

Adsorption and Anoxic Degradation of Typical PAHs in Bohai Coastal Sediments

Shuaijie Wang^{*a}, Lu Qin^a, Ying Liu^b, Yao Guan^a, XiaoShan Tan^a

^aSchool of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

^bChina Electronics Engineering Design Institute, Beijing 100142, China
wangshuaijie@ysu.edu.cn

This paper aims to disclose the adsorption and anoxic degradation processes of three typical polycyclic aromatic hydrocarbons (PAHs) in the coastal sediments of China's Bohai Sea region. The PAHs are naphthalene (Nap), phenanthrene (Phe) and pyrene (Pyr). Several sediments samples were collected from Qinhuangdao Port, and subjected to adsorption and biodegradation experiments. Then, pseudo-first-order and pseudo-second-order kinetic models were tested to explain the kinetics of liquid-solid phase adsorption systems. It is discovered that the adsorption of the three PAHs on the coastal sediments matched pseudo-second-order kinetics, revealing that adsorption processes were essentially chemical reactions. In terms of equilibrium adsorption capacity, the three PAHs are ranked as Pyr>Phe>Nap. Next, Freundlich and Langmuir models were employed to fit the experimental data. The fitting results show that the adsorption of Nap, Phe and Pyr on the coastal sediments can be explained as mono-molecular layer adsorption. All the adsorptions of Nap, Phe and Pyr were exothermic reactions. In the anoxic sediments, 93.2% of Nap was removed after 30h, 96.6% of Phe was removed after 7d, and 98.1% of Pyr was removed after 42d. The detected metabolites of Nap were [4,4-dimethyl-2-cyclohexene-1-ol], [1-carboxyl,2-hydroxy, 4-methyl-cyclohexane], the metabolites of Phe were [3-ethoxy ethyl benzoate], [Phthalate (2-methyl propyl) ester] and the metabolites of Pyr were [2-methyl succinic acid, double (2-methyl propyl) ester], [Phthalate (2-methyl propyl) ester], [Phthalic acid butyl ester, 14 alkyl ester]. The findings shed new light on the research of PAHs adsorption and anoxic degradation in coastal sediments.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are toxic, potentially carcinogenic and mutagenic. Sixteen PAHs compounds have been included in the European Union and US EPA priority pollutant lists (Chang et al., 2002; Lu et al., 2012; Quan et al., 2009). In recent years, the PAHs pollution has spread to the marine environment due to damaging human activities like oil spill, incomplete combustion of fossil fuel, etc. (Mirandola and Lorenzini, 2016). The highly hydrophobic PAHs could be strongly adsorbed on the organic matters in sediment, resulting in massive accumulation in coastal areas (Chen and Chen, 2011; Wang et al., 2012). The PAHs in the coastal sediments poses a direct risk to organisms and an indirect risk to humans (Haritash and Kaushik, 2009). Therefore, it is highly necessary to remove the PAHs from costal sediments and minimize their adverse effects. Among the various removal techniques, bioremediation has gained prominence in recent years (Chang et al., 2002; Fuchedzhieva et al., 2008; Haritash and Kaushik, 2009). During the bioremediation of PAHs, the catabolic activity of microbes mainly uses oxygen as terminal electron acceptors. However, the polluted sediments are mostly anoxic due to the limited amount of oxygen in subsurface sediments (Dou et al., 2009). Therefore, the predominant metabolic mode of PAHs removal from costal sediments lies in anoxic biodegradation.

In China, the Bohai Sea region is one of the regions most heavily polluted by the PAHs. Lin et al. (2005) investigated the spatial distribution of the PAHs in surface sediments of the Bohai Sea region, and discovered that the highest concentration of total PAHs was located in the coastal area at Qinhuangdao with a detection rate of 43 %. The results show that PAHs have presented a high ecological risk to the local area. In light of the above, this paper explores the adsorption and anoxic degradation behaviour of the typical PAHs in Bohai

coastal sediments. The samples were collected from Qinhuangdao Harbour. The typical PAHs include naphthalene (Nap), phenanthrene (Phe) and pyrene (Pyr). The purpose is to lay a scientific basis for artificial restoration of Bohai coastal sediments.

2. Materials and methods

2.1 Chemicals

The Nap (purity=99%), Phe (purity=99%) and Pyr (purity=99%) were supplied by Anshan Tianchang Chemical Company. The dichloromethane (analytical grade) was purchased from Qinhuangdao Chemical Reagent Factory.

2.2 Sampling

The samples of coastal water and sediments were collected from Qinhuangdao Harbour, China's Hebei Province. The sampling location for sediments was 10~20cm deeper than the surface sediment. The samples were sieved to remove plants and other debris, and stored at 4°C for further study. The fresh sediment contained 8.73% of water. For the coastal water samples, the salinity was 31‰, and the pH values were 7.4~8.2. The contents of Nap, Phe and Pyr in the sediment samples were 33.4µg/kg, 118.2µg/kg and 165.9µg/kg, respectively.

2.3 Adsorption experiments

Adsorption kinetics:

100µg Nap was added to a 50mL conical flask, which contained 10g sterilized sediment and 10mL deionized water. Then, the flask was shaken on an oscillator at 25°C and 175rpm. Finally, the residues of the PAH in water was measured at 0, 10, 20, 30, 60, 90, 180, 300 and 420min by ultraviolet spectrophotometry. The same steps and parameters were applied to the Phe and Pyr.

Adsorption isotherm:

Different amounts of Nap were added to six 50mL conical flasks, which contained 10g sterilized sediment and 10mL deionized water. The dosage was 50µg, 100µg, 160µg, 200µg, 240µg and 320µg, respectively. Then, the flasks were shaken on an oscillator at 25 °C (35 °C, 45 °C) and 175rpm. Finally, the residue of the PAH in water was measured at the moment of adsorption equilibrium. Except for dosage, the same steps and parameters were applied to the Phe and Pyr. For the Phe and Pyr, the dosage was 4µg, 10µg, 50µg, 100µg, 160µg and 200µg respectively.

2.4 Biodegradation experiments

Fresh coastal sediments, each equivalent to 10g dry sediment, were placed in several 50mL conical flasks. An appropriate amount of PAHs were added, respectively, into the sediment to obtain a concentration of 20µg/g (Nap/sediment), 10µg/g(Phe/sediment) and 10µg/g (Pyr/sediment). To maintain a moist environment, 3mL seawater was added to each flask to cover the sediment. The flasks were then placed on an oscillator and shaken for 2h at 200rpm. Then, the flasks were blanketed with nitrogen, sealed up, and left for incubation at 23±1°C. The residues of PAHs in the sediments were determined at different intervals.

2.5 Analytical techniques

The PAHs were extracted from the sediments using 10mL dichloromethane. After oscillation, ultrasonic extraction, cleaning and quantitative dilution, the residues dissolved in dichloromethane were taken for ultraviolet spectrophotometry analysis. The optimal wavelength of absorption was 274nm for Nap, 249nm for Phe, and 238nm for Pyr. The recovery rate of Nap residues in the sediment samples at 5, 10 and 20µg/g fell in 100.9%~109.0%, with the relative standard deviation (RSD) ranging from 2.65% to 4.77%; the recovery rate of Phe residues in the sediment samples at 1, 5 and 10µg/g fell in 108.3%~115.0%, with the RSD ranging from 2.85% to 3.05%; the recovery rate of Pyr residues the sediment samples at 1, 5 and 10µg/g fell in 102.5%~118.4%, with the RSD ranging from 4.03% to 4.27%. The metabolic products were analysed by an Agilent 7890 Series Plus gas chromatograph linked to a quadrupolar mass spectrometer (Agilent 5975C).

3. Results and Discussions

3.1 Adsorption of PAHs on Bohai coastal sediment

(1) Adsorption kinetics

Featuring high octanol-water partition coefficient (K_{ow}) and low water solubility, organic pollutants like PAHs easily adsorbed by sediments in the coastal environment. According to the adsorption behaviour curves (Figure 1) of Nap, Phe and Pyr on coastal sediments, the adsorption capacities of the three PAHs increased

rapidly in the initial 20min, the adsorption rates slowed during 20–60min, and no further adsorption was observed after 60min. Therefore, 60min was regarded as the moment of adsorption equilibrium for the three PAHs.

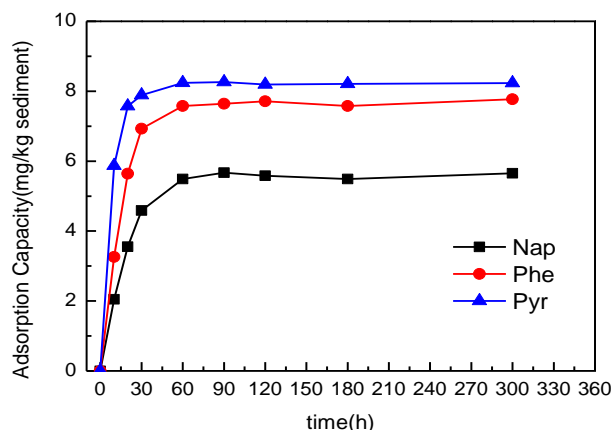


Figure 1: Adsorption curves of Nap, Phe and Pyr on Bohai coastal sediment

Two kinetic models, i.e. pseudo-first-order and pseudo-second-order kinetic models, were tested to explain the kinetics of liquid-solid phase adsorption systems. The pseudo-first-order and pseudo-second-order equations can be expressed as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 \times t$$

$$t/Q_t = 1/(k_2 \cdot Q_e^2) + t$$

where Q_e and Q_t (mg/kg) are the equilibrium adsorption capacity and the adsorption capacity at time t , respectively, k_1 (min^{-1}) and k_2 ($\text{kg}/(\text{mg} \cdot \text{min})$) are the adsorption rate constants for the pseudo-first order and pseudo-second order kinetics, respectively. The fitting results were shown in Table 1.

Table 1: Adsorption kinetic parameters of the pseudo-first-order and pseudo-second-order models

PAHs	pseudo-first-order model			pseudo-second-order model			Experimental adsorbance (mg/kg)
	k_1 (min^{-1})	Q_e (mg/kg)	correlation coefficient	k_2 ($\text{kg}/(\text{mg} \cdot \text{min})$)	Q_e (mg/kg)	correlation coefficient	
Nap	0.0873	7.17	0.9814	0.023	5.78	0.9989	5.65
Phe	0.1505	22.33	0.9033	0.027	7.73	0.9982	7.58
Pyr	0.1491	12.21	0.9741	0.086	8.28	0.9998	8.24

From Table 1, it can be seen that the pseudo-second-order kinetic model had a higher fitting degree than pseudo-first-order kinetic model; the experimental equilibrium adsorption capacities obtained by the pseudo-second-order kinetic model were closer to the theoretical results than those obtained by the pseudo-first-order kinetic model. The results show that the adsorption of the three PAHs on the coastal sediments is consistent with pseudo-second-order kinetics, and that chemical adsorption played a major role in the adsorption process. In terms of equilibrium adsorption capacity, the three PAHs are ranked as Pyr>Phe>Nap. This is because the K_{ow} of Nap, Phe and Pyr increases with the number of benzene rings. The greater the K_{ow} , the easier the PAHs to be adsorbed by sediments.

(2) Adsorption isotherm

Figure 2 displays the adsorption isotherms of Nap, Phe and Pyr at different temperatures. As shown in Figure 2, there was a nonlinear relationship between the equilibrium adsorption amount of PAHs on the sediments (Q_e) and the equilibrium concentration of PAHs in the solution (C_e). Besides, the adsorption amount was negatively correlated with the temperature, as long as the latter fell within the scope of the experimental temperature. The results show that the adsorptions of the three PAHs onto coastal sediments were exothermic reactions.

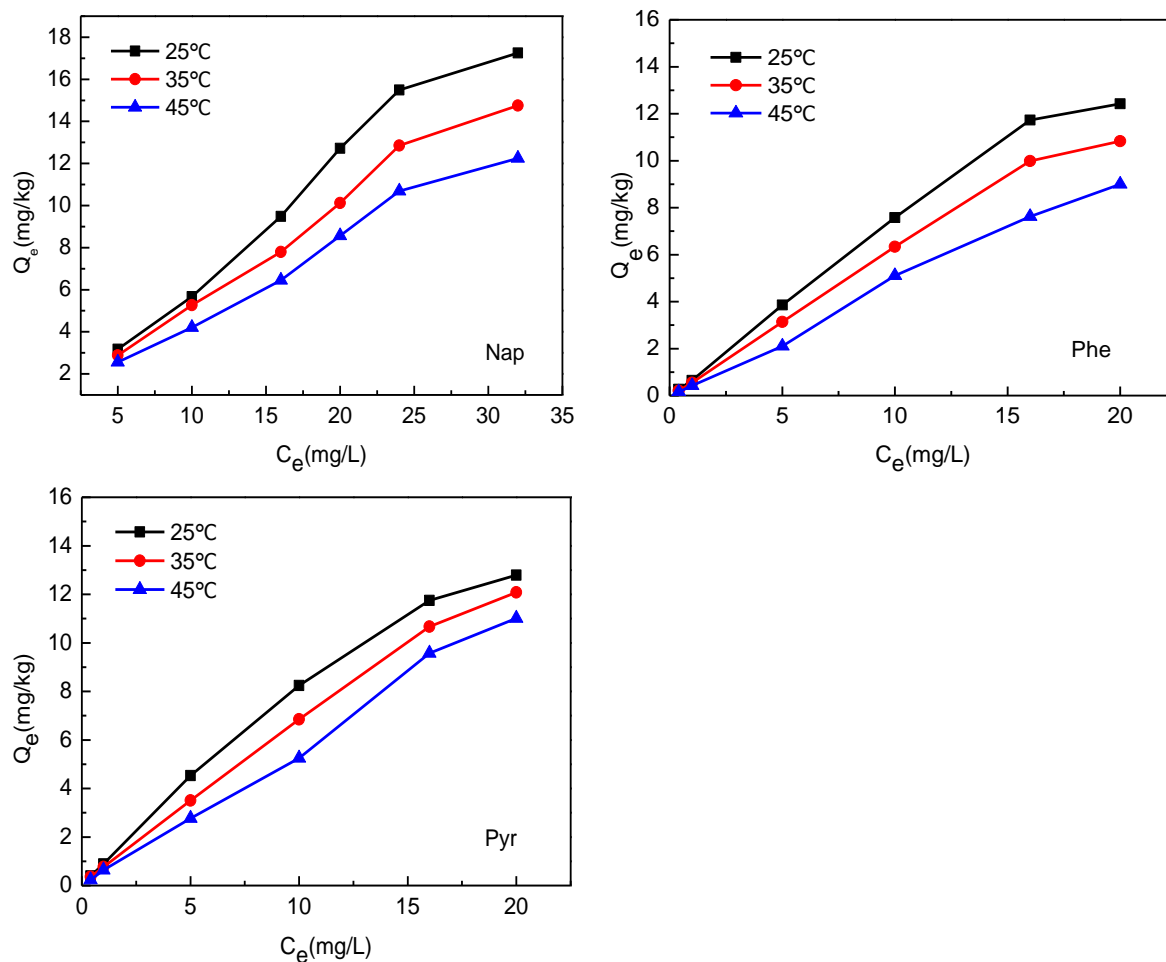


Figure 2: Adsorption isotherms of three PAHs on sediment at different temperatures

In view of the similar adsorption isotherms at 25 °C, 35 °C and 45 °C for three PAHs, the adsorption isotherms at 25 °C were chosen to be fitted. Freundlich and Langmuir models were employed to fit the experimental data.

The two models are expressed as:

Freundlich model: $Q_e = K_F \times C_e^n$

Langmuir model: $Q_e = Q \left[\frac{C_e}{C_e + A} \right]$

where Q (mg/kg) is the maximum adsorption capacity, K_F and n are empirical coefficients, A is a constant related to adsorption energy. The fitting results were shown in Table 2.

Table 2: The fitting results of adsorption isotherm models

PAHs	Langmuir model		Freundlich model		
	A	correlation coefficient	n	K_F	correlation coefficient
Nap	257.3	0.9941	0.9695	0.653	0.9886
Phe	252.7	0.9996	1.012	0.687	0.9971
Pyr	22.11	0.9980	0.9110	0.916	0.9968

As can be seen from Table 2, both Langmuir model and Freundlich model fitted the adsorption of the three PAHs well. In comparison, the better fitting effect belonged to the Langmuir model. This means the adsorption of Nap, Phe and Pyr on the coastal sediments can be explained as mono-molecular layer adsorption.

3.2 Anoxic degradation of PAHs in coastal sediment

(1) Anoxic degradation behaviour

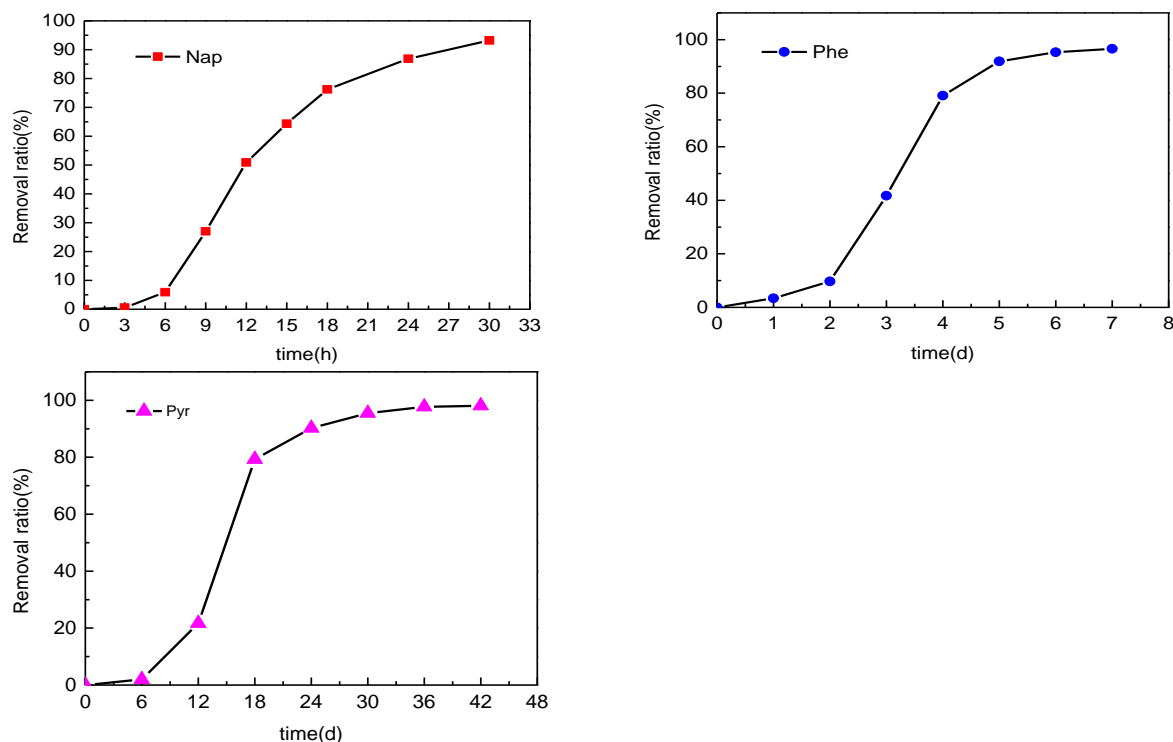


Figure 3: Anoxic degradation curves of the three typical PAHs

The removal ratio (%) was calculated as follows:

$$\text{Removal ratio} = (C_0 - C_t) / C_0 \times 100\%$$

where C_0 is the initial concentrations of the PAHs; C_t is the instantaneous concentrations of the PAHs. As shown in Figure 3, the Nap, Phe and Pyr added into Bohai coastal sediments were well utilized after a certain period of time under the action of native PAH-degrading microbes. The effective use is attributable to the abundance of microorganisms and presence of electron acceptors (e.g. NO_2^- , NO_3^- and SO_4^{2-}) in natural coastal sediments. The microbes could use the electron acceptors to degrade PAHs in the sediments to different degrees. Overall, 93.2% Nap was removed after 30h, 96.6% of Phe was removed after 7d, and 98.1% of Pyr was removed after 42d.

The pseudo-first-order kinetic model was often introduced to depict the pollutant biodegradation in sediments/soil.

$$\ln C_t = -k \cdot t + \ln C_0$$

where k is the degradation rate constant obtained by linear regression of the data $\ln C_t$ versus the incubation time (t). The fitting results are given in Table 3.

Table 3: The degradation rate constants (k) and regression coefficients (R^2)

PAHs	k	R^2
Nap	0.0967h^{-1}	0.9685
Phe	0.5601d^{-1}	0.9284
Pyr	0.1108d^{-1}	0.9576

Table 3 shows that the experimental data were well fitted with the results of the pseudo first-order kinetic model. Hence, the degradation rates were proportional to the concentrations of Nap, Phe and Pyr.

(2) Metabolism of PAHs

Through gas chromatography-mass spectrometry (GC-MS) detection, two metabolites of Nap, two metabolites of Phe and three metabolites of Pyr were detected during the anoxic degradation process in Bohai coastal sediments (Table 4).

Table 4: Metabolites of Nap, Phe and Pyr

PAHs	Metabolites
Nap	4,4-dimethyl-2-cyclohexene-1-ol 1-carboxyl,2-hydroxy, 4-methyl-cyclohexane
Phe	3-ethoxy ethyl benzoate Phthalate (2-methyl propyl) ester
Pyr	2-methyl succinic acid, double (2-methyl propyl) ester Phthalate (2-methyl propyl) ester Phthalic acid butyl ester, 14 alkyl ester

4. Conclusions

This paper investigates the adsorption and anoxic degradation behaviours of Nap, Phe and Pyr in Bohai coastal sediments. The main conclusions are listed as follows.

First, the adsorption equilibriums of Nap, Phe and Pyr were achieved within 60min. The adsorption kinetics could be described by the pseudo-second-order kinetic model. The adsorption processes of the three PAHs were essentially chemical reactions.

Second, the adsorption isotherms of Nap, Phe and Pyr were nonlinear. The Langmuir model simulated the adsorption processes of the three PAHs more accurately than the Freundlich model, indicating that the adsorption of Nap, Phe and Pyr on the coastal sediments can be explained as mono-molecular layer adsorption. All the adsorptions of Nap, Phe and Pyr were exothermic reactions.

Third, in the anoxic sediments, 93.2% of Nap was removed after 30h, 96.6% of Phe was removed after 7d, and 98.1% of Pyr was removed after 42d. The detected metabolites of Nap were [4,4-dimethyl-2-cyclohexene-1-ol], [1-carboxyl,2-hydroxy, 4-methyl-cyclohexane], the metabolites of Phe were [3-ethoxy ethyl benzoate], [Phthalate (2-methyl propyl) ester] and the metabolites of Pyr were [2-methyl succinic acid, double (2-methyl propyl) ester], [Phthalate (2-methyl propyl) ester], [Phthalic acid butyl ester, 14 alkyl ester].

Reference

- Chang B.V., Shiung L.C., Yuan S.Y., 2002, Anaerobic biodegradation of polycyclic aromatic hydrocarbon in soil, *Chemosphere* 48, 717-724, DOI: 10.1016/S0045-6535(02)00151-0.
- Chen C.W., Chen C.F., 2011, Distribution, origin, and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in sediments of Kaohsiung Harbor, Taiwan, *Marine Pollution Bulletin*, 63(5-12), 417-423, DOI: 10.1016/j.marpolbul.2011.04.047.
- Dou J., Liu X., Ding A., 2009, Anaerobic degradation of naphthalene by the mixed bacteria under nitrate reducing conditions, *Journal of Hazardous Materials*, 165(1), 325-331, DOI: 10.1016/j.jhazmat.2008.10.002.
- Fuchedzhieva N., Karakashev D., Angelidaki I., 2008, Anaerobic biodegradation of fluoranthene under methanogenic conditions in presence of surface-active compounds, *Journal of Hazardous Materials*, 153(1-2), 123-127, DOI: 10.1016/j.jhazmat.2007.08.027.
- Haritash, A.K., Kaushik C.P., 2009, Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review, *Journal of Hazardous Materials*, 169(1-3), 1-15, DOI: 10.1016/j.jhazmat.2009.03.137.
- Lin X.M., Liu W., Chen J.L., Xu S.S., Tao S., 2005, Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in surface sediments from Bohai Sea, *Acta Scientiae Circumstantiae*. 25(6), 362-368.
- Lu X.Y., Li B., Zhang T., Fang H.H.P., 2012, Enhanced anoxic bioremediation of PAHs-contaminated sediment, *Bioresource Technology*, 104(1), 51-58, DOI: 10.1016/j.biortech.2011.10.011.
- Mirandola A., Lorenzini E. 2016, Energy environment and climate: from the past to the future, *International Journal of Heat and Technology*, 34(2), 159-164, DOI: 10.18280/ijht.340201.
- Quan X.C., Tang Q., He M.C., Yang Z.F., Lin C.Y., Guo W., 2009, Biodegradation of polycyclic aromatic hydrocarbons in sediments from the Daliao River watershed, China, *Journal of Environmental Sciences*, 21(7), 865-871, DOI: 10.1016/S1001-0742(08)62354-2.
- Wang Z.-Y., Xu Y., Wang H.-Y., Zhao J., Gao D.-M., Li F.-M., Xing B., 2012, Biodegradation of Crude Oil in Contaminated Soils by Free and Immobilized Microorganisms, *Pedosphere*, 22(5), 717-725, DOI: 10.1016/S1002-0160(12)60057-5.