. The four steps are: Hazard Identification, Dose-Response Assessment, Exposure Assessment and Risk Characterization [29]. Within these steps, the contaminants of concerns are identified, the dose is calculated, according to each exposure pathway identified for exposed population, the risk is estimated, and the optimal solution for remediation is found. The dose calculation involves the establishment of hazardous contaminants, taking into account the legislation thresholds, and furthermore they help to risks determination. In order to determine if the risks are non-carcinogenic or carcinogenic for human health, the risks are estimated for each contaminant identified in polluted soil and for each exposure pathway (ingestion, dermal contact, or inhalation) characteristic to the contaminants found in soil [30].

The carcinogenic risk was estimated for the *industrial scenario*. The individual risks for each chemical and for ∑PAHs were estimated, and they were compared with the acceptable risk (Fig. 4.). The acceptable risk is the probability of cancer occurrence, in one million people (10^{-6}) according to WHO [31] and between 10^{-6} and 10^{-4} according to U.S. EPA [32].

If the results for estimated risk exceed the acceptable risk, then it be decided what remediation treatment to apply for soil remediation.

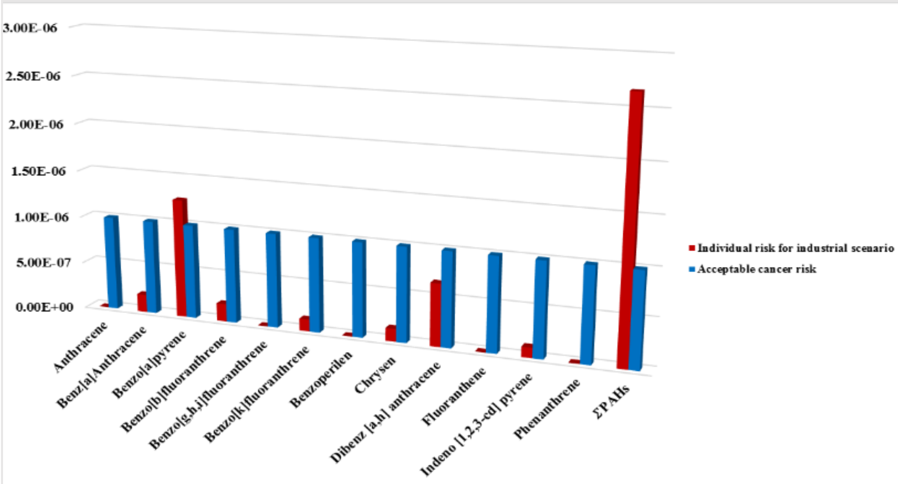

Fig. 4. The carcinogenic risk for industrial scenario

In case of industrial scenario, the investigated soil is human carcinogenic for Benzo[a]pyrene ($1.26x10^{-6}$) and ∑PAHs ($2.67x10^{-6}$). In order to decrease the carcinogenic risks when population is exposed to the investigated contaminated soil, it was decided to apply a remediation treatment.

3.3. Non-oxidative remediation treatment

The achieved results indicated that risk results are pessimistic for human's health and consequently, a treatment method should be applied to the contaminated soil. The remediation treatment applied in the current experimental work and research study was pyrolysis. It was chosen this method of remediation, because the level of pollution with PAHs of soil is not so high, and the purpose is that the soil could be reintroduced in natural cycle of nature [33]. In order to evaluate the pyrolysis efficiency and soil behavior before and after the proposed remediation strategy is applied, initial characteristics of contaminated soil were analyzed (Table 3).

Table 3

Characteristic of contaminated soil

Characteristic	Measure Unit	Value	Method
pH (in aqueous extract 1:5)	-	8.2	SR-ISO 10390:2015
K(in aqueous extract 1:5)	$mg/kg_{d.m.}$	5.0	ISO 9964-1:1993
P(in aqueous extract 1:5)	$mg/kg_{d.m.}$	29.79	STAS 7184/7-87
Cr VII(in aqueous extract 1:5)	$mg/kg_{d.m.}$	<0.1	EPA 7196A:1992
Total Nitrogen	$mg/kg_{d.m.}$	1.8	SR ISO 11261:2000
K	$mg/kg_{d.m.}$	9045.69	EPA 7000A:1992
Total Phosphorus	$mg/kg_{d.m.}$	293.64	STAS 7184/14-79
Total Organic Carbon	$\%_{d.m.}$	4.49	STAS 7184/21-82
Humus	$\%_{d.m.}$	7.74	STAS 7184/14-79
Chlorides	$mg/kg_{d.m.}$	14.04	STAS 7184/7-87

The pyrolysis treatment was performed using a tubular fixed bad reactor NABERTHERM (type RO 60/750/13), located in Renewable Energy Sources Laboratory, Faculty of Power Engineering, University POLITEHNICA of Bucharest (Fig. 5.)

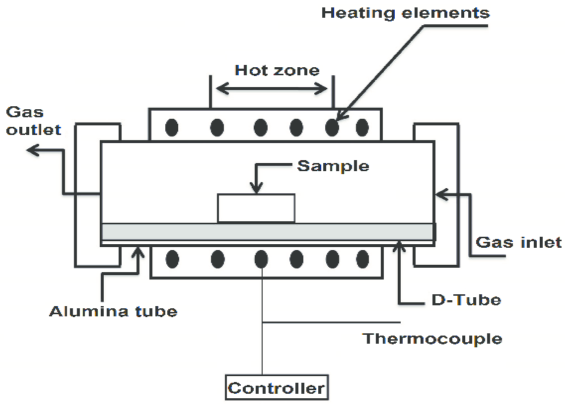

Fig. 5. Diagram of tubular electric furnace [34]

The end products of pyrolysis process are: solids (coke), liquids (tar, water and heavy carbons), and gaseous (water vapor, carbon dioxide, carbon monoxide, methane, benzene, etc. [35].

The pyrolysis process was applied as a solution for remediation of petroleum products contaminated soil. In order to study the efficiency, the thermal treatment was performed to different conditions of pyrolysis process (Table 4).

Table 4

Pyrolysis operating conditions

Process parameter	Unit	Value		
Temperature	°C	400	600	800
Duration of the experiment	h	4	4	2
Time of retention	min	60	30	30
Mass flow rate	g	600	600	600

3.3.1. Evaluation of the remediation degree through the pyrolysis treatment

The solid by-product resulted after thermal treatment, was analyzed in a specialized accredited laboratory. Among these results are the characteristics of soil after the pyrolysis treatment and the chemical concentrations for each analyzed compound of PAHs group.

In the next table (Table 5) are presented the characteristics of treated soil at 400 °C, 600 °C, and 800 °C.

Table 5

Characteristic of contaminated soil

Characteristic	Measure Unit	Value 400 °C	Value 600 °C	Value 800 °C
pH (in aqueous extract 1:5)	-	7.47	7.44	10.82
K (in aqueous extract 1:5)	$mg/kg_{d.m.}$	14.86	17.23	36.13
P (in aqueous extract 1:5)	$mg/kg_{d.m.}$	1.06	1.43	0.574
Total Nitrogen	$mg/kg_{d.m.}$	1.05	0.976	0.56
K	$mg/kg_{d.m.}$	9816.51	9754.01	9909.05
Total Phosphorus	$mg/kg_{d.m.}$	299.8	354.99	327.95
Total Organic Carbon	$\%_{d.m.}$	1.01	0.961	0.78
Humus	$\%_{d.m.}$	1.74	1.66	1.34
Chlorides	$mg/kg_{d.m.}$	97.1	43.28	42.09

For chemical concentrations the results were performed according to current standard in force SR ISO 13877:1999 [36]. The chemical concentrations for all contaminants of concern analyzed are presented in next table (Table 6).

Table 6

The PAHs compounds from coke

Chemical	Chemical concentration – pyrolysis 400 °C [$mg/kg_{d.m.}$]	Chemical concentration – pyrolysis 600 °C [$mg/kg_{d.m.}$]	Chemical concentration – pyrolysis 800 °C [$mg/kg_{d.m.}$]
Acenapthene	0.001	0.0008	0.0005
Anthracene	0.003	0.002	0.001
Benzo[a]anthracene	0.003	0.001	0.0008
Benzo[b]fluoranthene	0.001	0.0008	0.0006
Benzo[k]fluoranthene	0.001	0.0008	0.0006
Benzo[g,h,i]perylene	0.001	0.0008	0.0006
Benzo[a]pyrene	0.001	0.0008	0.0006
Crysene	0.001	0.003	0.002
Dibenzo[a,h]anthracene	0.001	0.0008	0.0006
Fluoranthene	0.001	0.0008	0.0006
Fluorene	0.003	0.003	0.002
Indeno[1,2,3-c,d]pyrene	0.001	0.0008	0.0006
Naphtalene	0.022	0.022	0.021
Phenanthrene	0.004	0.003	0.004
Pyrene	0.002	0.001	0.001

The main purpose of applying the thermal treatment is that the resulted solid material could be reintroduced in natural circuit. Thus, they were considered three scenarios to assess human health risk, in order to evaluate the most appropriate process parameters associated with the risk potential (Table 7).

Table 7

Scenarios proposed

Scenario	Pyrolysis conditions	∑PAHs concentration	Use of soil
Scenario 1	400 °C, 60 min	0.0460	Industrial use
Scenario 2	600 °C, 30 min	0.0414	Industrial use
Scenario 3	800 °C, 30 min	0.0365	Industrial use

To evaluate the efficiency of the thermal remediation treatment applied to contaminated soil, the risk was estimated, for each temperature (Fig. 5.).

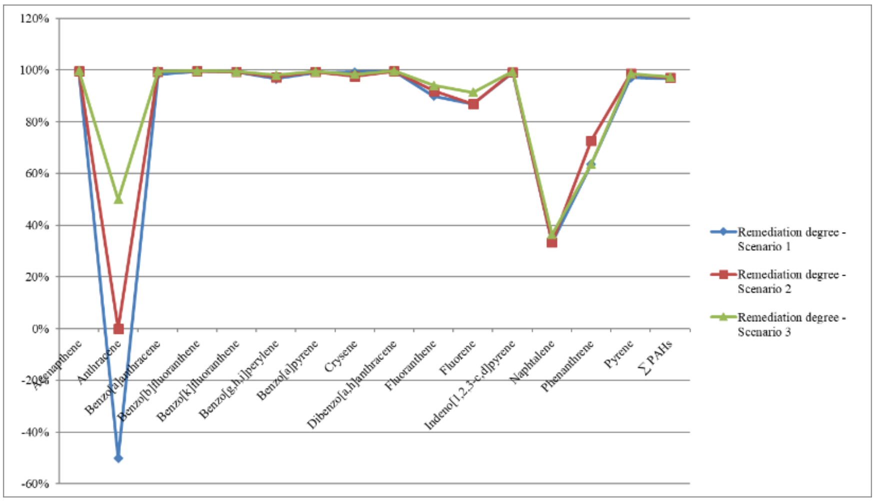

Fig. 5. The remediation degree according to the pyrolysis process at 400 °C, 600 °C, and 800 °C

The risk was calculated for ∑PAHs (sum of the individual risks of each compound of PAHs group found in contaminated soil) (Fig. 6.).

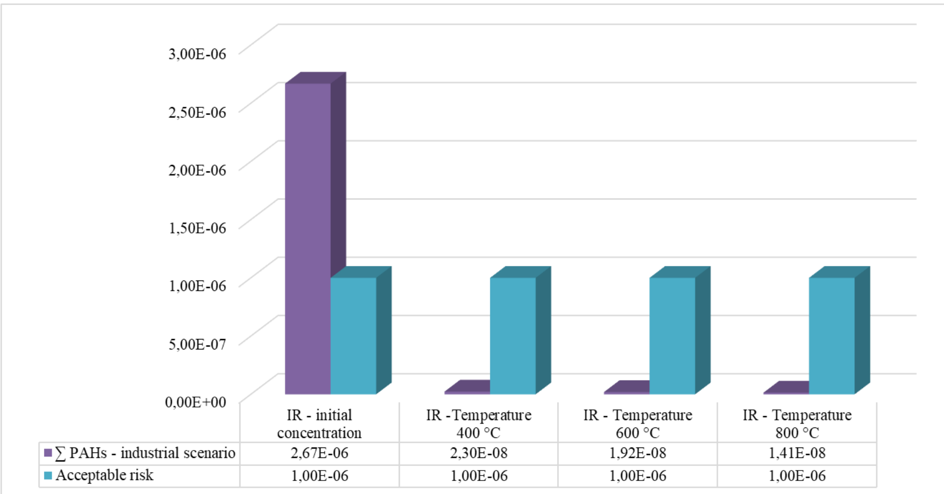

Fig. 6. Individual risk for ∑PAHs – initial concentration, and pyrolysis at 400°C, 600°C, 800°C

From Fig. 6. it can be noticed that the risk is decreasing considerable when the thermal treatment is applied. If the estimated risk for ΣPAHs initial concentrations was $6.12x10^{-3}$ for industrial use, while after the thermal treatment was applied to soil, the risks decreased to $2.30x10^{-8}$, $1.92x10^{-8}$ and respectively $1.41x10^{-8}$, according to the considered temperature. From the individual risk results estimated for each scenario, it can be observed that de risk become non-carcinogenic for human's health in case of Scenario 1 ($2.30x10^{-8} < 1x10^{-6}$).

4. Conclusions

The experimental results revealed that PAHs concentrations in soil can decreased significantly and the carcinogenic risk can be considerable reduced, when the pyrolysis process is applied to contaminated soils with petroleum products. According to the soil destination after the thermal method is applied to contaminated soil, the risk on human's health could be non-carcinogenic. According to the results, if the use of soil after the remediation treatment is the industrial one, the human's exposure to soil is harmless for health. The results for individual risk obtained using the soft REMPET shows that the exposure to contaminated soil with crude oil will be non-carcinogenic after pyrolysis at 400 °C. This remediation treatment is efficient for soil polluted with oil, because the costs of it are not so high, and the carcinogenic risk for humans could be minimized or eliminated. Disadvantages for this remediation treatment could be its application on large installations, because of the soil transport issues, and the soil bio-chemical properties damage, at high temperatures.

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