

What Can Rainwater Dissolve From Bitumen Shingle Roof Materials?

Adrienn Horváth¹, Adrienne Clement²

¹(Department of Sanitary and Environmental Engineering, Budapest University of Technology and Economics, Hungary)

²(Department of Sanitary and Environmental Engineering, Budapest University of Technology and Economics, Hungary)

ABSTRACT

Batches of lab steeping tests were carried out on two different bitumen shingles with and without antecedent UVA radiation exposure in order to characterize them regarding the possible effects on roof runoff. In this study, simple water quality parameters like pH, conductivity and chemical oxygen demand, and a specific pollutant group, PAHs were determined. Results show a temperature dependency concerning conductivity, organic matter and PAHs. Significant differences were detectable between the two types of investigated shingles for all studied parameters, presumably because of their different composition. The COD_{cr} concentrations were several times higher in the steeping water of shingles pre-treated with UVA radiation, indicating that UVA radiation could break down their hardly decomposing organic matter content, including PAHs.

Keywords – Bitumen, PAH, steeping; temperature, UVA radiation

I. INTRODUCTION

Previously little attention was paid to the roof runoff quality as it was considered clean or at least cleaner than that of road runoff or waste water [1]. Among others, Rocher et al. [2] published that the concentrations of some components, such as the polycyclic aromatic hydrocarbons (PAHs), total aliphatic hydrocarbons (TPH) and some major elements (Ca, K, Mg, Na, P and S) measured in roof runoff show seasonal changes. Higher loads of previously mentioned pollutants measured during the winter time (wash-off origin of accumulated materials) are attributed to elevated emissions due to heating [2].

PAHs are formed by incomplete combustion or pyrolysis of organic material, and some of them have mutagenic and carcinogenic properties. The US EPA has determined 16 PAHs as priority pollutants, which are the following: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz (a) anthracene, chrysene, benzo(b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, indeno (1,2,3-cd) pyrene dibenzo (a,h) anthracene and benzo (g,h,i) perylene. The classification of the 16 PAHs was based on toxicity, exposure and quantification of risk to humans, and frequency of occurrence at hazardous waste sites [3].

The main sources of PAHs in urban regions are the combustion of fuels, exhaust gases from motor vehicles, the wear of asphalt pavement surfaces, car tires and flat roof insulation. The bitumen in all of these applications has the chance to contact with rainwater, which can leach components from it.

Brandt and De Groot [4] executed static and dynamic leaching tests with different petroleum bitumens. They found that static tests show the same leaching behavior against time: in the first days diffusion-controlled processes are dominating, after 3-6 days concentrations reach equilibrium. In the case of dynamic leaching tests, equilibrium was reached after 30h. In the samples they found only PAHs with four rings or less, because these have the relatively highest water solubility.

The photodegradation of PAHs was widely investigated in different solutions and on different surfaces [5-11]. It was concluded that photodegradation highly depends on the surface of the adsorbent [5, 12-13]. Some studies found that the degradation of the investigated PAHs increased with rising temperature, as well [14-15].

In some research runoff water from roofs covered by bitumen or tar felt was studied, but the concentration of PAHs were not measured [16] or were below detection limit [17-19] or the atmospheric deposition was declared as source [20].

PAHs were found in the roof runoff from bitumen shingled roof in our previous study [21]. The sums of the PAHs, excluding naphthalene, acenaphthylene and acenaphthene but including benzo (e) pyrene, were 1.72 µg/l. Phenanthrene (0.24 µg/l), fluoranthene (0.28 µg/l), pyrene (0.23 µg/l) and the chrysene (0.30 µg/l) were found in the highest concentrations in the samples. The mean sum of the same PAH components measured in precipitation at site of Balaton, Hungary, collected during winter time [22-23] were lower (0.595-1.331 µg/l) than the roofwater, and the concentrations in summer

precipitation (after the heating season ceased) were even lower (0.096-0.586 µg/l).

These results induce the question whether the high PAH concentrations in roof runoff water originate only from atmospheric deposition, or the roof material also contributes to them. To study the effect of bitumen shingle in the quality of runoff leaching tests have been performed with and without antecedent UVA radiation.

II. MATERIAL AND METHOD

Steeping tests: Two different types of bitumen shingled roof material were studied, produced by two different manufacturers. Type A was an oxide-bitumen shingle, and type B was an elastomer modified bitumen shingle. The former was rigid, easy to break, while the latter was rather elastic. These differences stem from the different modification methods of the bitumen material used. Oxide-bitumen is made from distilled-bitumen blown with oxygen to increase its heat resistance while the elastomer modified bitumen contains plastic additives to improve its physical properties. The manufacturers did not give any information about the composition of their products, so it was not possible to compare the two shingle type in detail. The specific weight of shingle Type A was 4.1 kg/m², and Type B 4.9 kg/m².

Static steeping tests were executed at 5, 20, 30, 40 and 60 °C air temperatures, controlled by a thermostat. Test pieces of both shingle types were soaked in 500 ml distilled water for 1 day. In parallel, 3 tests were run in the same temperature. After 1 day the solutions were poured together, and the measurements were executed from that 1.5 liter water. The mean weight of the shingle test pieces was 188.6 g per 500 ml. The liquid-surface ratio was 32.2 l/m² in case of shingle Type A, and 40.8 l/m² in Type B. These ratios are higher than the average intensity of rain in Hungary, and the leaching time also high, but the bitumen shingles are usually used as waterproofing on flat roofs where the rainwater could remain for longer time. A blank test was made in parallel with the steeping tests for each studied temperature. The pH of the blank and the steeping water was measured before and after the tests to study the degree of pH change attributed to the shingle. Conductivity, turbidity, suspended solid content, chemical oxygen demand (COD) and PAH concentrations were measured following the test.

Two batches of experiments were executed with both shingle types. One batch was done with the test pieces exposed to approximately 424 W/m² UVA (340 nm) radiation at 80 °C, which is equal to the annual average irradiation in Hungary. The other batch consisted of the same steeping test, performed without radiation. The UV test apparatus used was as ATLAS UVtest fluorescent/UV instrument.

Measured components: pH values were measured with a WTW 330i probe, while conductivity was measured using a WTWCond 330i probe.

The suspended solid content was determined by filtering 100 ml of the samples through a previously dried and measured 0.45 µm membrane filter, then the filter was dried in 105 °C for 2 hours. The suspended solid content was then measured gravimetrically. The method used corresponds to the Hungarian Standard MSZ 448-33:1985.

The chemical oxygen demand was determined by using both potassium permanganate (CODps) and potassium dichromate (CODcr) as oxidants, in order to compare the content of the easily and hardly decomposable organic matter. The methods used were the Hungarian Standard method MSZ 448-20:1990 and MSZ ISO 6060:1991 respectively.

The PAH concentrations in the samples were measured according to the Hungarian Standard method MSZ 1484-6:2003 (GC-MSD/liquid-liquid extraction) by an accredited laboratory.

III. RESULTS AND DISCUSSIONS

pH: The pH of the blank water before the test varied between 4.7 and 5.7 in all cases, and the measured changes after one day were negligible. The pH rose with increasing temperature, changes compared to the blank water, varied between 2.1 and 4.7. The increment of the pH could be attributed to the dissolution of materials from the shingles. In the case of irradiated shingles the increment of pH was lower, especially in shingle B. ('Fig. 1.')

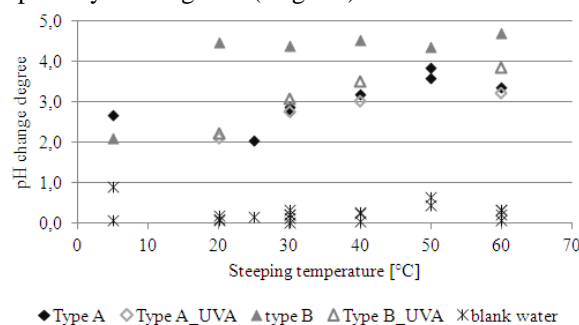


Fig. 1 The pH changes of water after steeping test at different temperatures, with and without antecedent UVA radiation of the investigated roof material

Conductivity: In contrast to the pH values, conductivities measured after one day of soaking were lower in all samples of type B than type A. In the case of shingle A, values varied between 170 and 270 µS/cm, while for type B between 99 and 197 µS/cm. An increase in conductivity with the elevation of steeping temperature was observable in both cases, indicating higher dissolution rate at higher temperatures. The UVA radiation did not affect the conductivity significantly ('Fig. 2.')

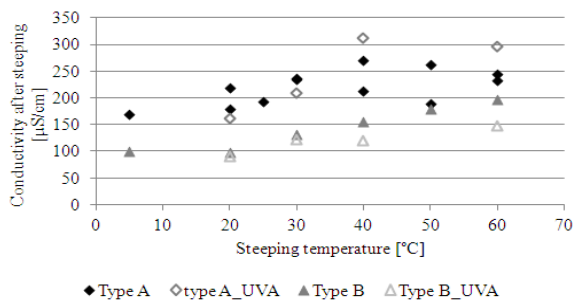


Fig. 2 The conductivity of water after steeping test at different temperatures, with and without antecedent UVA radiation of the investigated roof material

Chemical oxygen demand: ‘Fig. 3’. show the effect of steeping concerning COD_{ps} and COD_{cr} ,

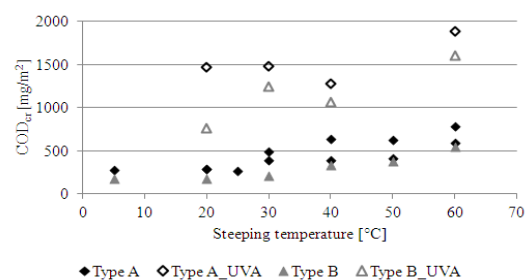
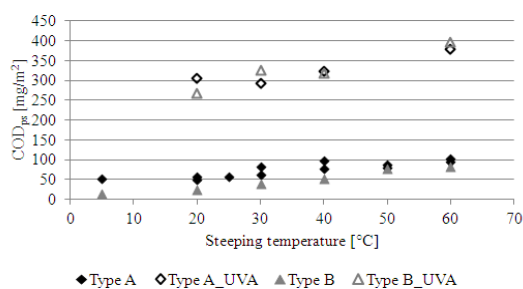


Fig. 3 COD according to the potassium-permanganate (left) and potassium-dichromate (right) method for the two shingle types after steeping, with and without antecedent UVA radiation

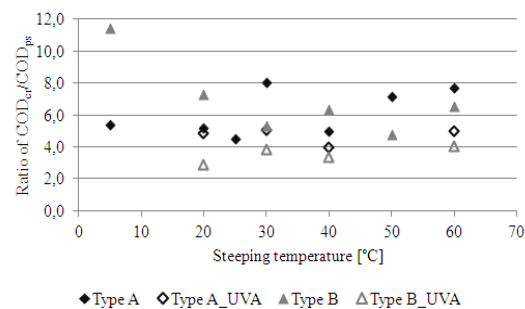
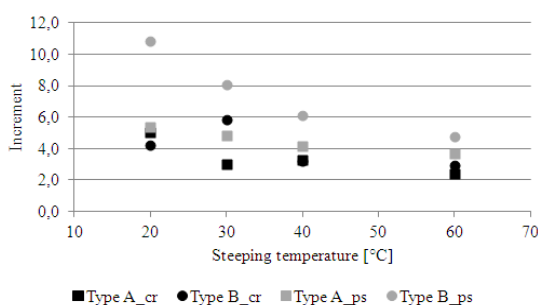


Fig. 4 The increment of COD_{cr} and COD_{ps} in comparison to samples without antecedent UVA radiation (left) and the ratio of COD_{ps} and COD_{cr} of the samples without and with antecedent UVA radiation (right)

The ratio of the COD_{cr} and COD_{ps} in samples without antecedent UVA radiation varied between 4.5-8.1 in shingle type A, and 4.8-11.4 in shingle type B. These ratios indicate that the hardly decomposable organic matter dominates in the leachate. In the samples with antecedent UVA radiation these ratios were considerably lower, 3.9-5.0 and 3.3-4.0 respectively (Fig. 4. right). The decrease is attributed to the decomposition of the organic materials to easily oxidizable ones due to the irradiation.

Polycyclic aromatic hydrocarbons: The total PAH-16 concentrations in the test batch without antecedent UVA radiation were found to be 3.7, 4.5, 1.8, 3.9 and 1.9 times higher at temperatures 5, 20, 30, 40 and 60 °C respectively in the steeping water samples of shingle type A than in those of shingle

respectively. The minor difference between the shingles can be assigned to the different bitumen modification methods, or the different origin of mineral oil used, however this is only a hypothesis, as the manufacturers didn't give any information about the primary materials or the technology. A slight increase in COD can be observed with rising temperatures for all samples, which can be attributed to the higher release rate of organic matter from the bitumen at higher temperatures. Furthermore, a significant increase in COD was observable in the samples with antecedent UVA radiation in comparison to the samples that were not irradiated ('Fig. 4.' left.). This phenomenon was clear for both COD_{ps} and COD_{cr} ,

type B ('Table 1' and 'Table 2'). Furthermore, not only the concentrations of total PAHs were higher, but also the number of detectable components was higher in the samples of shingle type A. From shingle type A, fluorene, phenanthrene, fluoranthene and chrysene was detectable at almost every temperature, while acenaphthene, pyrene, benz(a)anthracene and benzo(e)pyrene were found only at higher temperatures. From shingle type B only phenanthrene was found in all samples, and chrysene in the samples of 30, 40 and 60 °C experiments.

Regarding temperatures, the two types of bitumen shingles showed inverse behavior both without and with antecedent UVA radiation. With antecedent UVA radiation, only chrysene (at two temperatures) and benz(a)anthracene (at one temperature) was found in the samples of shingle

type A. However in samples of shingle type B, phenanthrene (at all temperatures), chrysene and benzo(e)pyrene (at three temperatures), benz(a)anthracene (at two temperatures), and fluoranthene and pyrene (at one temperature) was measured. The outcomes of the experiments were inconsistent at temperatures 30 and 40 °C for shingle type A, and at 40 °C for shingle type B, therefore

further investigation is required. Comparing the PAH concentrations with COD_{cr} the two shingle types behaved similar in samples without irradiation while after UVA radiation their behavior were different ('Fig. 5.'). The UVA radiation increased the COD_{cr} of the samples, but the total PAH concentrations did not vary considerably.

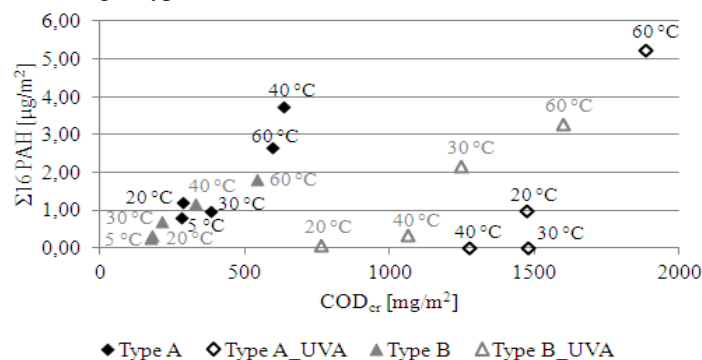


Fig. 5 The Total PAH concentration of the samples in function of the chemical oxygen demand measured with potassium-dichromate

The Hungarian surface waters quality standard (10/2010. (VIII. 18.) VM), in accordance with the EU legislation (2008/105/EC directive), lays down EQS (Environmental Quality Standards) values for pollutants classified as priority substances at Community level. This include the following PAHs: anthracene, fluoranthene, benzo(b)fluoranthene+benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene+benzo(g,h,i)perylene. All measured concentrations of these substances in our steeping water samples were

lower than the EQS. On the other hand, comparing the dissolved PAH concentrations with the groundwater quality standard (6/2009. (IV. 14.) KvVM-EüM-FVM), it can be seen that in some cases, especially in the samples of higher temperatures, the concentrations exceed the contamination limits (Tables 1 and 2). The concentrations of Chrysene and Benzo(e)pyrene (0,02 µg/l and 0,01 µg/l respectively) are exceeding these limits the most.

Table 1 PAH concentrations in the solutions after steeping shingle type A at different temperatures without and with antecedent UVA radiation.

Temperature [°C]	without UVA radiation					with UVA radiation				DL ----
	5	20	30	40	60	20	30	40	60	
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.002
Acenaphthene	nd	nd	nd	0.006	0.005	nd	nd	nd	nd	0.002
Fluorene	nd	0.012	0.013	0.028	0.023	nd	nd	nd	nd	0.002
Phenanthrene	0.024	0.031	0.034	0.059	0.056	nd	nd	nd	nd	0.002
Anthracene	nd	nd	nd	0.010	nd	nd	nd	nd	nd	0.002
Fluoranthene	0.008	0.009	nd	0.014	0.013	nd	nd	nd	nd	0.002
Pyrene	nd	nd	0.013	0.024	0.020	nd	nd	nd	nd	0.002
Benz(a)anthracene	nd	nd	nd	0.011	0.008	nd	nd	nd	0.170	0.005
Chrysene	0.016	0.021	nd	0.051	0.038	0.063	nd	nd	0.160	0.005
Benzo(b)fluoranthene	nd	nd	nd	0.013	nd	nd	nd	nd	nd	0.005
Benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Benzo(e)pyrene	nd	nd	nd	0.009	0.006	nd	nd	nd	nd	0.005
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Sum 16 PAH	0.048	0.073	0.060	0.225	0.169	0.063	nd	nd	0.330	
Sum 16 PAH (µg/m2)	0.78	1.21	0.96	3.76	2.65	0.97	nd	nd	5.25	

Concentrations in µg/l, except where is defined

DL: detention limit

nd: not detected

grey background – concentration higher than the contamination limits determined in Hungarian groundwater quality standard

Table 2 PAH concentrations in the solutions after steeping shingle type B at different temperatures without and with antecedent UVA radiation.

Temperature [°C]	without UVA radiation					with UVA radiation				DL ----
	5	20	30	40	60	20	30	40	60	
Acenaphtylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.002
Acenaphtene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.002
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.002
Phenanthrene	0.013	0.016	0.026	0.037	0.056	0.002	0.020	0.004	0.038	0.002
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.002
Fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd	0.011	0.002
Pyrene	nd	nd	nd	0.008	nd	nd	0.010	nd	nd	0.002
Benz(a)anthracene	nd	nd	nd	nd	nd	nd	0.010	nd	0.032	0.005
Chrysene	nd	nd	0.007	0.012	0.033	nd	0.033	0.006	0.020	0.005
Benzo(b)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Benzo(e)pyrene	nd	nd	nd	nd	nd	nd	0.036	0.006	0.061	0.005
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.005
Sum 16 PAH	0.013	0.016	0.033	0.057	0.089	0.002	0.109	0.016	0.162	
Sum 16 PAH (µg/m²)	0.26	0.33	0.68	1.17	1.82	0.04	2.16	0.32	3.26	

Concentrations in µg/l, except where is defined

DL: detention limit

nd: not detected

grey background – concentration higher than the contamination limits determined in Hungarian groundwater quality standard

IV. CONCLUSION

Answering to the question raised in the introduction, it was proven that the bitumen shingle can significantly contribute to the PAH and chemical oxygen demand of roof runoff.

The pH of the samples increased after the steeping test in both investigated bitumen roof shingle types. The increment was larger in the case of the elastomer modified bitumen shingle. In samples which received UVA radiation prior to the steeping test, the pH change was detectable only in the case of the elastomer modified bitumen shingle. The conductivity of the samples increased with increasing temperature, but UVA radiation did not affect significantly the conductivity of the steeping water.

The COD of the samples also increased with increasing temperature, because of the higher release rate of organic matter. In both investigated materials the measured COD values were higher in the samples with antecedent UVA radiation, but the ratio of hardly and easily decomposable organic matter decreased. This indicates that the UVA radiation was

able to break down parts of the hardly decomposable organic matter to measurable components.

The PAH concentration of the water after the steeping was found to be depending on the ambient temperature, the type of the shingle, and the presence of UVA radiation. Studying the PAH concentrations in function of COD_{Cr}, the shingles without prior UVA radiation behaved similarly, but the irradiated samples showed differences. It is supposed, that the UVA radiation decomposed the PAHs to a higher degree in shingle type A, because the PAH-16 and the COD_{Cr} was also higher than in the samples of shingle B.

The differences in the measured component values in same conditions are attributed to the different manufacture technology and origin of their raw material. It is important to mention that the PAH measurements have significant standard errors, as the digestion methods depend on the type of samples and the measured components sometimes are close to the detention limit.

Furthermore, in this pilot study the shingles received one year UVA radiation. In the reality the

roofing materials are irradiated with the whole range of wavelength and are washed off frequently. Because of the previously mentioned reasons, more research with higher resolution would be necessary to establish.

REFERENCES

- [1] J. Zobrist, S. R. Müller, A. A. Ammann, T. D. Buchelli, V. Mottieri, M. Ochs, R. Schoenenberger, J. Eugster, M. Boller, Quality of roof runoff for groundwater infiltration, *Water Research*, 34(5), 2000, 1455 - 1462.
- [2] V. Rocher, S. Azimi, J. Gasperi, L. Beuvin, M. Müller, R. Moilleron, G. Chebbo, Hydrocarbons and metals in atmospheric deposition and roof runoff in central Paris, *Water, Air and Soil Pollution* 159(1), 2004, 67 - 86.
- [3] ATSDR (Agency for Toxic Substances and Disease Registry). *Toxicological profile for polycyclic aromatic hydrocarbons*. (U.S. Department Of Health And Human Services, Public Health Service. Agency for Toxic Substances and Disease Registry. August 1995).
- [4] H. C. A. Brandt, P. C. De Groot, Aqueous leaching of polycyclic aromatic hydrocarbons from bitumen and asphalt, *Water Research* 35(17), 2001, 4200 - 4207.
- [5] T. D. Behymer, R. A. Hites, Photolysis of Polycyclic Aromatic Hydrocarbons Adsorbed on Simulated Atmospheric Particulates, *Environmental Science and Technology* 19, 1985, 1004 - 1006.
- [6] K-M Lehto, E. Vuorimaa, H. Lemmetyinen, Photolysis of polycyclic aromatic hydrocarbons (PAHs) in dilute aqueous solutions detected by fluorescence, *Journal of Photochemistry and Photobiology A: Chemistry* 136, 2000, 53–60.
- [7] J. S. Miller, D. Olejnik, Photolysis of polycyclic aromatic hydrocarbons in water, *Water Research* 35(1), 2001, 233-243.
- [8] M. Nadal, J. J. Wargent, K. C. Jones, N. D. Paul, M. Schuhmacher, J. L. Domingo, Influence of UV-B radiation and temperature on photodegradation of PAHs: Preliminary Results, *Journal of Atmospheric Chemistry* 55, 2006, 241-252.
- [9] K. Ram, C. Anastasio, Photochemistry of phenanthrene, pyrene, and fluoranthene in ice and snow, *Atmospheric Environment* 43, 2009, 2252-2259.
- [10] L. Zhang, P. Li, Z. Gong, A. A. Oni, Photochemical behaviour of benzo[a]pyrene on soil surface under UV light irradiation, *Journal of Environmental Sciences* 18(6), 2006, 1226-1232.
- [11] L. Zhang, P. Li, Z. Gong, X. Li, Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using TiO₂ under UV light, *Journal of Hazardous Materials* 158, 2008, 478–484.
- [12] A. Mallakin, D. G. Dixon, B. M. Greenberg, Pathway of anthracene modification under simulated solar radiation, *Chemosphere* 40, 2000, 1435-1441.
- [13] J. Niu, J. Chen, D. Martens, X. Quan, F. Yang, A. Kettrup, K-W. Schramm, Photolysis of polycyclic aromatic hydrocarbons adsorbed on spruce [*Picea abies* (L.) Karst.] needles under sunlight irradiation, *Environmental Pollution* 123, 2003, 39-45.
- [14] Y. Wang, L. Fengkai, L. Zhulu, X. Zheng, T. Yubin, Photolysis of anthracene and chrysene in aquatic systems, *Chemosphere* 38(6), 1999, 1273-1278.
- [15] L. Zhang, Ch. Xu, Z. Chen, X. Li, P. Li, Photodegradation of pyrene on soil surface under UV 225 light irradiation, *Journal of Hazardous Materials* 173, 2010, 168-172.
- [16] M. Chang, M. W. McBroom, R. Scott Beasley, Roofing as a source of nonpoint water pollution, *Journal of Environmental Management* 73, 2004, 307–315.
- [17] C. Despins, K. Farahbakhsh and C. Leidl C, Assessment of rainwater quality from rainwater harvesting systems in Ontario, Canada, *Journal of Water Supply: Research and Technology-AQUA* 58(2), 2009, 117-134.
- [18] K. Lamprea, V. Ruban, Micro pollutants in atmospheric deposition, roof runoff and storm water runoff of a suburban Catchment in Nantes, France. *11th International Conference on Urban Drainage*, Edinburgh, Scotland, UK., 2008.
- [19] C. B. Mendez, J. B. Klenzendorf, B. R. Afshar, M. T. Simmons, M. E. Barrett, K. A. Kinney, M. J. Kirisits, The effect of roofing material on the quality of harvested rainwater, *Water Research* 45, 2011, 2049-2059.
- [20] J. Förster, Patterns of roof runoff contamination and their potential implications on practice and regulation of treatment and local infiltration, *Water Science and Technology* 33(6), 1996, 39-48.
- [21] A. Horváth, Roof runoff quality and reduction possibility of the pollutants, *Pollack Periodica* 6(1), 2011, 107–116.
- [22] E. Bodnár, J. Hlavay, Atmospheric deposition of polycyclic aromatic hydrocarbons on the Lake Balaton, Hungary, *Microchemical Journal* 79, 2005, 213-220.
- [23] Gy. Kiss, Z. Varga-Puchony, B. Tolnai, B. Varga, A. Gelencsér, Z. Krivácsy, J. Hlavay, The seasonal changes in the concentration of polycyclic aromatic hydrocarbons in precipitation and aerosol near Lake Balaton, Hungary, *Environmental Pollution* 114, 2001, 55-61.