Removal of Pesticides from Wastewater by the Use of Constructed Wetlands

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ABSTRACT
The purpose of the work was to determine the efficiency of domestic wastewater treatment contaminated with a mixture of pesticides at varying deposit load. The efficiency of purification in the case of eight pesticides equaled 99.8%, and the removal effect of azoxystrobin reached 93%, while that of thiachloprid – 96%. The constructed wetland ensured high removal of organic matter expressed as BOD and COD, as well as reduction in the concentration of nitrogen and phosphorus compounds. Studies showed a clear impact of the deposit load on the effectiveness of pesticide removal, BOD and COD parameters, total phosphorus, and total nitrogen.

Keywords: constructed wetland, organic matter, pesticides.

INTRODUCTION

The quantitative and qualitative differences in the wastewater composition depend on their place of origin. Among the identified organic impurities present in wastewater, micro-pollutants are a significant group. This group includes organochlorine pesticides and polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), di-2-ethylhexyl phthalate (DEHP) and polychlorinated dibenzodioxins and dibenzofurans (PCDD and PCDF) [Nawirska 2007; Li et al. 2012; Grotowska et al. 2018]. This is mainly related to the wide application of chemical plant protection products in agriculture in order to obtain more abundant crops of better quality [Ignatowicz 2008, 2009; Łozowicka 2010; Głowacki et al. 2014]. The presence of such a large number of pesticide contaminants in water and wastewater necessitates searching for more and more efficient and possibly the most economical methods of their disposal.

Untreated wastewater causes harmful, often irreversible changes and two types of interactions can be distinguished: direct toxic and inhibitory influence of the wastewater containing toxic substances and indirect caused by an unfavorable change of the aquatic environment, which in turn is detrimental and inhibits the development of aquatic organisms [Wrzosek et al. 2009]. Direct adverse effects occur when wastewater contains toxic substances in the quantities exceeding safe limits. Among the group of pesticides, pyrethroids and organophosphorus insecticides, used to fight pests in orchards, some fungicides and herbicides are the most toxic. They are especially dangerous for aquatic organisms, among others, fish that tend to accumulate pesticides [Kwiatkowska et al. 2012; Research Laboratories Greenpeace 2015; Ignatowicz 2009, 2011].

Pesticides are one of many chemical pollutants in domestic and industrial wastewater. They are used to care for kitchen gardens, cultivation, cleaning and protection of farm animals. Due to significant variations in the composition of wastewater from small farms, high concentrations of organic matter, ammonium nitrogen and low content of organic carbon, they are difficult to purify by using classical biological processes. For more than twenty years, constructed wetlands have become more and more popular. There are known applications of constructed wetland systems for
the treatment of wastewater from farms, especially in the United States and Japan [Kato et al. 2007; Haley et al. 2007]. Among the wastewater treated in vertical (VF) and horizontal flow (HF) systems, there were also wastewater from agro-food processing containing contaminants susceptible to the biochemical degradation processes [Puchlik 2018]. This solution was used in the United States for wastewater from sugar factories, as well as in New Zealand and the United Kingdom for wastewater from meat plants [Obarska Pempkowiak et al. 2010]. The interest in this convenient and pro-ecological solution is so large since they can work on any plot, regardless of ground conditions and size of the plot. A high purification effect is obtained at low expenditures for construction and operation, while the plants colonizing the deposits take up nitrogen and phosphorus compounds. An extremely important element is that it does not use chemicals commonly used in conventional wastewater treatment plants, as well as the lack of waste typical of the activated sludge method, and these systems are easily blended into the landscape. There are few scientific reports on the effectiveness of pesticide removal and they concern individual pesticides.

The aim of this work was to present the use of constructed wetland method for the treatment of the household wastewater containing pesticides, originating from the use of plant protection products in households, for the protection of orchards and fields, lawn care, washing chemically protected fruits and vegetables.

MATERIAL AND METHODS

The paper presents the research conducted in the years 2016–2017 regarding the removal of pesticides contained in domestic and industrial wastewater on the constructed wetland deposit. The bed with square dimensions of 75 cm × 75 cm and a depth of 90 cm, was built in a system with a vertical flow of wastewater. The deposit had four layers of filling, from the top: layer I (sand 0–2 mm, 0.15 m), layer II (gravel 2–8 mm, 0.15m), layer III (gravel 8–20 mm, 0.20 m), layer IV (stones 20–80 mm, 0.15 m), on which the common reed (*Phragmites australis*) was planted.

The aim of the study was to assess the effectiveness of the treatment plant and removal of selected pesticides from domestic wastewater in the constructed wetland treatment plant at different loads of the deposit: 0.01 m³/m²/d, 0.02 m³/m²/d, 0.03 m³/m²/d. The raw and purified wastewater samples were collected for the physicochemical analyses (Table 1). The following contents were determined in the raw wastewater samples taken in accordance with the obligatory methodology:

- COD – dichromate method according to: PN-74/C-04578.03,
- BOD – manometric method applying the OxiTop Standard system,
- \(P_{\text{tot.}}\) – spectrophotometric method according to: PN-EN ISO 6878:2006
- \(N_{\text{tot.}}\) – spectrophotometric method on the UV-VIS Pharo 300 spectrophotometer,
- \(N-\text{NH}_4^+\) – spectrophotometric method PN-ISO 7150–1:2002,
- \(N-\text{NO}_3^-\) – PN – spectrophotometric method 82/C-04576/08.

The assessment of pesticide removal effectiveness on the deposit was determined using domestic wastewater with the addition of a mixture of pesticides at a concentration of 500 μg/dm³ each (Table 2). The most commonly used active ingredients of pesticides from the group of fungicides, insecticides and herbicides were selected for the study. The pesticide concentration values were determined by means of liquid chromatography using a liquid chromatograph coupled with an LC/MS/MS mass spectrometer at the Institute of Plant Protection – National Research Institute applying a Waters liquid chromatograph apparatus and AB SCIEX mass spectrometer. The chromatographic analysis was performed using an Eksigent Ultra LC-100 liquid chromatograph coupled to a QTRAP 6500 mass spectrometer (AB Sciex Instruments, Foster City, CA).

RESULTS AND DISCUSSION

The assessment of the contamination removal effectiveness was evaluated as the quotient of the difference in the concentrations of chemical contaminant in the inflow and outflow to the concentration on the inflow.

While analyzing the effectiveness of organic substance removal in the treatment plant, a significant decrease in the values of BOD and COD was found (Table 1). BOD in raw wastewater
ranged from 480 to 3500 mgO₂/dm³, with an average value of 1025.71 mgO₂/dm³. Depending on the applied load of the deposit, these values have decreased significantly. The lowest value of this parameter was obtained after the treatment of wastewater on a deposit with a flow of 0.01 m²/m²/d (the average was 15 mgO₂/dm³), while in the remaining – above 300 mgO₂/dm³. In the case of COD, the values in raw wastewater ranged from 651 to 4400 mgO₂/dm³. The highest COD value was exhibited by the wastewater treated on a deposit with a flow of 0.02 m²/m²/d, but more than 9 times lower (671 mgO₂/dm³) than raw wastewater. The smallest values (from 69.00 to 148.00 mgO₂/dm³) of this parameter characterized the wastewater treated on a deposit at 0.01 m²/m²/d flow. This applies not only to BOD and COD, but also to the concentrations of ammonium nitrogen. Its values (mean 68.37 mg N/dm³) decreased by 30 times at 0.02 m²/m²/d and 7 times at 0.01 and 0.03 m²/m²/d. Own research confirms the impact of constructed wetland primarily on the course of nitrification and denitrification reactions, causing the transformation of ammonium nitrogen to nitrogen gas. The effectiveness of this process is also influenced by the abiotic factors, such as temperature, pH, concentration and ratio of individual ions, synergistic and antagonistic effects of various elements, and biotic factors – the presence of competitors, pests or herbivores [Puchlik et al. 2016]. In our own research, the effect of deposit load on the effectiveness of biogenic elements accumulation was demonstrated. The minimum value of BOD/COD ratio for raw wastewater was 0.7 and the maximum value was 0.8, with the average 0.6. The concentration of nitrogen and phosphorus is very important from the point of view of the treatment plant operation evaluation. Total nitrogen in all wastewater samples decreased and nitrogen in the form of nitrates dropped in two cases (deposit loads of 0.02 and 0.03 m²/m²/d). The concentration of total nitrogen decreased by 8 times (0.02 m²/m²/d), and nitrate nitrogen by about 2 times (Table 1). A significant reduction in the concentration of total phosphorus in the treated wastewater in the deposit was observed. The efficiency of wastewater treatment in the case of ammonium nitrogen was very high at the load of 0.03 m²/m²/d, which could have resulted from a significant increase in the concentration of nitrogen in raw wastewater. According to the research carried out by Warzęzak et al. [Warzęzak et al. 2013], the effectiveness of removing organic contaminants from the constructed wetland wastewater treatment plant in Przyborów after 16 years of operation, was high during the research period and was from 88% to 97% for BOD, and from 85% to 97% for COD. In the tested constructed wetland treatment plant, the nitrification process was found, as evidenced by the reduction of ammonium nitrogen to 95%. Total nitrogen was removed from wastewater with an efficiency of up to 86%. The phosphorus compounds removed during the spring period were around 70%, phosphates and total phosphorus

Table 1. Characteristics of raw and treated wastewater.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Arithmetic mean</th>
<th>Raw wastewater</th>
<th>Wastewater treated</th>
<th>q₀ 0.01 m²/m²/d</th>
<th>q₀ 0.02 m²/m²/d</th>
<th>q₀ 0.03 m²/m²/d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>min-max</td>
<td></td>
<td></td>
<td>1025.71–3500.00</td>
<td>15.00–20.00</td>
<td>350.00–434.50</td>
</tr>
<tr>
<td>BOD</td>
<td>mgO₂/dm³</td>
<td>1025.71–3500.00</td>
<td>1025.71–3500.00</td>
<td>15.00–20.00</td>
<td>350.00–434.50</td>
<td>300.00–423.00</td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>mgO₂/dm³</td>
<td>1733.29–651.00</td>
<td>1733.29–651.00</td>
<td>103.67–480.00</td>
<td>423.00–367.00</td>
<td>300.00–479.00</td>
<td></td>
</tr>
<tr>
<td>N_tot</td>
<td>mgN/dm³</td>
<td>2.00–12.00</td>
<td>2.00–12.00</td>
<td>2.00–12.00</td>
<td>2.00–12.00</td>
<td>2.00–12.00</td>
<td></td>
</tr>
<tr>
<td>N-NH₄⁺</td>
<td>mgN/dm³</td>
<td>488.00–600.00</td>
<td>488.00–600.00</td>
<td>11.00–8.00</td>
<td>11.00–8.00</td>
<td>11.00–8.00</td>
<td></td>
</tr>
<tr>
<td>N-NO₃⁻</td>
<td>mgN/dm³</td>
<td>35.00–115.00</td>
<td>35.00–115.00</td>
<td>3.50–1.20</td>
<td>3.50–1.20</td>
<td>3.50–1.20</td>
<td></td>
</tr>
<tr>
<td>P₆</td>
<td>mgP/dm³</td>
<td>20.34–120.00</td>
<td>20.34–120.00</td>
<td>3.53–0.50</td>
<td>3.53–0.50</td>
<td>3.53–0.50</td>
<td></td>
</tr>
<tr>
<td>P-P₄-H₂O</td>
<td>mgP/dm³</td>
<td>20.26–120.00</td>
<td>20.26–120.00</td>
<td>1.53–0.50</td>
<td>1.53–0.50</td>
<td>1.53–0.50</td>
<td></td>
</tr>
</tbody>
</table>

* q₀ – hydraulic load
around 80%. Obarska-Pempkowiak et al., Kato et al. claim that the aquatic and wetland habitat vegetation have the feature that allows oxygen to be transported to the roots, due to which life processes take place in submerged organs [Kato et al. 2007; Obarska-Pempkowiak 2010]. Due to transporting oxygen to the roots, an aeration zone, in which microorganisms purify wastewater from pesticide contamination, is created. It is in this site that the carbon compounds are oxidized as a result of aerobic bacteria action and the nitrification process of ammonium nitrogen takes place [Kowalik 2004]. High efficiency of purification is ensured by the presence of both aerobic and anaerobic zones, in which the dephosphatation and denitrification processes takes place. A significant part of the components obtained from the decomposition is used by microorganisms in life processes. The products of bacterial metabolism leave the deposit in the form of gases, mainly carbon dioxide originating from the decomposition of organic matter. Puchlik et al. [2016] in the studies regarding the effectiveness of azoxystrobin fungicide removal, obtained very high efficiency (98.1%). This has also been confirmed in our own research. Nearly 99.8% removal of the pesticide occurred at the 0.01 m³/m²/d deposit load. Slightly lower efficiency was obtained on the deposit with a load of 0.02 m³/m²/d and close to 0.03 m³/m²/d. Thiacloprid was detected in the samples of purified wastewater; its highest concentration was found at a hydraulic load of 0.03 m³/m²/d. A similar tendency was noted by Puchlik et al. [2016] in the case of chlorpyrifos ethyl insecticide; however, the efficiency of its removal was higher than that of azoxystrobin (99%).

The following conclusions were drawn based on the research:
• The technology of constructed wetland deposits is a highly effective method of removing pesticides.
• Constructed wetland wastewater treatment plants can be successfully used in the treatment of domestic wastewater with a large share of agricultural wastewater.
• Fungicides, insecticides and herbicide were removed from the wastewater with comparable high efficiency. The efficiency of purification in the case of eight pesticides was 99.8%, and the removal effect for azoxystrobin reached 93%, while thiacloprid – 96%.
• The studies revealed a clear impact of the deposit load on the effectiveness of pesticide removal and concentrations of BOD, COD, total phosphorus, and total nitrogen.

REFERENCES

Table 2. Concentration of pesticides in raw and treated wastewater.

<table>
<thead>
<tr>
<th>Pesticides / Dose 500 [µg/dm³]</th>
<th>Wastewater treated [µg/dm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q₀, 0.01 m²/m²/d</td>
</tr>
<tr>
<td>Azoksystrobina</td>
<td>0.2–0.6</td>
</tr>
<tr>
<td>Boskalid</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Epokzykonazol</td>
<td>&lt;0.1</td>
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<tr>
<td>Fenarymol</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Fenazachina</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Nikosulfuron</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Procymidon</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Pyraklostrobina</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Thiaclopyrd</td>
<td>1.1–1.2</td>
</tr>
<tr>
<td>Trifloksystrobina</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>