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BETX REMOVAL FROM MOTORWAY RUNOFF ON CONSTRUCTED WETLANDS**

1. INTRODUCTION

The elaboration of the rational method to treat stormwater is one of the most urgent challenges of the modern environmental engineering, both in Poland [6] and worldwide [4, 12]. As the result of urban development the significant increase of stormwater amount has been occurred – its rational management is more and more important, and mixing it with municipal wastewater, widely applied in Poland, is the outdated and inefficient solution. The problem is especially important and difficult in a case of stormwater from motorways and parking lots [3, 6] – this kind of runoff has to be pretreated before releasing to the wastewater network and to the wastewater treatment plant. It is caused by the oil derivatives presence in this kind of wastewater. Oil derivatives due to their widespread occurrence and high harmfulness both for human health and environment are micropollutants of special importance. Among them the specific group are aromatic hydrocarbons, including benzene, toluene, ethylbenzene and xylenes, which sum is described and measured as BETX. In recent years more aromatics hydrocarbons have been added into fuels for antiknock purposes, as a result of lead-containing additives elimination [5]. Due to their high toxicity and hazardousness [9], [10, 5] elaborating the efficient method of BETX removal from runoff is an important task. In countries with the developed highway infrastructure, constructed wetlands are more and more widely applied to treat runoff from highways and parking lots [8, 2, 11] – they guarantee effective and economic stormwater treatment in the place of its formation [7, 1].

To assess the possibility to use the technology in our country, the decision has been made to initiate the pilot researches on the oil derivatives removal from wastewater on constructed wetlands. In particular the effectiveness of BETX removal from synthetic model wastewater on model constructed wetlands has been examined.

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2. EXPERIMENTAL PROCEDURES

The experiments have been conducted with using of the model constructed wetland pots, since March 25 to June 12 2008, under the influence of atmospheric conditions, however pots were located under the roof to avoid stormwater inflow into analyzed wastewater.

Experiments have been done in 9 model pots to simulate constructed wetland beds planted with Common Reed (*Phragmites Australis*), Common Osier willow (*Salix Viminalis*) and without macrophytes (control bed). Three concentrations of synthetic wastewater have been applied to the experiment pots to simulate the concentrations in real stormwater from motorways, and parking lots, and filling stations and car washing stations. The monitored parameter was the concentration of benzene, toluene, ethylbenzene, p,m,o-xylene (BETX). Gas chromatography has been used to analyzed these compounds. Additional two pots with reed and osier have been applied with fresh water. They have been constructed as the comparison for the observations how oil derivatives influence the plants development in the experimental beds applied with wastewater. Three values of detention time have been analyzed: 0 h (the direct flow of wastewater through a bed), 3 h and 6 h.

2.1. Bed models

As the constructed wetland (CW) bed models, the 20-liter plastic containers (pots) have been used. Each container was equipped with a ball valve in its bottom. Such a construction has enabled to collect wastewater from the whole container (samples from the experimental pots have never been mixed). Pots have been filled with gravel (class I, quality I, fraction 8–12 mm) up to ¾ of their volume. The gravel producer is Kopalnia Odkrywkowa Surowców Drogowych in Rudawa.

2.2. Plants

The willow seedlings, in a form of 35 cm cuttings, were received from the private willow husbandry (March 17 2008). They were kept in a fridge, and two days before their planting they were put into water in a warm and sunlit room, to start them to root.

Reed seedlings were collected from the public field in Szczyglice close Wiślica (March 25 2008). They had been kept in water until the experiments started.

Plants were planted March 28 2008; willow seedlings have been planted in four model pots (6 cuts in each), reed seedlings – in four (8 in each), three pots were filled only with gravel, without plants.

Plants were regularly watered every 3 days. Since May 8 2008 the application of synthetic wastewater with oil derivatives has been started (the three concentrations of oil have been used). This was to saturate beds with oil and adopt plants to new conditions. The acclimatization period lasted for 9 days. In that time wastewater was changed every 72 hours, the single dose of wastewater was 4,5 liters for each container.

2.3. Model wastewater

Synthetic model wastewater has been produced as the mixture of water and diesel oil. It was prepared every time, just before its application to the model pots. In all experiments

the same diesel oil has been used (EKODIESEL), it was purchased once in a suitable amount from the filling station „Orlen", Kraków, ul. Armii Krajowej.

Three different BETX concentrations of model wastewater have been simulated: 1.08 μg/dm^3 and 5.91 μg/dm^3 and 9.01 μg/dm^3 (benzene respectively: 0.01 μg/dm^3 and 0.02 μg/dm^3 and 0.03 μg/dm^3; toluene: 0.10 μg/dm^3 and 0.57 μg/dm^3 and 1.07 μg/dm^3; ethylbenzene: 0.16 μg/dm^3 and 0.97 μg/dm^3 and 1.50 μg/dm^3; p,m,o-xylene: 0.81 μg/dm^3 and 4.36 μg/dm^3 and 6.40 μg/dm^3) – see the first column of the Table 1. These concentrations represent the levels of hydrocarbons leaking to the natural environment in runoff from motorways and parking lots. These three concentrations have been simulated by adding respectively: 0.025 ml and 0.05 ml and 0.1 ml of diesel fuel to 1 liter of water.

Table 1

BETX concentrations in relationship to initial concentration and experimental constructed wetland bed and detention time

Initial concentration [μg/dm^3]	BETX concentration [μg/dm^3]								
	Control Bed (CB)			Phragmites Australis Bed (PA)			Salix Vinimalis Bed (SV)		
	0h[a]	3h	6h	0h	3h	6h	0h	3h	6h
Benzene									
0,01	0,01	0,02	nd[b]	nd	0,01	0,01	0,02	nd	0,02
0,02	0,01	0,02	0,01	0,02	0,01	0,01	nd	0,01	0,01
0,03	0,03	0,01	0,01	0,02	0,01	nd	0,01	nd	0,01
Toluene									
0,10	0,11	nd	nd	nd	nd	nd	0,09	0,01	nd
0,57	0,01	0,05	nd	0,05	nd	nd	nd	nd	nd
1,07	0,04	0,02	0,01	0,04	nd	nd	nd	nd	nd
Ethylbenzene									
0,16	0,06	nd	nd	nd	nd	nd	nd	nd	nd
0,97	0,06	0,01	nd	nd	nd	nd	nd	nd	nd
1,50	nd	nd	nd	0,02	nd	nd	nd	nd	nd
p,m,o-xylene									
0,81	0,19	nd	nd	nd	nd	nd	0,01	nd	nd
4,36	0,14	0,03	nd	nd	nd	nd	nd	nd	nd
6,40	0,15	nd	0,04	0,20	nd	nd	nd	nd	nd
BETX									
1,08	0,36	0,02	0,00	0,01	0,01	0,01	0,12	0,02	0,02
5,91	0,22	0,10	0,01	0,07	0,01	0,01	0,01	0,01	0,01
9,01	0,22	0,04	0,06	0,27	0,01	0,01	0,01	nd	0,01

a – detention time; b – not detected

2.4. BETX measurement

The BETX concentration has been analyzed with the gas chromatograph with a mass spectrometer detector (GC-MS) Trace Ultra and DSQ-II by the Thermo, with helium as carrier gas. The Rxi^{TM}–1ms capillary column by Restek has been used (100% polydimethylsiloxane; film thickness 0.25 μm; column length 30 m; column diameter 0.25 mm). The BETX have been extracted with the Head-Space method and determined on GS-MS due to the Polish Standard PN-ISO 11423-1. The samples have been incubated in 90°C for 40 minutes, the column has been heated from 31°C (0 min) to 200°C (0 min) with the temperature rate of 16°C/min.

3. RESULTS

The experiments results have been presented in the Table 1 and shown in the Figures 1–5. The Figure 1 presents the benzene concentrations, which have been measured in the effluents from control beds (CB) and reed *Phragmites Australis* beds (PA) and willow *Salix Viminalis* beds (SV), after detention times: 0 h and 3 h and 6 h. The analogical graphs have been presented in the picture 2 for toluene, in the Figure 3 for ethylbenzene, in the Figure 4 for p,m,o-xylene, and in the Figure 5 for the sum of all measured hydrocarbons (BETX).

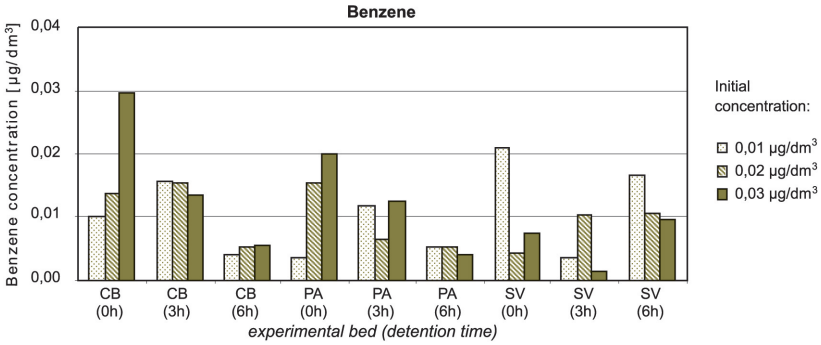

Fig. 1. Benzene concentrations in effluent from the experimental constructed wetlands

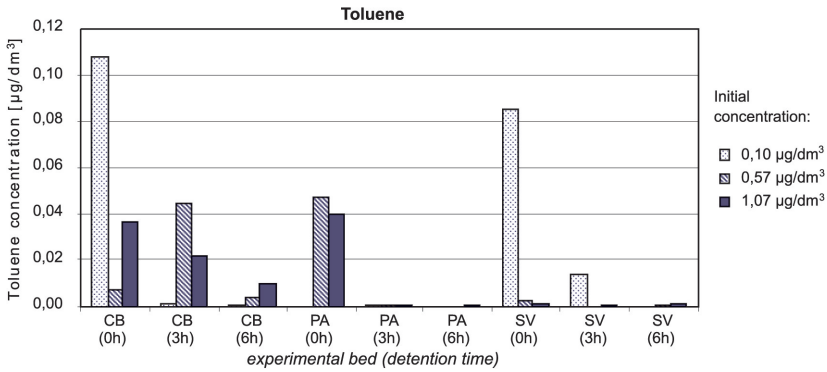

Fig. 2. Toluene concentrations in effluent from the experimental constructed wetlands

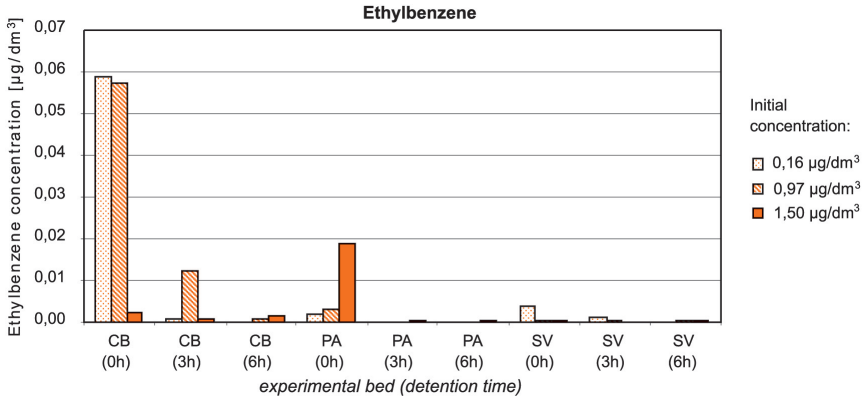

Fig. 3. Ethylbenzene concentrations in effluent from the experimental constructed wetlands

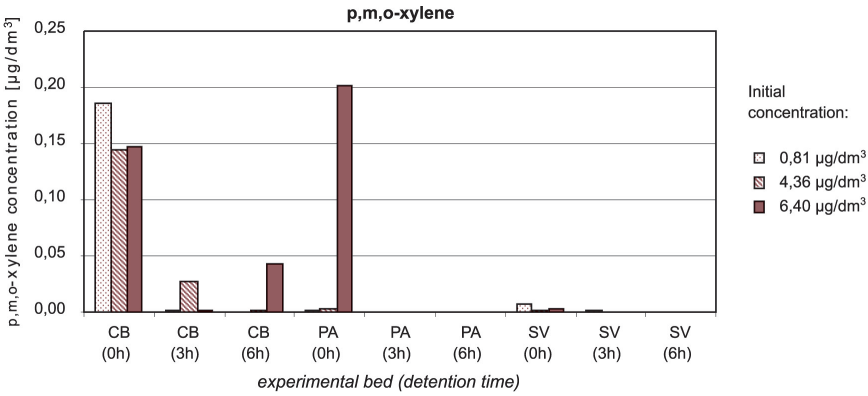

Fig. 4. p,m,o-xylene concentrations in effluent from the experimental constructed wetlands

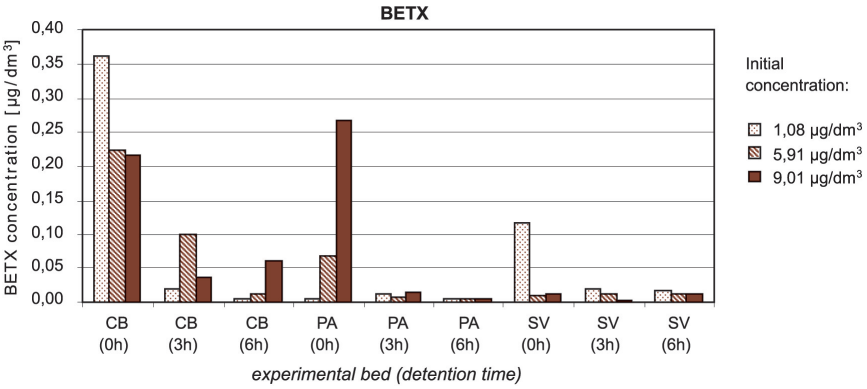

Fig. 5. BETX concentrations in effluent from the experimental constructed wetlands

4. DISCUSSION OF RESULTS

4.1. Benzene removal

Benzene, which has the highest water solubility (1,8 g/dm^3 in 20°C) in a comparison with the other examined aromatic hydrocarbons, was removed with the lowest efficiency by the experimental CW beds. Generally, the best results of the benzene removal by all examined CW beds have been observed for the highest benzene concentrations in the model synthetic wastewater (0.03 μg/dm^3) and for the longest detention time (6 h); the reed bed (PA) has reached the 88% level of the benzene removal, for the willow bed (SV) – 72%. In a case of wastewater with the lowest benzene concentration (0.01 μg/dm^3) the higher level of benzene was observed in the effluent than in the influent, thus the removal efficiency was negative. This fact could be explained by rinsing benzene out of the beds which had been earlier conditioned, especially for such low concentrations – close to the benzene detection limit – this effect could be significant, and could has resulted in the increase of the benzene concentration in the effluents.

4.2. Toluene removal

The water solubility of toluene is much lower than benzene (0.5 g/dm^3 in 20°C), and the toluene removal efficiency by the experimental CW beds was higher. For the control beds the toluene removal efficiency has been observed on the level 92–99%. For reed beds the complete toluene removal has been observed for all initial concentrations, both for 3 h and 6 h detention times. Similar for willow beds; the complete toluene removal (99.9%) has been observed for the initial toluene concentrations 0.57 μg/dm^3 and 1.07 μg/dm^3, both for 3 h and 6 h detention times. For the lowest toluene initial concentration (0.10 μg/dm^3) the complete removal has been observed only for 6 h detention time.

4.3. Ethylbenzene removal

The ethylbenzene removal efficiency by the experimental CW beds was very high; generally this compound was almost completely removed (99–100%) in all examined cases. Only for the control bed (without plants) for 0h detention time the lower ethylbenzene removal efficiency has been observed: 63% for the initial ethylbenzene concentration 0.16 μg/dm^3; and 94% for 0.97 μg/dm^3 concentration; and 99.8% for 1.50 μg/dm^3 ethylbenzene concentration in an influent. Ethylbenzene has the very low water solubility, which explains so high effectiveness of the model CW beds in its removal.

4.4. p,m,o-xylene removal

Xylenes (water solubility 0.2 g/dm^3 in 20°C) similar to ethylbenzene, were very well removed from wastewater in the performed pot experiments. Almost the total p,m,o-xylene removal has been observed in all examined cases, beside the detention time 0 h on the control bed, for which case the efficiency was 77% for the initial p,m,o-xylene concentration 0.81 μg/dm^3, and 97% for 4.36 μg/dm^3, and 98% for 6.40 μg/dm^3.

4.5. BETX removal

The removal efficiency of the sum of examined hydrocarbons (BETX) was very high: 98–100%. The beds with plants have demonstrated the higher BETX removal efficiency than the control beds. The lowest BETX removal efficiency has been observed for the beds with the lowest initial BETX concentration – 1.08 μg/dm^3, but it was very high anyway (98%). Only for 0 h detention time on the control bed the efficiency was as low as 66%.

4.6. Plants condition

After experiments, in all willow pots the changes have been noticed in a form of slower growth and yellow leaves. Reed was a plant species much more resistant to oil derivatives influence – any kind of negative changes have not been observed; even its faster growth has been observed in a comparison to the reed pot feeding with fresh water.

5. CONCLUSIONS

The research experiments have shown the high potential of constructed wetlands to efficiently remove BETX from wastewater. The relationship between the examined aromatic hydrocarbons removal efficiency and their water solubility has been observed; the less water-soluble compounds have been better removed by the experimental CW beds. The lowest effects have been obtained for benzene – the compound, which is the most toxic among examined hydrocarbons and has the highest water solubility. However its removal efficiency was relatively high anyway – exceed 80%.

The experiments have proved the higher BETX removal efficiency by the beds with plants in a comparison to the control beds. The willow beds have demonstrated the better efficiency for 0h detention time, bur for the longer detention times the BETX removal was more efficient on the reed beds.

Reed is a plant resistant to oil derivatives influence – any kind of negative changes have not been observed during experiments.

The experiments results have confirmed the thesis that the constructed wetlands are the promising alternative for the conventional treatment methods, and they should be considered as an valuable option in designing and constructing the systems to treat motorways and parking lot runoff contaminated with oil derivatives.

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