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THE INFLUENCE OF REED *Phragmites australis* ON AN EFFICIENCY OF OIL-DERIVATIVES REMOVAL

WPŁYW TRZCINY POSPOLITEJ *Phragmites australis* NA SKUTECZNOŚĆ USUWANIA ZANIECZYSZCZEŃ ROPOPOCHODNYCH

Abstract: Constructed wetlands are the effective mean of stormwater management, also in a case of runoff from highways, parking lots and other surfaces contaminated with oil-derivatives, which are potential risk for environment, human health and biological wastewater treatment units. The mechanisms of oil-derivatives removal on wetland beds are complex and not fully understood, however the most important role seem to be played by adsorption on mineral filling, the activities of microorganisms and higher plants. The goal of the presented research is to evaluate the role of macrophytes in oil-derivatives removal processes, as well as to assess the plants' resistance to the high concentrations of these pollutants. The research was conducted as pot experiments, with the usage of reed *Phragmites australis* and model solutions, simulating runoff from surfaces contaminated with oil-derivatives, in three concentrations (0.01, 0.02 and 0.05% of diesel fuel) and three detection times (24, 48 and 96 h). Both in raw and treated solutions, following parameters were measured: pH, conductivity, the sum of aliphatic hydrocarbons C7-C40 and their individual concentration. The research results were used to define the removal efficiency of the studied contaminates, especially oil-derivatives, on constructed wetlands beds, as well as to assess the macrophytes' influence on these processes. The state and conditions of plants were also observed to assess their reaction on the examined concentrations of oil substances.

Keywords: stormwater treatment, constructed wetlands, oil-derivatives, aliphatic hydrocarbons, reed *Phragmites australis*

Introduction

One of the most urgent challenges of the sustainable water management, both in Poland [1, 2] and world-wide [3, 4], is to develop the rational methods of stormwater treatment and management. In recent years, as a result of urbanization processes, changes in the patterns of land-use and land-cover, and especially sealing of the municipal surfaces, a significant increase of stormwater amount has been observed [5]. The problem of proper management of stormwater is especially complex and important in case of run-off from roads, parking lots and other kinds of road transport infrastructure [6, 7]. Due to the presence of specific contaminants, especially oil-derivatives and other petroleum products, it is necessary to pre-treat stormwater from such areas, before it is discharged to the municipal wastewater system or into the environment.

In case of countries with a developed network of roads and motorways, constructed wetlands and other natural based solutions are applied increasingly more often to treat and manage stormwater coming from the road infrastructure [8, 9]. They guarantee the effective stormwater treatment in-situ, therefore minimizing the costs and negative environmental effects.

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Despite the simplicity of these objects, the mechanisms and dynamics of pollutants' removal by constructed wetlands are complicated and complex, and not fully understood and studied [10]. It is particularly difficult to comprehend and describe these mechanisms in a case of oil-derivatives, however the main paths of removing, which are reported for these compounds, are volatilization, biological or microbial degradation with the activity of macrophytes and microorganisms, sorption and sedimentation in mineral filling [11]. However there is a limited number of articles and research reports, which would allow us to predict the effectiveness and role of these mechanisms for different oil-derivatives and constructed wetlands technical parameters, thereby to accurately plan and design such the facilities.

The goal of the pot experiments presented in this paper was to evaluate (and isolate) the influence of plants on effectiveness of the oil-derivatives removal, and also to determine the plants resistance towards high concentrations of these compounds. They were complementary studies to the research project on semi-technical objects, treating stormwater from the gas filling station and car service [12].

Materials and methods

The experiments, mentioned in the previous paragraph, were carried out in pots in a form of glass vessels, with volume of 3 dm^3. The studies were conducted on model solutions, which were produced with Ekodiesel by Orlen. The whole quantity of diesel fuel was purchased once, thus the identical fuel was used for all experiments. Three types of model solutions were prepared with following concentrations of oil-derivatives: 0.01 (by adding 0.1 cm^3 of diesel fuel per one liter of water), 0.02 and 0.05%. The experiments were performed with common reed (*Phragmites australis*) and were performed for three values of retention time: 24, 48 and 96 h.

The following parameters were measured both in raw and treated solutions: pH, conductivity, the concentration of all individual aliphatic hydrocarbons C7-C40, the total concentration of sum of aliphatic hydrocarbons C7-C40 (Σn-alkanes). The extraction of aliphatic hydrocarbons was conducted with liquid-liquid method with n-pentane used as solvent. Then they were analyzed with gas chromatograph with mass spectrometer (GC-MS) - Trace Ultra DSQ-II by Thermo. The capillary column Rxi^{TM-}5ms by Restek company was used (film thickness 0.5 µm; column length 30 m; diameter 0.25 mm) and helium as carrier gas (flow rate 0.6 cm^3/min). The analysis of each sample lasted 90 minutes and the following temperature programme was used: from 35ºC (6 min) to 130ºC (0 min) with temperature increase 8ºC/min, and then from 130ºC (0 min) to 250ºC (0 min) with temperature increase 5ºC/min and from 250ºC (0 min) to 335ºC (10 min) with temperature increase 1ºC/min. The detection limit for each individual analyzed alkane was 0.02 µg/dm^3.

Results and discussion

Total concentration of aliphatic hydrocarbons

Figure 1 presents the total concentration of all aliphatic hydrocarbons in a function of retention time. The values of Σn-alkanes for model solutions with the initial concentrations of 0.01, 0.02 and 0.05%, were respectively 28.69, 52.12 and 121.32 mg/dm^3. As a result of treatment in experimental pots, the decrease in hydrocarbons concentrations was observed. For the solution with the initial concentration of 0.01%, the concentration of aliphatic hydrocarbons dropped to the level of 17.08 mg/dm^3 in the pots without plants, and to 5.48 mg/dm^3 in the pots with plants, which is respectively 40 and 81% lower than for the raw model solution (28.69 mg/ dm^3). The higher decrease in the concentration of n-alkanes was observed after 48 h. For the pots without plants, the hydrocarbons concentration was 12.48 mg/dm^3 (a decrease by 56% in compare with the initial concentration), and 2.77 mg/dm^3 for the pots with plants (90%). After the longest studied retention time (96 h) the lowest concentrations of the aliphatic hydrocarbons were observed - in case of pots without plant, this concentration decreased to 3.42 mg/dm^3 (88%), and in case of pots with plants to 0.68 mg/dm^3. Generally the higher values of Σn-alkanes removal efficiency were observed for the longer retention times.

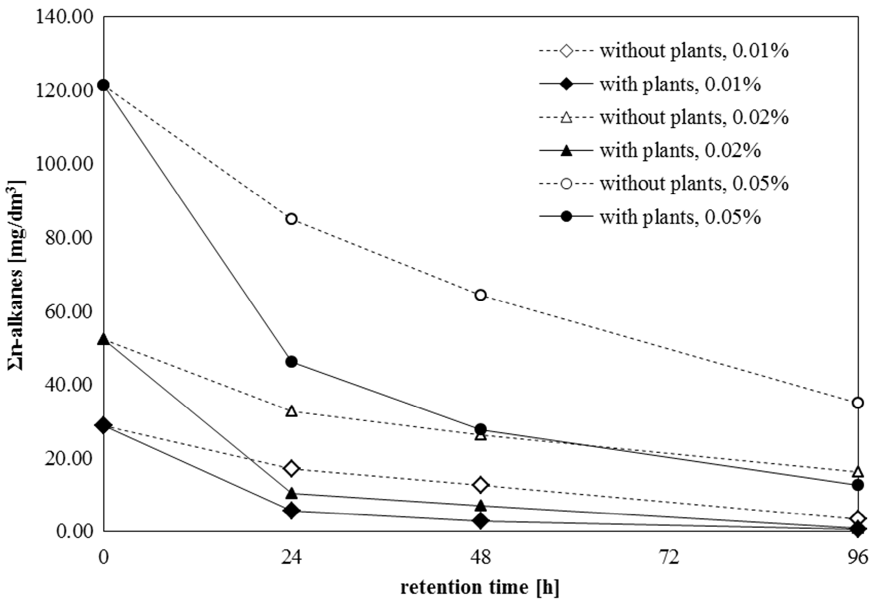

Fig. 1. The total aliphatic hydrocarbons concentration (Σn-alkanes) in a function of retention time, for solutions with the initial concentrations of diesel fuel: 0.01, 0.02 and 0.05%

The similar relationships were observed for the model solution 0.02%, in which the initial concentration of Σn-alkanes was 52.12 mg/dm^3. In case of the pots without plants, Σn-alkanes concentration for 24 h retention time was 32.59 mg/dm^3 (increased by 37%), for 48 hours - 26.39 mg/dm^3 (49%), and for 96 h - 16.12 mg/dm^3 (69%). In case of samples collected from the pots with plants, greater levels of effectiveness in hydrocarbons removal were observed. For 24 h retention time the concentration of Σn-alkanes decreased to

10.31 mg/dm^3, for 48 h - 7.09 mg/dm^3, for 96 h - 0.98 mg/dm^3, what correspond to the effectiveness of 80, 86 and 98%, respectively.

For the model solution with the highest initial concentration 0.05% (Σn-alkanes 121.32 mg/dm^3), the significant decrease in the oil-derivatives concentration was also observed. In a case of samples without plants, for retention time of 24 h Σn-alkanes concentration decreased to the level of 84.96 mg/dm^3 (30% lower than the initial concentration), for 48 h to 64.37 mg/dm^3 (47%), and for 96 h to 34.99 mg/dm^3 (71%). In a case of samples with plants, these values were respectively: 46.01 mg/dm^3 (62%), 27.58 mg/dm^3 (77%) and 12.67 mg/dm^3 (90%).

It is clearly visible from the above results, that plants caused the more efficient removal of oil-derivatives. To evaluate and isolate their role in these processes, the percentage share of their influence was calculated, as the effectiveness of hydrocarbons removal in a pot with plants minus this effectiveness in a pot without plants. For the model solution of 0.01%, the plant isolated influence was the highest for 24 h (40%), and it was decreasing along with the longer values of retention time, reaching 34% for 48 h and 10% for 96 h. The similar patterns were observed for the higher initial concentrations, thus for the initial concentration of 0.02% the isolated plants influence on n-alkanes removal was 32% for 24 h, 30% for 48 h, 18% for 96 h. While for the initial concentration of 0.05% they were respectively: 43, 37 and 29%. These results have verified the thesis that plants have important role in n-alkanes removal, especially for short retention times this effect was very clear and strong. However the plants influence on the hydrocarbons removal depends not only on retention time, but also on the initial n-alkanes concentration.

Sensitivity of plants towards the presence of petroleum products

During and upon completion of the studies presented above, there were also observations over the plants condition carried out. They were realized for 8 pots, subjected to regular inspections: two pots for each diesel fuel concentration in the model solutions (0.01, 0.02, 0.05%), and two control pots, which were planted with macrophytes, but only watered (without model diesel).

Table 1 presents the results of these observations the plants upon completion of the studies. In majority of cases, presence of mold and discoloring of the plants tissues were observed. Conditions of the experiment were handled with the worst by the plants from one of the pots with the highest initial diesel concentration (0.05%) - it dried out, mildewed, its leaves and stems became yellow-brown, its rhizome was brown-green, with only one new sprout. No significant differences were observed in case of conditions of the plants from the control pots (without the petroleum products), and from the pots with the lowest studied concentration (0.01%) - they handled the experimental conditions in a similar good way. First signs of yellowing became visible in both groups, but just the leaves' tips were dried out. The mold appeared on the plants regardless the initial diesel concentration. It may be generally stated that the laboratory conditions were not advantageous for the plants, and they were the main factor shaping the plants conditions, although negative influence of the petroleum products was observable in case of the initial concentration of 0.02%, and even more observable for 0.05% concentration.

Within the course of the studies discussed above, the evaluated plants were also weighted in order to determine their loss in weight, as a result of exposure to toxic petroleum products. However, no unambiguous relationships were observed, and the loss of weight resulted rather from the conditions, which the pot studies were carried out in, or it was accidental, it did not depend on the oil-derivatives concentration in a pot, which is why it was decided not to present or discuss those results.

Table 1

Plants condition upon completion of the pot studies over removal of the petroleum products

Pot; Initial concentration	Condition
Control sample 1, 0.00%	• no new sprouts • the rhizome started to get moldy • new roots
Reference sample 2, 0.00%	• leaves tips started to dry out, their other parts remained green • no mold on the plant • no new sprouts • the rhizome started to get moldy
Pot 1, 0.01%	• the rhizome started to get moldy • no new sprouts
Pot 2, 0.01%	• leaves tips started to dry out, their other parts remained green • no mold on the rhizome, however it is dry, yellow-brown in color • no mold on the plant • no new sprouts • new roots
Pot 1, 0.02%	• leaves tips started to dry out, their other parts remain green • the rhizome is green-brown • no mold • new roots
Pot 2, 0.02%	• yellowish leaves and the stem • the rhizome is green-brown • 3 new sprouts, on covered with mold
Pot 1, 0.05%	• the plant dried out • mold on the stem, leaves and the rhizome • the leaves and stem are yellow-brown • the rhizome is brown and greenish • a new sprout at the greenish rhizome
Pot 2, 0.05%	• no mold • brown-green rhizome • now new sprouts • from the old sprouts: 2 dried out, 1 started do dry out, 1 remained green

Conclusions

Results of experiments on assessment of the influence of reed *Phragmites australis* on an efficiency of aliphatic hydrocarbons removal from the model solution with oil-derivatives allow to draw the following conclusions:

- The high values of removal effectiveness was observed for the experimental pots. The macrophytes play the important role in these processes of n-alkanes' removal. They were responsible for removing 10-43% of alkanes, which were originally in treated solutions. The stronger plants influence were observed for higher values of retention times, however it also depends on the initial concentration of hydrocarbons in a solution.

- The higher initial hydrocarbons concentrations and longer retention time caused an decrease in plants influence on alkanes removal - in these cases the process of hydrocarbons vaporing to the atmosphere are probably more intensive than their biological degradation processes driven by the plants.
- While analyzing the removal effectiveness of individual aliphatic hydrocarbons, it may be observed than an increase of retention time causes more effective removal of a wider range of hydrocarbons; for short retention times C14-35 hydrocarbons were effectively removed, and elongation of this time allowed highly effective removal of even the heaviest C39 and C40 hydrocarbons.
- The relatively low sensitivity of plants on the influence of oil-derivatives, they survived the experiments in a relatively good conditions for all analyzed initial diesel concentrations. However some negative changes were observable for the initial concentration of 0.02%, and even more observable for 0.05%.

These results have positively verified the thesis that plants play an important role in n-alkanes removal, especially for short retention times (24 h) this effect was very clear and strong. It is of great utilitarian importance, because in case of difficult weather conditions (high flow rates and short treatment time) it guarantees the effective removal of oil-derivatives.

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WPŁYW TRZCINY POSPOLITEJ *Phragmites australis* NA SKUTECZNOŚĆ USUWANIA ZANIECZYSZCZEŃ ROPOPOCHODNYCH

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Abstrakt: Oczyszczalnie hydrofitowe są efektywnym sposobem zagospodarowania wód deszczowych, w tym również spływów powierzchniowych z dróg, parkingów i innych powierzchni zanieczyszczonych związkami ropopochodnymi, które stanowią zagrożenie dla środowiska naturalnego, zdrowia ludzi, a także systemów biologicznego oczyszczania ścieków. Mechanizmy usuwania związków ropopochodnych przez złoża hydrofitowe są złożone i nie w pełni poznane, jednak najważniejszą rolę wydaje się pełnić adsorpcja na wypełnieniu mineralnym złoża, działanie mikroorganizmów w nim bytujących oraz aktywność roślin wyższych. Celem prezentowanych badań jest określenie wpływu roślinności na skuteczność usuwania zanieczyszczeń ropopochodnych, a także ocena odporności roślin na wysokie stężenia tych związków. Badania przeprowadzono w formie doświadczeń wazonowych z wykorzystaniem trzciny pospolitej (*Phragmites australis*) oraz ścieków modelowych, symulujących spływy powierzchniowe z powierzchni zanieczyszczonych ropopochodnymi, o trzech stężeniach (0,01, 0,02 i 0,05% oleju napędowego), dla trzech czasów retencji ścieków (24, 48 i 96 h). W ściekach surowych oraz w ściekach po odpowiednim czasie zatrzymania oznaczano następujące parametry: odczyn pH, przewodność elektryczną właściwą, sumę węglowodorów alifatycznych C7-C40 oraz stężenia pojedynczych węglowodorów z tej grupy. Wyniki tych badań posłużyły do określenia efektywności usuwania badanych zanieczyszczeń, w szczególności ropopochodnych, przez złoża hydrofitowe i do określenia wpływu roślinności w tym zakresie. Poza tym prowadzono obserwacje stanu i kondycji roślin, co pozwoliło określić ich odporność na badane stężenia związków ropopochodnych.

Słowa kluczowe: hydrofitowe oczyszczanie wód deszczowych, ropopochodne, węglowodory alifatyczne, trzcina pospolita *Phragmites australis*